# Phosphorous removal and recovery methods. An application on a real municipal wastewater treatment plant.

*Original Citation:*
Phosphorous removal and recovery methods. An application on a real municipal wastewater treatment plant / De Sario, Simona. - ELETTRONICO. - (2023). [10.60576/poliba/iris/de-sario-simona_phd2023]

*Published version*
DOI:10.60576/poliba/iris/de-sario-simona_phd2023

Publisher: Politecnico di Bari

## Abstract

Phosphorous (P) is a key element in the global food supply but its availability is coming to an end, because P is a non-renewable resource. Furthermore, the accumulation of phosphorous in the wastewater is one of the main causes of eutrophication. This, in addition to P depletion, leads to the need to adopt technologies to remove and recover P from the wastewater treatment plants (WWTP), also in a circular economy perspective. Specifically, the removal and recovery of P concentration from the sludge line of WWTP may result into an improvement in the P removal from the mainstream of WWTP. Many studies have been focused on this topic in the last years and many methods linked to both P removal and recovery are available in the scientific literature. These include biological- and chemical-based technologies and many experimental pilot plants have been realized to test the best plant configuration also from an economic and operational point of view. In some cases, the products of the chemical precipitation could be reused in agriculture, as in the case of the struvite and hydroxyapatite that can be used as slow-release fertilizers. Both struvite and hydroxyapatite precipitation take place according to determinate pH values and reagents kinds and doses. According to the National Strategy of Intelligent Specialization (SNSI), the theme of research, financed by the Italian Ministry of University and Research (MUR) through the National Operational Programme "Research and Innovation 2014- 2020" (PhD fellowship, grant number DOT130UZWT n. 2), consists in looking at the water purification world as a "Smart Factory". After the analysis of P removal and recovery methods currently present in scientific literature, P recovery in form of struvite and hydroxyapatite from the centrate deriving from a centrifuge of the WWTP of Andria Municipality was investigated at varying pH values and reagents kinds and concentrations. The analyses were carried out both physically and informatic (using the Visual MINTEQ software) and led to comparable results. The best result found at the end of the experimental campaign highlighted a maximum P recovery of 87.3% leading to an estimated quantity of 92.0 tons/years and 33.2 tons/years of struvite and hydroxyapatite, respectively, recovered from the WWTP of Andria. By an economic estimation of the reagent costs, the consumption of them is almost 50% of the mean P market value. Testing the method on other WWTP and carrying out an analysis of the potential environmental impacts (Life Cycle Assessment) could lead to a large-scale application of the method.

DICATECh
2023
**Simona de Sario**
**Phosphorous removal and recovery methods. An application on a real municipal wastewater treatment plant.**
11

D.R.S.S.
Doctor of Philosophy in Environmental and Building Risk and Development

**POLITECNICO DI BARI**

11
2023

Coordinator: Prof. Eng. Michele Mossa

XXXV CYCLE
ICAR/02 Hydraulic and marine constructions and hydrology
ICAR/03 Sanitary and environmental engineering

DICATECh
Department of Civil, Environmental, Building Engineering and Chemistry

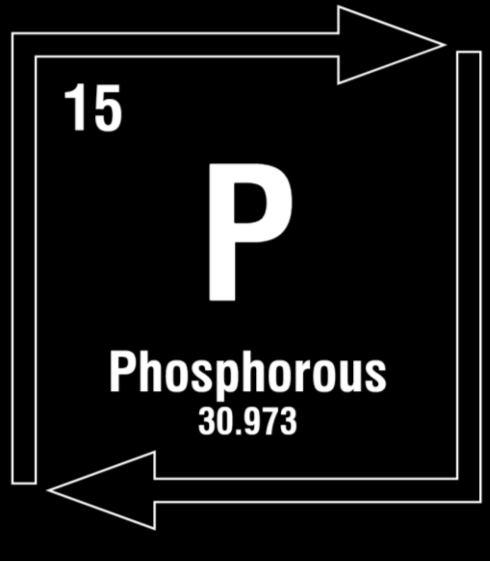
Simona de Sario

# Phosphorous removal and recovery methods. An application on a real municipal wastewater treatment plant

Prof. Eng. Umberto Fratino
Prof. Eng. Danilo Spasiano
*DICATECh - Department of Civil, Environmental, Building Engineering and Chemistry*

Eng. Piervito Lagioia
*Acquedotto Pugliese S.p.A.*

Prof. Eng. Angela Gorgoglione
*Universidad de la República, Montevideo (Uruguay)*



Politecnico
di Bari

# LIBERATORIA PER L'ARCHIVIAZIONE DELLA TESI DI DOTTORATO

Al Magnifico Rettore

del Politecnico di Bari

La sottoscritta Simona de Sario nata a Foggia il 10/10/1990 residente a Foggia in via Arpi 6 (cap 71121) e-mail simona.desario@poliba.it iscritta al 3° anno di Corso di Dottorato di Ricerca in Rischio e Sviluppo Ambientale, Territoriale ed Edilizio ciclo XXXV ed essendo stata ammessa a sostenere l'esame finale con la prevista discussione della tesi dal titolo:

*Phosphorous removal and recovery methods. An application on a real municipal wastewater treatment plant.*

**DICHIARA**

1) di essere consapevole che, ai sensi del D.P.R. n. 445 del 28.12.2000, le dichiarazioni mendaci, la falsità negli atti e l'uso di atti falsi sono puniti ai sensi del codice penale e delle Leggi speciali in materia, e che nel caso ricorressero dette ipotesi, decade fin dall'inizio e senza necessità di nessuna formalità dai benefici conseguenti al provvedimento emanato sulla base di tali dichiarazioni;
2) di essere iscritto al Corso di Dottorato di ricerca Rischio e Sviluppo Ambientale, Territoriale ed Edilizio ciclo XXXV, corso attivato ai sensi del "*Regolamento dei Corsi di Dottorato di ricerca del Politecnico di Bari*", emanato con D.R. n.286 del 01.07.2013;
3) di essere pienamente a conoscenza delle disposizioni contenute nel predetto Regolamento in merito alla procedura di deposito, pubblicazione e autoarchiviazione della tesi di dottorato nell'Archivio Istituzionale ad accesso aperto alla letteratura scientifica;
4) di essere consapevole che attraverso l'autoarchiviazione delle tesi nell'Archivio Istituzionale ad accesso aperto alla letteratura scientifica del Politecnico di Bari (IRIS-POLIBA), l'Ateneo archivierà e renderà consultabile in rete (nel rispetto della Policy di Ateneo di cui al D.R. 642 del 13.11.2015) il testo completo della tesi di dottorato, fatta salva la possibilità di sottoscrizione di apposite licenze per le relative condizioni di utilizzo (di cui al sito http://www.creativecommons.it/Licenze), e fatte salve, altresì, le eventuali esigenze di "embargo", legate a strette considerazioni sulla tutelabilità e sfruttamento industriale/commerciale dei contenuti della tesi, da rappresentarsi mediante compilazione e sottoscrizione del modulo in calce (Richiesta di embargo);
5) che la tesi da depositare in IRIS-POLIBA, in formato digitale (PDF/A) sarà del tutto identica a quelle **consegnate**/inviate/da inviarsi ai componenti della commissione per l'esame finale e a qualsiasi altra copia depositata presso gli Uffici del Politecnico di Bari in forma cartacea o digitale, ovvero a quella da discutere in sede di esame finale, a quella da depositare, a cura dell'Ateneo, presso le Biblioteche Nazionali Centrali di Roma e Firenze e presso tutti gli Uffici competenti per legge al momento del deposito stesso, e che di conseguenza va esclusa qualsiasi responsabilità del Politecnico di Bari per quanto riguarda eventuali errori, imprecisioni o omissioni nei contenuti della tesi;
6) che il contenuto e l'organizzazione della tesi è opera originale realizzata dal sottoscritto e non compromette in alcun modo i diritti di terzi, ivi compresi quelli relativi alla sicurezza dei dati personali; che pertanto il Politecnico di Bari ed i suoi funzionari sono in ogni caso esenti da responsabilità di qualsivoglia natura: civile, amministrativa e penale e saranno dal sottoscritto tenuti indenni da qualsiasi richiesta o rivendicazione da parte di terzi;
7) che il contenuto della tesi non infrange in alcun modo il diritto d'Autore né gli obblighi connessi alla salvaguardia di diritti morali od economici di altri autori o di altri aventi diritto, sia per testi, immagini, foto, tabelle, o altre parti di cui la tesi è composta.

Luogo e data, Bari, __/__/____

Firma Simona de Sario

La sottoscritta, con l'autoarchiviazione della propria tesi di dottorato nell'Archivio Istituzionale ad accesso aperto del Politecnico di Bari (POLIBA-IRIS), pur mantenendo su di essa tutti i diritti d'autore, morali ed economici, ai sensi della normativa vigente (Legge 633/1941 e ss.mm.ii.),

**CONCEDE**

- al Politecnico di Bari il permesso di trasferire l'opera su qualsiasi supporto e di convertirla in qualsiasi formato al fine di una corretta conservazione nel tempo. Il Politecnico di Bari garantisce che non verrà effettuata alcuna modifica al contenuto e alla struttura dell'opera.
- al Politecnico di Bari la possibilità di riprodurre l'opera in più di una copia per fini di sicurezza, back-up e conservazione.

Luogo e data, Bari __/__/____ Firma

# D.R.S.S.

**POLITECNICO DI BARI**

11

Doctor of Philosophy in Environmental and Building Risk and Development

2023

Coordinator: Prof. Eng. Michele Mossa

Michele Mossa

XXXV CYCLE
ICAR/02 Hydraulic and marine constructions and hydrology
ICAR/03 Sanitary and environmental engineering

DICATECh
Department of Civil, Environmental, Building Engineering and Chemistry

Simona de Sario

Simona de Sario

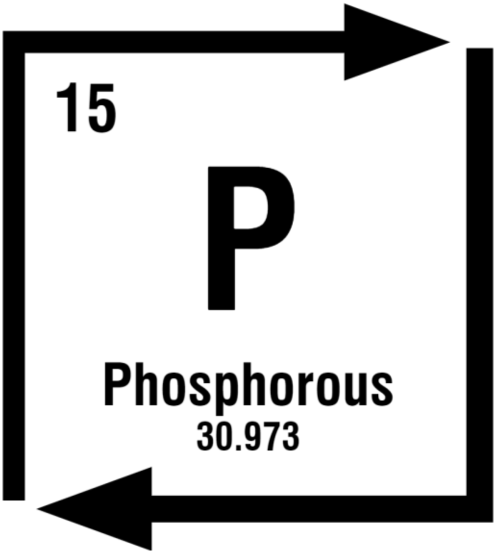
# Phosphorous removal and recovery methods. An application on a real municipal wastewater treatment plant

Prof. Eng. Umberto Fratino
Prof. Eng. Danilo Spasiano
*DICATECh - Department of Civil, Environmental, Building Engineering and Chemistry*

Danilo Spasiano

Eng. Piervito Lagioia
*Acquedotto Pugliese S.p.A.*

Prof. Eng. Angela Gorgoglione
Universidad de la Repùblica, Montevideo (Uruguay)



# D.R.S.S.

**POLITECNICO DI BARI**

11

2023

Dottorato di Ricerca in Rischio e Sviluppo ambientale, territoriale ed edilizio

Coordinatore: Prof. Ing. Michele Mossa

XXXV CICLO
ICAR/02 Costruzioni idrauliche e marittime e idrologia
ICAR/03 Ingegneria Sanitaria Ambientale

DICATECh
Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica

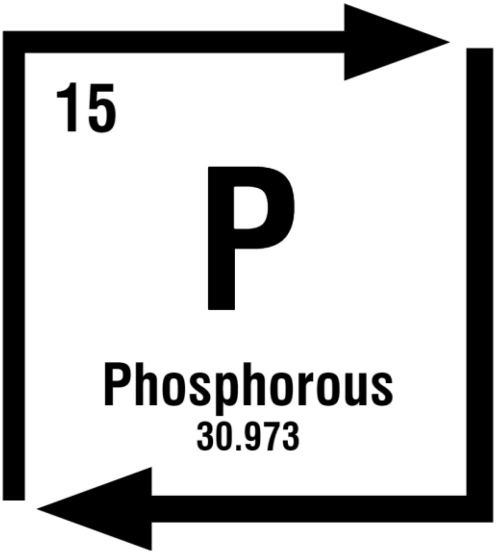
Simona de Sario

# Metodi di rimozione e recupero del fosforo. Applicazione su un reale impianto di trattamento delle acque reflue municipali

Prof. Ing. Umberto Fratino
Prof. Ing. Danilo Spasiano
*DICATECh - Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica*

Ing. Piervito Lagioia
*Acquedotto Pugliese S.p.A.*

Prof.ssa Ing. Angela Gorgoglione
*Universidad de la Repùblica, Montevideo (Uruguay)*



# ***EXTENDED ABSTRACT (eng)***

Phosphorous (P) is a key element in the global food supply but its availability is coming to an end, because P is a non-renewable resource. Furthermore, the accumulation of phosphorous in the wastewater is one of the main causes of eutrophication. This, in addition to P depletion, leads to the need to adopt technologies to remove and recover P from the wastewater treatment plants (WWTP), also in a circular economy perspective. Specifically, the removal and recovery of P concentration from the sludge line of WWTP may result into an improvement in the P removal from the mainstream of WWTP. Many studies have been focused on this topic in the last years and many methods linked to both P removal and recovery are available in the scientific literature. These include biological- and chemical-based technologies and many experimental pilot plants have been realized to test the best plant configuration also from an economic and operational point of view. In some cases, the products of the chemical precipitation could be reused in agriculture, as in the case of the struvite and hydroxyapatite that can be used as slow-release fertilizers. Both struvite and hydroxyapatite precipitation take place according to determinate pH values and reagents kinds and doses.

According to the National Strategy of Intelligent Specialization (SNSI), the theme of research, financed by the Italian Ministry of University and Research (MUR) through the National Operational Programme "Research and Innovation 2014- 2020" (PhD fellowship, grant number DOT130UZWT n. 2), consists in looking at the water purification world as a "Smart Factory".

After the analysis of P removal and recovery methods currently present in scientific literature, P recovery in form of struvite and hydroxyapatite from the centrate deriving from a centrifuge of the WWTP of Andria Municipality was investigated at varying pH values and reagents kinds and concentrations. The analyses were carried out both physically and informatic (using the Visual MINTEQ software) and led to comparable results.

The best result found at the end of the experimental campaign highlighted a maximum P recovery of 87.3% leading to an estimated quantity of 92.0 tons/years and 33.2 tons/years of struvite and hydroxyapatite, respectively, recovered from the WWTP of Andria. By an economic estimation of the reagent costs, the consumption of them is almost 50% of the mean P market value. Testing the method on other WWTP and carrying out an analysis of the potential environmental impacts (Life Cycle Assessment) could lead to a large-scale application of the method.

***key words***

Wastewater treatment plants, Phosphorous recovery, Struvite, Hydroxyapatite, Municipal wastewater, Sewage sludge, Fertilizer recovery, Chemical precipitation

## *EXTENDED ABSTRACT (ita)*

Il fosforo (P) è un elemento chiave nell'approvvigionamento alimentare mondiale ma la sua disponibilità sta giungendo al termine, dal momento che il fosforo è una risorsa non rinnovabile. Inoltre, l'accumulo di fosforo nelle acque reflue è una delle cause principali di eutrofizzazione. Ciò, in aggiunta al previsto esaurimento del fosforo, conduce alla necessità di tecnologie di rimozione e recupero dagli impianti di trattamento delle acque reflue, anche in prospettiva di un'economia circolare. Inoltre, la rimozione e la riduzione della concentrazione del fosforo dalla linea fanghi dell'impianto di trattamento può comportare un miglioramento della rimozione del fosforo dalla linea di trattamento principale dell'impianto. Molti studi si sono focalizzati su questo argomento negli ultimi anni e nella letteratura scientifica sono disponibili molti metodi legati alla rimozione e al recupero del fosforo. Questi studi includono metodi biologici e chimici e sono stati realizzati molti impianti pilota sperimentali per testare le migliori configurazioni impiantistiche, sia da un punto di vista economico che operativo. In alcuni casi il prodotto della precipitazione chimica può essere riutilizzato in agricoltura, come nel caso della struvite e dell'idrossiapatite che possono essere utilizzati come fertilizzanti a lento rilascio. Sia la formazione della struvite che quella dell'idrossiapatite avvengono in base a determinati valori di pH e di concentrazione dei reagenti ed entrambe richiedono precise condizioni di equilibrio chimico.

In accordo con la Strategia Nazionale di Specializzazione Intelligente (SNSI), il tema della ricerca, finanziato dal Ministero dell'Università e della Ricerca (MUR) attraverso il Programma Operativo Nazionale "Ricerca e Innovazione 2014-2020" (borsa di dottorato, grant number DOT130UZWT n. 2), consiste nel considerare il mondo della depurazione dell'acqua come una "Fabbrica Intelligente ".

Dopo l'analisi dei metodi di recupero e rimozione del fosforo attualmente presenti nella letteratura scientifica è stato indagato il recupero di fosforo, in forma di struvite ed idrossiapatite, dal centrato dell’impianto di trattamento delle acque reflue municipali del Comune di Andria, a diversi pH e diverse concentrazioni di reagenti. Le analisi sono state effettuate sia per via fisica che informatica (mediante il software Visual MINTEQ) ed hanno condotto a risultati comparabili tra loro.

Il miglior risultato riscontrato al termine della campagna sperimentale ha evidenziato un recupero massimo di P dell' 87.3% che ha portato ad una quantità stimata annua di 92,0 tonnellate e 33,2 tonnellate di struvite e idrossiapatite, rispettivamente, recuperati dall’impianto di depurazione di Andria. Da una stima economica dei costi dei reagenti, il loro consumo è risultato essere circa la metà del valore di mercato del fosforo. Testando il metodo su altri impianti di depurazione ed effettuando una analisi dei potenziali impatti ambientali (Life Cycle Assessment) si potrebbe giungere ad un'applicazione del metodo su larga scala.

## ***key words***

Impianto di trattamento delle acque reflue, Recupero del fosforo, Struvite, Idrossiapatite, Acque reflue urbane, Fanghi, Recupero di fertilizzanti, Precipitazione chimica

# INDEX

# *1. INTRODUCTION*

An innovation in the development model of the European industrial strategy was the introduction of the principle of "Extended Producer Responsibility" (EPR) which is based on the expectation that an industrial system can recover materials from previous uses to counteract the increasingly scarce availability of many raw materials, especially in Europe (Bompan & Brambilla, 2016). Based on this principle, manufacturers and importers, through a "Collective System", must ensure that their products are recovered and reused in the production cycles at the end of the useful life. This practice translates into a transition from a linear economy model to a circular economy, from which derive economic, social and environmental benefits.

Johan Rockström, director of the Stockholm Resilience Centre, proposed a new approach to global sustainability in which planetary boundaries are defined within which humanity could be expected to operate safely (Rockström et al., 2009) and, among these, appears the use of nitrogen (N) and phosphorus (P) under the thresholds.

The recovery and reuse of organic waste is in line with the strategic finding of nutrients to ensure that natural cycles continue uninterrupted. For example, the anaerobic co-digestion of sludge from WWTP and the organic fraction of municipal solid waste could lead to production of high quantities of biogas rich in methane, thus reducing the dependence on fossil fuels, and to the subsequent recovery of nutrients in form of marketable fertilizer (Di Costanzo et al., 2021).

Since 20% of the P used globally ends up in wastewater (Ott & Rechberger, 2012), this thesis has been focused on the removal and recovery of P from urban wastewater treatment plant through chemical or biological methods. In particular, the sewage sludge could be reused in agricultural field, but its physical and chemical characteristics have to be in compliance with the European (Directive 86/278/EEC) and national legislation. However, the adoption of the strategies and technologies reported in this thesis may result in the environmentally safe recovery of nutrients from wastewater and sludge in form of fertilizers, in agreement with the principles of the circular economy.

Specifically, several processes and patents aimed at recover P from WWTP in form of struvite ($NH_4MgPO_4 \cdot 6H_2O$) have been proposed. In fact, this mineral contains both P and N and, being poor soluble, avoid the fast leaching of nutrients, thus protecting groundwater from possible contamination.

These methods could be applied in many points of the WWTP, but most of them are designed to operate in the sewage sludge treatment cycle since higher concentrations of P are found (González-Morales et al., 2021). However, the presence of $Ca^{2+}$ ions could interfere in the struvite crystallisation process since it leads to the precipitation of calcium phosphate, such as the hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Le Corre et al., 2005). Nevertheless, also hydroxyapatite, like struvite, can be used as slow-release fertilizer, food additives and more (M. Chen & Graedel, 2016a). Typically, magnesium is the limiting compound for struvite precipitation and there is a need of its add to the solution for efficient P recovery in form of struvite (Fattah, 2012). However this supplement contributes to increase the costs for struvite production up to 75% (Kataki et al., 2016). By an economic point of view, a recent research (Muys et al., 2021) reports that struvite production has a cost ranging from 100 € per ton to 350 and 1000 € per ton (for Phosphogreen and Pearl projects, respectively).

Most of these studies have been carried out on biological sludge deriving from enhanced biological processes (EBPR). Consequently, little information is available in the literature regarding P recovery from the sewage sludge of WWTPs that do not rely on EBPR through precipitation under low (sub-stoichiometric) Mg concentrations.

The first phase of the research activities was in a large bibliographical review and, subsequently, the connection with AQP S.p.A., in order to define the wastewater treatment plant to be used for laboratory testing.

The chosen WWTP is in Andria (BAT, Apulia), where an on-site inspection was carried out.

After that, a characterization analysis of thickener supernatant, digestate and centrate in terms of phosphate concentration was carried out to locate the best sampling point for the P recovery tests. At the end of this phase, P recovery from digestate liquid fraction (centrate) was investigated at varying pH, reagent typologies ($MgCl_2$, NaOH, $Ca(OH)_2$, $CaCl_2$) and concentrations. The combined analysis of the solid (by X-Ray diffraction) and liquid phase determinations, together with a thermodynamic simulation to quantitatively estimate the amount and the nature of the precipitates, has led to the identification of two conditions that seem to be optimal for the recovery of phosphorus as struvite and hydroxyapatite.

Finally, a mass balance was performed to estimate the annual quantities of struvite and hydroxyapatite recovered by the investigated method, together with a preliminary economic assessment.

# CHAPTER 2. PHOSPHOROUS CYCLE AND MANAGEMENT

## 2.1. PHOSPHOROUS CYCLE

Phosphorus is a chemical element belonging to the V group of the periodic table. It is a non-metal and in nature is not possible to find it in its elementary (pure) state, due to its strong reactivity. For instance, it is very common to find it in the form of phosphates (usually $PO_4^{3-}$, with the general formula $H_nPO_4^{n-3}$, where *n* is an integer decreasing with pH), or salts of phosphoric acid ($H_3PO_4$). In line with common practice, N, P and potassium (K) should be referred to as ‘primary macronutrients’ (Regulation EU, 2019). In fact, some compounds containing P are involved in the vital functions at the base of life: P is present in the molecules of DNA, RNA, ATP (adenosine triphosphate ($C_{10}H_{16}N_5O_{13}P_3$), an indispensable substance for the synthesis of RNA) and phospholipids.

The natural P cycle, which has been established on geological time scales, primarily involves the erosion of minerals containing P in soil and watercourses. From here it is absorbed by microorganisms and plants and then by animals that feed on plants.

P returns to the soil by excretion from animals and by decomposition of plants and animals after death; over time, part of the P is lost in water streams and finally in the sea, where it is reincorporated into sedimentary rock for long periods of time (Tian et al., 2021) (Figure 2.1).

P is a particularly abundant element in the soil but it is present especially in an insoluble form and therefore not available for radical absorption by plants (van de Wiel et al., 2016). In addition, this process is highly sensitive to changes in pH and to the type (Moody et al., 2013) of soil. Furthermore, the P available for plants is function of the soluble fraction (e.g. $H_2PO_4^-$ ) in relation to the total.

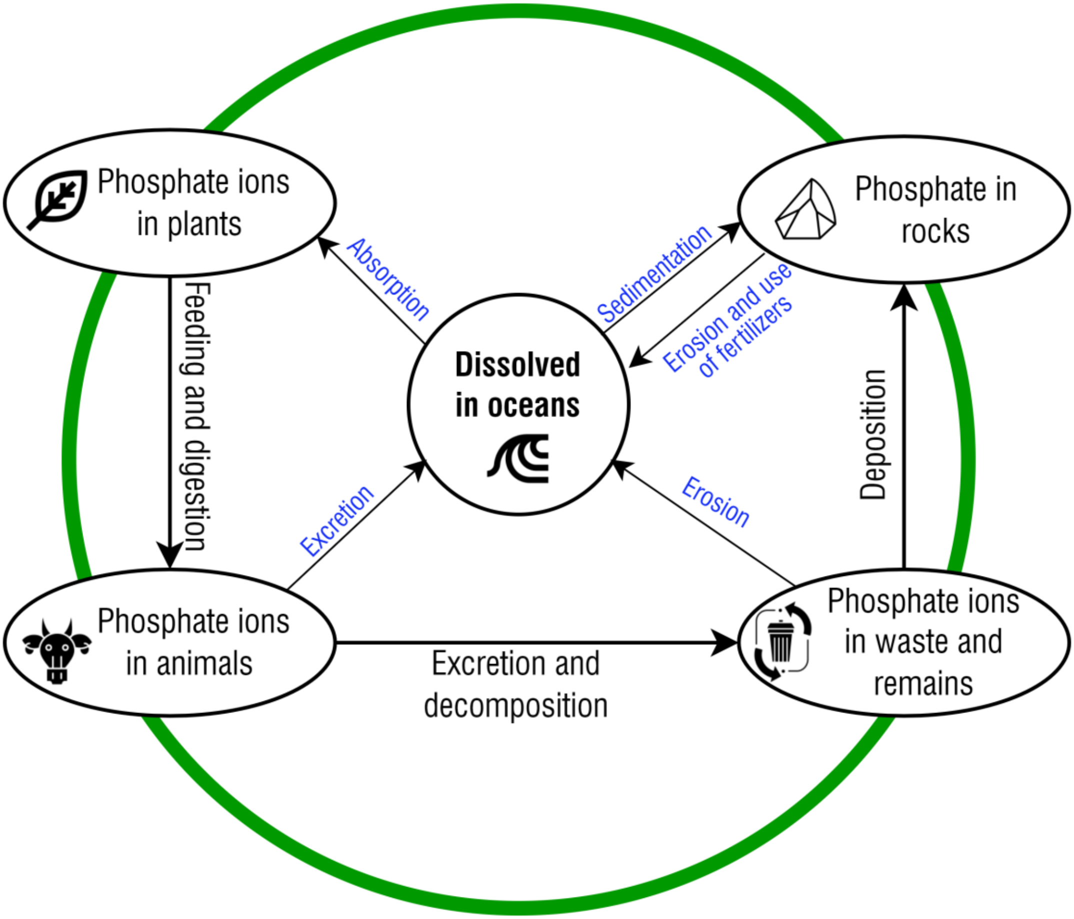


Figure 2.1. Phosphorous cycle.

Notably, most of the soluble inorganic P used in synthetic fertilizers is immobilized immediately after application in the field and thus converts into the form not available for the plant (Ibrahim et al., 2022). These synthetic fertilizers, that are useful to increase up to 50% the agricultural harvests (Stewart et al., 2005), are produced from the extracted phosphoric anhydride ($P_2O_5$) that can be of two types: sedimentary (80-90% of world production) and magmatic (10-20% of world production) (Canziani & Di Cosmo, 2018).

## *2.2. P LOSSES AND NEED FOR RECOVERY*

From extracting to distributing and using fertilizers for agricultural purposes, a certain amount of P may be lost. These losses are due to erosion phenomena triggered by rain and soil work, and about half ends up in aquatic ecosystems favoring the process of eutrophication. The latter involves the formation of large algae blooms that damage aquatic life, creating the so-called "dead zones" (Joyce, 2000).

A recent study on the EU15 former countries highlights that almost 20% of the P used for food, feed and non-food products, such as detergents, end up in industrial and urban wastewater treatment plant (WWTP) (Ott & Rechberger, 2012).

In particular, as reported also by another study (Ball Coelho et al., 2012; van Dijk et al., 2016):

- 70% of P comes from WWTP in form of sludge (not always reused in agriculture)
- 30% goes directly in the hydrosphere.

Part of P contained in fertilizer and in the sludge reused in the agriculture is washed away by the rain (and this cause migration of P to surface waters).

By another study on the EU27 countries showed that 27% of P imported in 2005 has been losses mainly in wastewater (55%), food waste (27%), and pet excreta (11%) (van Dijk et al., 2016).

These P sustainability issues are closely linked to other challenges, including nitrogen management, water treatment, food waste, soil erosion, contaminants and food safety (Rickson et al., 2015). P recovery and recycling can improve economy, mitigate nutrient pollution, as well as lead to the circular economy model.

Thanks to different government agencies and interorganizational platforms, many efforts have been made in recent years to develop recovery technologies. One example is the European Sustainable Phosphorus Platform (ESPP), which includes over 150 members from industry, research and politics. Its main objective is knowledge sharing, networking and facilitating discussion between the market, stakeholders and regulators.

Research in agriculture is also focusing on improving the efficiency of fertilizer use through the application of live microorganisms able to solubilize phosphorus, also called Phosphate-Solubilizing Microorganism (PSM) (Timofeeva et al., 2022). Specifically, some types of PSM are, for example, *Bacillus*, *Pseudomonas*, *Bulkolderia*, *Rhizobium*, *Erwinia*, and other. These can convert inorganic P into soluble P through the action of low molecular weight organic acids or by the action of hydroxyl and carboxyl groups that can bind the P cations.

In addition, to avoid erosion and leaching of P from agricultural fields, some kinds of slow P-release fertilizers, such as struvite, calcium and magnesium phosphates, have been suggested by EU in the Regulation EC No 1907/2006 (European Chemicals Agency, 2017) (Table 2.1).

| EC / List number regulatory REACH process names | | CAS number | Molecular formula |
|---|---|---|---|
| 232-075-2 | ammonium magnesium orthophosphate (struvite) | 7785-21-9 | $NH_4MgPO_4 \cdot 6H_2O$ (hydrate) |
| 231-826-1 | calcium hydrogen orthophosphate | 7757-93-9 | $CaHPO_4$ (anhydrous) |
| 231-823-5 | magnesium hydrogen orthophosphate | 7757-86-0 | $MgHPO_4$ |
| 235-330-6 | penta calcium hydroxide tris(orthophosphate) | 12167-74-7 | $Ca_5(PO_4)_3(OH)$ |
| 231-837-1 | calcium bis(dihydrogen orthophosphate) | 7758-23-8 | $Ca(H_2PO_4)_2$ (anhydrous); |
| 236-004-6 | magnesium bis(dihydrogen orthophosphate) | 13092-66-5 | $Mg(H_2PO_4)_2$ (anhydrous); |
| 231-840-8 | tricalcium bis(orthophosphate) | 7758-87-4 | $Ca_3(PO_4)_2$ |
| 231-824-0 | trimagnesium bis(orthophosphate) | 7757-87-1 | $Mg_3(PO_4)_2$ |

Table 2.1. Examples of phosphate salts as registered pursuant to Regulation EC No 1907/2006 (REACH) as fertilizers (Huygens et al., 2019).

## *2.3. PHOSPHOROUS MANAGEMENT*

The sustainable use of P is a strong interdisciplinary topic. In fact, in the scientific, politic and economic fields (Deselnicu et al., 2018; Withers, Elser, et al., 2015 (b); Withers, van Dijk, et al., 2015 (a)) there are several proposals aimed to enhance the efficiency of the P flow management and increase the P recycle in the anthropic activity.

To meet the demands of agriculture and food needs, from 1993, the global consumption of elemental P deriving from phosphate rocks (PR) raised by almost 3-4% per year and equaled 30.8 Tg in 2014 (M. Chen & Graedel, 2016b). By considering that the global PR reserves amount to almost $65\times10^3$ Tg, which could reach $290\times10^3$ Tg if hypothetical deposits and unprocessed rock of varying quality are considered (Van Kauwenbergh, 2010), and the constant increase of P demand, growing concerns over long-term security of P supply are arising (Desmidt, Ghyselbrecht, Zhang, Pinoy, Van der Bruggen, et al., 2015; Koppelaar & Weikard, 2013; Vaccari & Strigul, 2011). Global PR reserves are not evenly distributed around the world. Notably, three quarters are located in Morocco and North Africa, China, the United States and Russia and, so, concentrated in a limited number of countries, none of which is located in the EU, except for Finland which only produces a small amount of $P_2O_5$ (Ridder et al., 2012). The European Union is heavily dependent on these countries for the import of PR, and therefore in 2014 it included P in the list of 20 critical raw materials that are characterized by a great economic importance and a strong risk of procurement. It has been estimated that global PR reserves will last 3-4 centuries, but, excluding Morocco, all the other countries will deplete their reserves within the next century (Cooper et al., 2011). The causes of P depletion include intensive farming and agriculture (Garske et al., 2020).

To reduce the PR mining, the 5Rs strategy (Realign P inputs in agriculture, Reduce P losses in the hydrosphere, Recycle P in bio-resources, Recover P from waste, and Redefine the food system) has been suggested to EU countries (Withers, van Dijk, et al., 2015) and, from this suggestion, the European Parliament has proposed the promotion of the *"large scale fertilizer production in the EU from domestic organic or secondary raw materials"* (European Parliament, 2016).

The possibility of recovering P from these sources is dependent on (Canziani & Di Cosmo, 2018):

1) the EU directives (or specific national legislations), that can encourage a circular economy model;
2) compliance with the technical specifications and regulatory requirements of the recovered product;
3) socio-economic and environmental impacts, measurable with life cycle analysis of the product;

4) technical skills, better exploitation and use of existing infrastructures and business model of recovery processes and technologies;
5) market, which depends, as well as price, on the acceptability of products recovered by end users.

One of the “secondary raw materials” mentioned by European Parliament could be the sewage sludge since, as previously said, about 70% of P that passes in WWTP ends right in this phase. Recovery of P from sewage sludge must be in according to the 5 points listed and, regarding the point 1), the European and Italian regulatory framework that currently governing the treatment of sewage sludge and possible reuse in agriculture is set out in Table 2.2.

| **European Standard** | |
|---|---|
| 86/278/CE | Protection of the environment, in particular of the soil, in the use of sewage sludge in agriculture |
| 91/676/CE | Protection of water against pollution caused by nitrates from agricultural sources |
| 2008/98/CE | Waste management |
| EU 2019/1009 | Availability of EU fertilizer products on the market |
| **National Standard (IT)** | |
| D.Lgs 99/92 | Management of the use of sewage sludge in agriculture |
| D.Lgs 152/2006 | Environmental regulations |
| D.Lgs 121/2020 | Rules on the landfill of waste |

Table 2.2. Summary of the European and Italian regulatory framework.

# *CHAPTER 3. PHOSPHOROUS REMOVAL METHODS*

*This chapter has, in part, resulted in the review entitled "Phosphorous removal and recovery from urban wastewater: Current practices and new directions" by Di Capua,* ***de Sario****, Ferraro, Petrella, Race, Pirozzi, Fratino, Spasiano (Science of The Total Environment, 153750, 2022)* (Di Capua et al., 2022).

The average total P concentration in municipal wastewater typically ranges between 6 - 12 mg/L (Rittmann & McCarty, 2012; US EPA, 2007). P is present in urban wastewater generally in forms of orthophosphates and Poly-P which turn to orthophosphates after slow hydrolysis (T. Park et al., 2016). According to what is reported in some studies (Rittmann & McCarty, 2012; US EPA, 2007), the conventional secondary treatments can reduce total P level to 3-6 mg/L, that is higher than the typical limits of 1 mg/L, leading to a necessity of the supplemental methods to reduce total P in the final effluent and, as consequence, the risk of eutrophication.

P removal can be performed:

- via chemical methods (after and before the biological phase)
- via biological treatments (within the biological phase).

## *3.1. CHEMICAL AND CHEMICAL-PHYSICAL METHODS*

Chemical precipitation and sorption are generally reliable and effective processes for the removal of phosphates and have been used for many years to recover P from the liquid phase (X. Chen et al., 2009; W. Huang et al., 2017; Loganathan et al., 2014; Mitrogiannis et al., 2017; Spears et al., 2013; Y. Ye et al., 2017).

Chemical precipitation is applied to most wastewater systems and is based on the addition of a coagulant with consequent flocculation of insoluble compounds successively removed either by settling or by filtration. During this process, large quantities of chemical sludges are produced (Ding et al., 2012). Regarding sorption, currently there are some methods that allow to recover phosphorous removed for another uses, so these methods will be discussed in the Chapter 3 (PHOSPHOROUS RECOVERY METHODS).

### *3.1.2. CHEMICAL PRECIPITATION*

Chemical precipitation is carried-out with the final aim of phosphate recovery and the treatment is based on the choice of the appropriate coagulants which could be added before, after or during the conventional biological wastewater system (Burton & Stensey, 2003). Specifically, the removal of P from wastewater is based on the precipitation of phosphate into either biological solids or chemical precipitates (Total Suspended Solids = TSS) followed by separation from these insoluble compounds.
Calcium, magnesium, aluminum and iron ions are commonly employed as precipitators in (Metcalf&Eddy et al., 2014):

1) the primary wastewater treatment (pre-precipitation); 65-80% removal efficiency is achieved with a relatively low P concentration in the final effluent (<0.5 mg/l) while the alkalinity of the wastewater can influence reactant dosage;
2) in the post-precipitation treatment (after secondary biological treatment); low P concentration in the final effluent (<0.5 mg/l) is obtained together with higher removal efficiency (~95%) due to a more efficient chemical action ascribed to the conversion of the organic phosphates to orthophosphates during the biological step. This process is more expensive than the former (big tanks are required) and a dilute effluent is often obtained;

3) in the co-precipitation treatment (contemporary to the secondary treatment); this system is suitable for activated sludge reactors and chemical consumption is reduced because of the combined effect operated by the sludge recirculation and the sorption and precipitation processes. For this reason, this system is less expensive than the post-precipitation treatment also because tanks of moderate size are required, but chemical and biological sludges are not easily differentiated. In the present case, aluminum and iron ions are commonly employed as precipitators and P removal efficiency can reach value up to 93-99% (Costa et al., 2019; Filali-Meknassi et al., 2005).

Calcium and magnesium ions can be used as phosphate precipitators in the form of (hydr)oxides and salts (e.g. $MgO$, $Mg(OH)_2$, $CaO$, $Ca(OH)_2$, $MgCl_2$ and $CaCl_2$) (De-Bashan & Bashan, 2004; Y. Ye et al., 2017). Generally, in the case of calcium compounds, lime is the most used coagulant for the removal of phosphate which, as the pH value of the wastewater is higher than 8, precipitates as hydroxyapatite according to reaction 3.1:

$$10\ Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \qquad \text{(R. 3.1)}$$

This process is essentially a water softening treatment and the amount of lime to be added depends more on the alkalinity of the discharge than on the P content, accordingly, lime concentration is approximately 1.5 times the alkalinity as $CaCO_3$. Hydroxyapatite could be recycled by the phosphate industry. This treatment is used only in pre-precipitation or in post-precipitation systems and the major drawback of lime, which is cheaper than the Al and Fe salts, is the enormous quantity of sludge produced; in fact, the precipitation of hydroxyapatite takes place only after precipitation of the Ca and Mg carbonates. Other drawbacks derive from encrustation and corrosion problems together with a setup of systems for storage and reagent dosage (Beccari et al., 1993; Desmidt, Ghyselbrecht, Zhang, Pinoy, Bruggen, et al., 2015).

Generally, Magnesium ions are used as phosphate precipitators because they form struvite, according to reaction 3.2.

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \bullet 6H_2O \qquad \text{(R. 3.2)}$$

Struvite is a composition of equimolar concentration of magnesium, ammonium and phosphate and its precipitation is depending on pH, temperature and saturation index (Fattah, 2012). The precipitation of this crystal can be separated in the two phases: nucleation, which occurs when the ionic constituents form the crystalline embryo and can be homogeneous (if it occurs spontaneously) or heterogeneous (if helped by the presence of nuclei, such as example of suspended solid impurities on the walls of the pipes), and growth, which continues until the equilibrium is reached (Doyle & Parsons, 2002). Characteristics that make struvite a useful resource are the low solubility, the low content of heavy metals compared to PR, the reduction in the volume of sludge generated and the reduction of N and P in the sludge.

Experimentally, the needed amount of magnesium is much higher than the theoretical value because of the further precipitation of insoluble compounds after combination with the soluble organic substances (Tong & Chen, 2007). Moreover, the formation of struvite is facilitated by high concentrations of ammonia behaving as a N supplier and inducing a pH buffering effect (Pastor et al., 2008; Stratful et al., 2004), nonetheless, $MgKPO_4$ precipitation may also occur after reaction between $K^+$ and $PO_4^{3-}$ (H. Huang et al., 2011) with a consequent reduction of the struvite purity.

As reported before, pH value can affect the process of precipitation by calcium and magnesium ions because the concentration of free $NH^{4+}$ and $PO_4^{3-}$ and the solubility of precipitates can be influenced (Bi et al., 2014; H. Huang et al., 2015) with modification of the characteristics of the recovered phosphate (specific yield, dimension, purity). Hydroxyapatite and struvite tend to precipitate at wastewater pH higher than 8, whereas, at values higher than 10, the formation of struvite may be affected by the formation of gaseous ammonia and by the precipitation of calcium and magnesium hydroxides which may reduce hydroxyapatite and struvite formation. Finally, at so high pH, the precipitation of calcium carbonate instead of calcium phosphate is favored (Song et al., 2002).

The most common form of aluminum used for phosphorus precipitation is alum (Gibbons & Gagnon, 2011), a hydrated aluminum sulphate with about 9% by weight of aluminum. Alum is widely used for the precipitation of aluminum phosphates ($AlPO_4$) which can be obtained by the reaction described in the reaction 3.3 (Beccari et al., 1993):

$$Al_2(SO_4)_3 \bullet 14H_2O + 2PO_4^{3-} \leftrightarrow 2AlPO_4 + 3SO_4^{2-} + 14H_2O \qquad \text{(R. 3.3)}$$

It can be observed that, from the stoichiometry of the reaction, 1 mole of alum reacts with 2 moles of phosphate, but practically the amount of alum to be used is 1.5-2 times greater. This evidence is ascribed to the large number of competitive reactions which are basically dependent on the nature of wastewater and on the engineering aspects of the process. For this reason, this reaction is more complex and must be considered in light of the most important factors that affect the amount of precipitating reagent, i.e. the alkalinity, ionic strength, pH, the quantity and nature of the suspended solids, the presence of microorganisms or colloidal species, the intensity of mixing, the time of hydraulic residence and the age of the sludge (Beccari et al., 1993).

Another reaction may also occur, although less favorable from thermodynamic and kinetic point of view (Beccari et al., 1993; Jenkins et al., 1971) is that showed in reaction 3.4:

$$Al_2(SO_4)_3 \bullet 14H_2O + 6HCO_3^{-} \leftrightarrow 2Al(OH)_3 + 6CO_2 + 14\,H_2O + 3SO_4^{2-} \qquad \text{(R. 3.4)}$$

The coagulant dosage is a function of the phosphate removal required. Optimum pH is in the range of 5.5-6.5, and it can be reduced by exploiting the acid hydrolysis of the aluminum sulphate which can be obtained by the addition of a higher dosage of alum, dosage dependent on the alkalinity of the discharge.

The coagulation efficiency decreases as the P concentration decreases, accordingly, with a coagulant dosage in the range of 50-200 mg /L, about 80-90% of P removal efficiency can be achieved.

Ferric and ferrous ions in the form of chlorides and sulphates are widely used for the precipitation of phosphates from wastewater (H. Wu et al., 2015) by reactions 3.5 and 3.6 (Beccari et al., 1993):

$$FeCl_3 + PO_4^{3-} \leftrightarrow FePO_4 + 3Cl^- \qquad (R.\ 3.5)$$

$$FeCl_3 + 3HCO_3^- \leftrightarrow Fe(OH)_3 + 3CO_2 + 3Cl^- \qquad (R.\ 3.6)$$

From the reaction stoichiometry, the molar ratio between ferric chloride and phosphate is equal to 1:1 but, also in this case (and for the same reasons), practically the amount of ferric chloride to be used is 1.5-2 times greater.

The optimum ferric ions pH of precipitation is in the range of 4.5-5.5, but good removal efficiencies can be observed at higher values. Ferrous sulphate and chloride are efficient coagulants although phosphate precipitation occurs only after oxidation of the ferrous ion to ferric ion.

Iron salts are cheaper than aluminum salts and produce sludges which can be easily dehydrated, on the other hand lower removal efficiencies are obtained and problems of corrosion (acid hydrolysis of the salts) together with a colored effluent can be observed.

Moreover, aluminum and iron ions are not suitable as precipitators for application as fertilizers (Petzet & Cornel, 2012) because phosphate cannot be recovered since it is strongly bound in the sludge, thus generating little phosphate release with a remarkable increase of waste disposal costs and problems of soil nutrient uptake (Mehta et al., 2015; Petzet & Cornel, 2012).

## *3.2. BIOLOGICAL METHODS*

As already reported, P is present in DNA, RNA and ATP molecules. Thus, all known forms of life need P for their survival. For this reason, many P removing treatments are based on biological processes based on the accumulation of P in the biomass, which is subsequently removed from the water. As an example, in a conventional activated sludge (CAS) system P is uptake by microorganisms for catabolism or adsorbed on extracellular polymeric substances (EPS). The amount of P removed in a CAS system is only 7-18 g P per kg COD removed, resulting in a 20-30% reduction of the influent TP concentration (Henze et al., 1997). However, in the last decades, the scientific community has undertaken action to purpose more efficient biological P-removal treatments. Specifically, some unconventional biological P-removal processes are listed in Table 3.1, 3.2, 3.3. More details about these treatments are explained in the following paragraphs.

| Process configuration | Location | Removal efficiency (%) | Reference |
|---|---|---|---|
| $A^2O$ | Moscow (USA) | 91.2-99.1 | (Coats et al., 2017) |
| MUCT | Madison(USA) | >75 | (Zilles, Hung, et al., 2002) |
| Orbal | Mazomanie (USA) | 87.3 | (Zilles, Peccia, et al., 2002) |
| $A^2O$ | Thorneside (Australia) | 72.7 | (Pijuan et al., 2008) |
| 5-stage Bardenpho | (Australia) | >95 | |
| $A^2O$ | (China) | 96-96.8 | (J. Wang et al., 2014) |
| Inverted $A^2O$ | (China) | 95.4-97 | |
| MUCT | (Australia) | 52 | (Beer et al., 2006) |
| 3-stage Bardenpho | (Australia) | 96 | |
| Carousel/UCT | (Australia) | 99.2 | |
| 3-stage Bardenpho | (Australia) | 88 | |
| MUCT | (Australia) | 97.3 | |
| Carousel/UCT | (Australia) | 75 | |
| MUCT | (Australia) | <80 | |
| MUCT | (Australia) | 98.3 | |
| MUCT | (Australia) | 83.3 | |
| Side-stream RAS | Apex (USA) | 94.4 | (Onnis-Hayden et al., 2020) |
| Side-stream RAS plus carbon | West Kelowna (Canada) | 97.1 | |
| Modified Johannesburg with SSM | Cedar Creek (USA) | 67 | |
| Johannesburg with UMIF | Henderson (USA) | 91.6 | |
| Carousel MUCT | Hardenberg (The Netherlands) | 94.5 | (López-Vázquez et al., 2008) |
| Carousel MUCT | Deventer (The Netherlands) | 87.1 | |

| Process configuration | Location | Removal efficiency (%) | Reference |
|---|---|---|---|
| Carousel $A^2O$ | Katwoude (The Netherlands) | 95.6 | |
| Carousel $A^2O$ | Hoek van Holland (The Netherlands) | 92.9 | |
| Carousel $A^2O$ | Venlo (The Netherlands) | 97 | |
| $A^2O$ | Waarde (The Netherlands) | 90 | |
| Sidestream P-stripping | Haarlem Waarderpolder (The Netherlands) | 95 | |
| 5-stage step feeding | (Singapore) | 80.7 | (Qiu et al., 2019) |
| $A^2O$ | (Singapore) | 100 | |
| Inverted $A^2O$ | (Singapore) | 76.8 | |
| $A^2O$ | Lisbon (Portugal) | 43 | (Lanham et al., 2013) |
| $A^2O$ | Setúbal (Portugal) | 85 | |
| $A^2O$ | Hjørring (Denmark) | 92 | |
| Biodenitro® configuration with side-stream RAS | Aalborg (Denmark) | 94 | |
| Biodenitro® configuration with side-stream RAS | Aalborg (Denmark) | 96 | |
| A2O plus primary sludge fermentate | Hillsboro (USA) | 82 | (D. Wang et al., 2019) |
| Side-stream RAS plus primary sludge fermentate (S2EBPR) with continuous mixing | Hillsboro (USA) | 84 | |
| Side-stream RAS plus primary sludge fermentate (S2EBPR) with intermittent mixing | Hillsboro (USA) | 93 | |

Table 3.1. Full-scale applications of suspended biomass biological systems for P removal.

| Process configuration | Location | Removal efficiency (%) | Reference |
|---|---|---|---|
| AGS | Garmerwolde (The Netherlands) | 86.6 | (Pronk et al., 2015) |
| AGS | Lubawa (Poland) | 95 | (Świątczak & Cydzik-Kwiatkowska, 2018) |
| AGS | Epe (The Netherlands) | 98 | (Toja Ortega et al., 2021) |
| AGS | Gansbai (South Africa) | 82 | (Giesen et al., 2013) |
| AGS | Ryki (Poland) | 94.7 | (Giesen et al., 2016) |
| IFAS-EBPR | Denver (USA) | >88 | (Onnis-Hayden et al., 2011) |
| IFAS-EBPR | (China) | 81 | (Bai et al., 2016) |
| IFAS-EBPR | Guri (South Korea) | 48.3 | (Kwon et al., 2010) |
| Biofilm carriers-A2O | Xi'an (China) | 97 | (Xiao et al., 2016) |

Table 3.2. Biofilm-based applications for full-scale P removal.

| Process configuration | Location | Removal efficiency (%) | Reference |
|---|---|---|---|
| HRAP | Christchurch (New Zealand) | 22-49 | (Sutherland et al., 2014) |
| HRAP | Cambridge (New Zealand) | 32.7-51.9 | (Sutherland et al., 2017) |
| HRAP | Rabat (Morocco) | 66 | (El Hamouri, 2009) |
| Algal pond | Thessaloniki City (Greece) | 26-65 | (Papadopoulos et al., 2014) |
| Algal pond | Lawrence (USA) | <90.6 | (Sturm & Lamer, 2011) |

Table 3.3. Algae-based biological systems for P removal at full- and pilot-scale.

### *3.2.1. BIOLOGICAL P REMOVAL BY SUSPENDED BIOMASS PROCESSES*

To increase the efficiency of P removal up to 90%, the adoption of intermittent anaerobic/aerobic conditions and the development of a phosphorous accumulating organism (PAO) enriched culture was already proposed in the second half of the seventies (Barnard, 1974; Nicholls & Osborn, 1979). This process, known as EBPR, is mainly facilitated by some specialized microorganisms, such as Tetrasphaera- and Accumulibacter-related organisms, which respectively constitute the 27-35% and the 3-24% of the total biomass volume (Cydzik-Kwiatkowska & Zielińska, 2016; Stokholm-Bjerregaard et al., 2017). The behavior of these microorganisms is a controversial topic, and it is still being studied. However, the points that seem to be recognized by the whole scientific community are reported below and depicted in Figure 3.1.

Under anaerobic conditions, Tetrasphaera-related microorganisms can assimilate some rapidly biodegradable substrates (RBS) (such as glucose, glutamate, aspartate, and glycine) to ferment them and synthetize glycogen and new cells (Marques et al., 2017). Both RBS fermentation and polyphosphate (Poly-P) degradation provide the required energy, with a consequent release of phosphates and low molecular weight organic compounds (such as lactate, acetate, and succinate) (Nguyen et al., 2011). The last are adsorbed and stored as polyhydroxyalkanoates (PHA) in the cells of Accumulibacter-type bacteria thanks to the energy deriving from both the hydrolysis of Poly-P and the glycolysis of intracellular glycogen (He & McMahon, 2011). Both Tetrasphaera-related microorganisms and bacteria associated to Accumulibacter release phosphates during the anaerobic step due to the hydrolysis of Poly-P. Due to the scarcity of exogenous energy and carbon sources being already depleted during the anaerobic phase, during the subsequent anoxic and/or aerobic phase the stored glycogen and PHA are oxidized aerobically or anoxically to provide carbon and energy required for the production of new cells and for assimilation of phosphates and the consequent restoration of Poly-P reserve (Kristiansen et al., 2013).

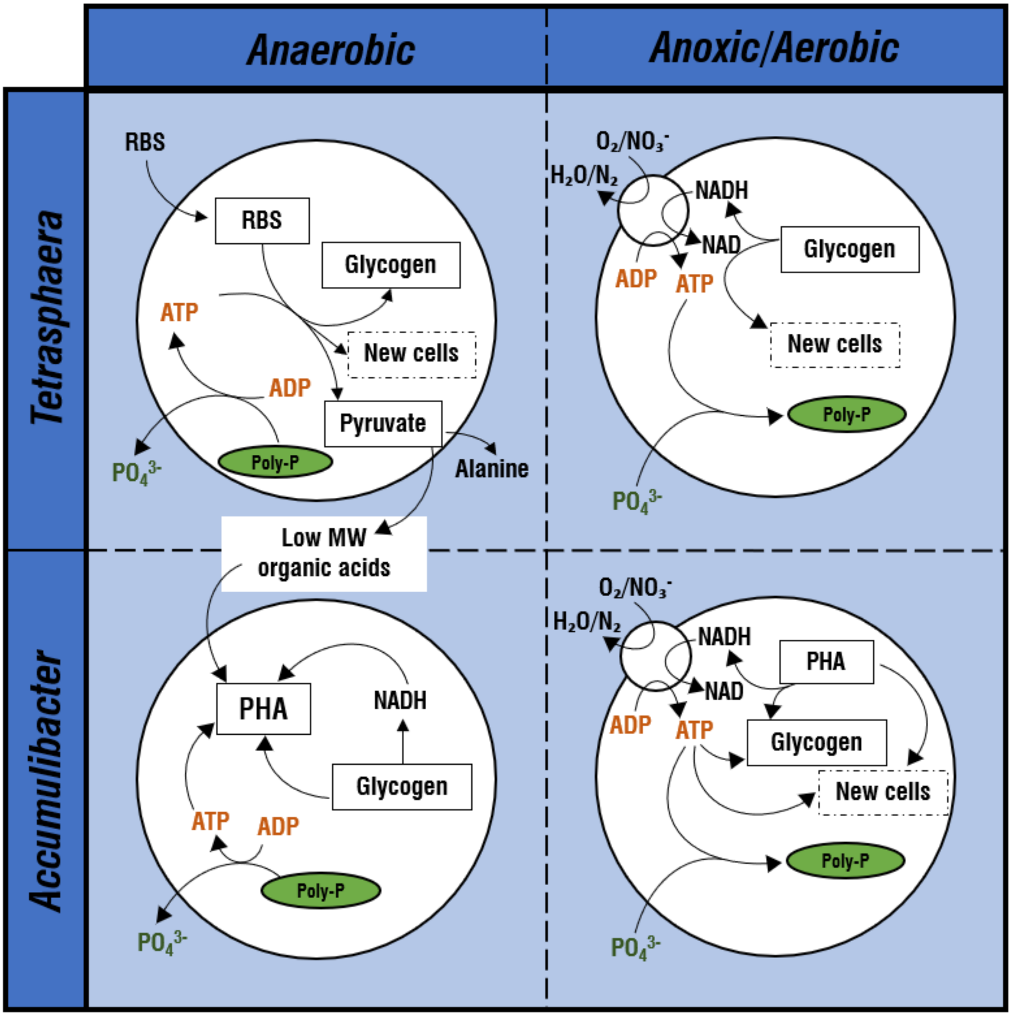


Figure 3.1. Short description of the micro-organisms Tetrasphaera and Accumulibacter in an EBPR system.

Phosphate uptake under aerobic conditions exceed the amount released during the anaerobic phase, resulting in a net P uptake also defined as *luxury* uptake. The so called denitrifying PAO (DPAO), that are bacteria capable of anoxic oxidation of stored carbon compounds, include both Tetrasphaera- and Accumulibacter-related microorganisms, although *Tetrasphaera* has shown lower anoxic P uptake compared to *Accumulibacter* (Marques et al., 2018). Both *Tetrasphaera* and *Accumulibacter* contributed for the 24-70% to the TP removed (14.84-37.52 mg P/g TSS) in eight different WWTPs performing EBPR, the rest being attributed to the activity of chemical precipitation and/or unknown PAO (Fernando et al., 2019). P content in the biomass of EBPR systems can reach up to 100 mg P/g TSS (150 mg P/g VSS), that is 6.7 times higher than that typically found in typical activated sludge (around 15 mg P/g TSS and 20 mg P/ g VSS) (Henze et al., 2008).

EBPR in WWTPs is commonly achieved in concomitance with N removal. In order to this, several configurations can be applied, as it shown in Figure 3.2.

Among these, the $A^2O$ configuration is the easiest, as it simply adds to the classical pre-denitrification system an anaerobic basin receiving recycle sludge from the secondary settler. The $NO_3^-$ contained in recycle sludge can be used by denitrifying bacteria to oxidize part of the COD used for the synthesis of PHA (*Accumulibacter*) and glycogen (*Tetrasphaera*) and limit the subsequent aerobic P uptake.

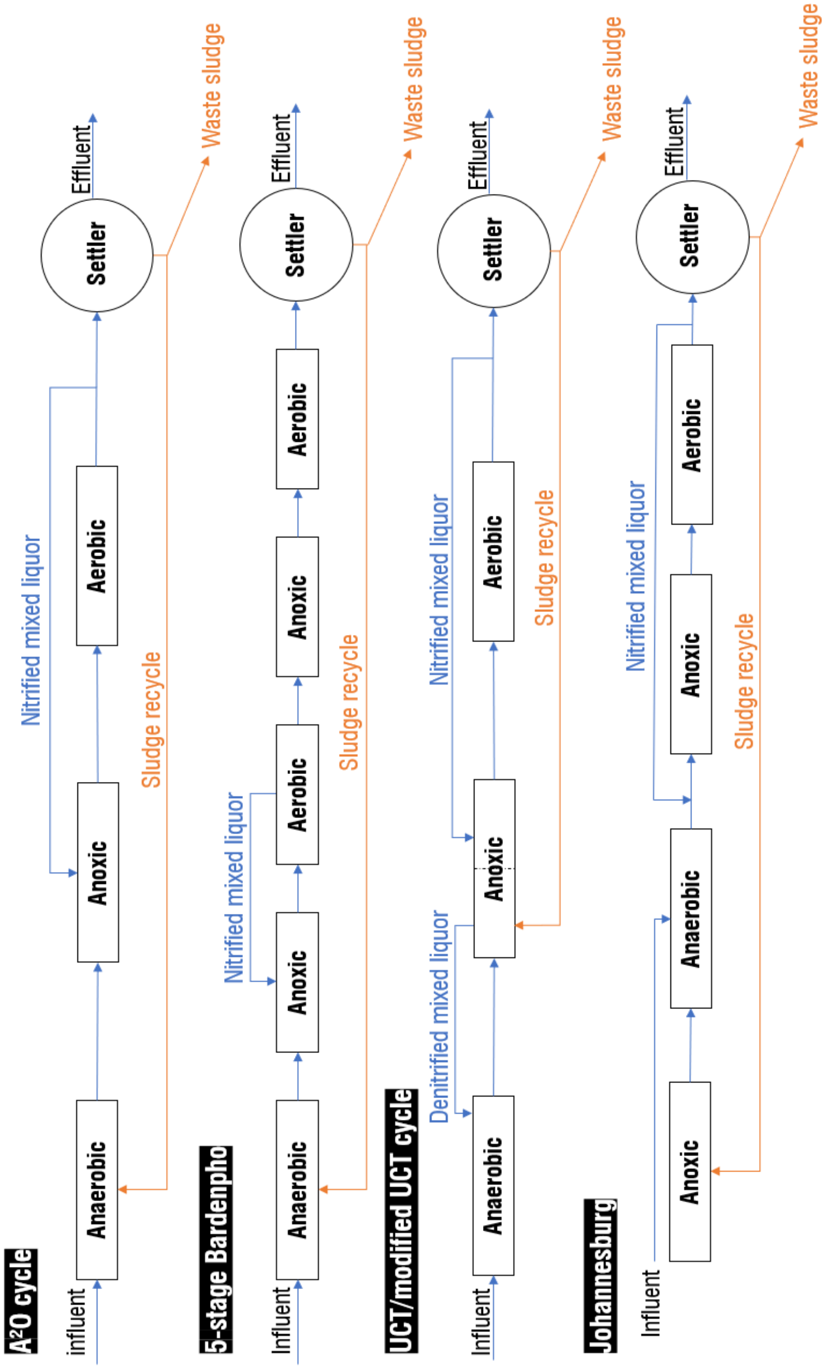


Figure 3.2. WWTP cycles for combined biological P and N removal from wastewater.

### *3.2.2. MICROBIAL BIOFILMS: A SIMPLIFIED APPROACH TO P REMOVAL FROM WASTEWATER*

In the last years, the research focused on alternative technologies with the objective to simplify plant operation and strongly limit the number of basins and recycles required for EBPR while reducing investment and operational costs. In particular, the use of sequencing batch reactor (SBR) has gained increasing interest because allows a full control of operational conditions and the complete removal of P, N and C in a single basin by alternating aeration to non-aeration phases. In order to allow the simultaneous growth of ammonium oxidizing bacteria (AOB), nitrite oxidizing bacteria (NOB), PAO and DPAO, biofilm processes are advantageous compared to suspended-growth systems, as mass transport limitations within the biofilm create ecological niches allowing the coexistence of different types of bacteria**.** The most used biofilm system used for P removal (both from industrial and municipal wastewater) are aerobic granular sludge (AGS) and moving bed film reactor (MBBR).

AGS granules have a core which stays anaerobic under non-aeration phase (feast) and turns partially to aerobic/anoxic during the aeration phase (famine) due to oxygen penetration and NOB activity. On the external layer of the granules (where oxygen is more available) nitrifiers (AOB and NOB) develop, resulting in $NO_x^-$ production which is diffuses into the internal layers of the granule, how is illustrated in the Figure 3.3**.** A recent applications of the AGS technology is the combined removal of phosphorus, nitrogen and carbon from domestic wastewater. Campo et al., 2020 investigated the C/N/P removal performance of AGS treating real domestic wastewater with low C/N as well as the impact of high solid retention time (SRT) on the process. With a lab-scale reactor P removal equal to 96% and C and N removal of 84% and 71%, respectively, was obtained when treating wastewater with molar ratio C/N equal to 3.8, resulting in effluent P concentrations $< 0.1$ mg/L (on average).

Instead, MBBR systems allow the formation of a multi-layered biofilm including nitrifiers, denitrifies, PAO and DPAO. By coupling simultaneous nitrification denitrification

(SND) to EBPR by operating the MBBR in SBR mode and allowing the alternation of aerobic and anaerobic phases is possible obtain the simultaneous removal of carbon and nutrients (Helness & Ødegaard, 2001; Yin et al., 2015). Also, MBBRs have been recently applied in continuous-flow mode for combined removal of P, N and C under stable microaerobic conditions (Iannacone et al., 2019) or by alternating aerobic and microaerobic phases (Iannacone et al., 2020, 2021). Through the alternation of dissolved oxygen (DO) concentration of 0.2-3 mg/L (HRT = 1 d) and feed C/N and C/P of 3.6 and 11, respectively, the highest P removal efficiency (83-86% on average) was achieved, with also complete C removal and N removal equal to 80% via SND (Iannacone et al., 2021). Microbial characterization of the MBBR biofilm strongly suggested that P uptake was mainly carried out by bacteria belonging to the genus *Hydrogenophaga*, which dominated the biofilm microbiome under IA conditions**.** Previous studies reported that when acetate is used as source of organic carbon, *Hydrogenophaga* has the ability to accumulate P under aerobic conditions with an uptake rate comparable to those observed in full-scale EBPR systems (Iannacone et al., 2020; Jørgensen & Pauli, 1995). The organic carbon saved by denitritation ($NO_3^-$ reduction to $NO_2^-$) can support P uptake under low-COD conditions, that is typical of domestic wastewaters, as is suggested from the higher P removal under ia conditions when coupled to shortcut SND than to complete SND (Campo et al., 2020; Chai et al., 2019).

Iannacone et al. (2021, 2020) have proved that the anaerobic phase is not mandatory for P removal from wastewater and this was previously demonstrated by Pijuan et al. (2006), that reports the establishment of feast and famine phases also under aerobic conditions in the presence of acetate: during the feast phase, acetate is stored as PHA within the cells, glycogen is degraded and P-$PO_4^{3-}$ is released from the cells. The famine phase begins when all acetate is consumed and consists in the exploitation of PHA reserves for glycogen and poly-P synthesis, leading to a net P uptake.

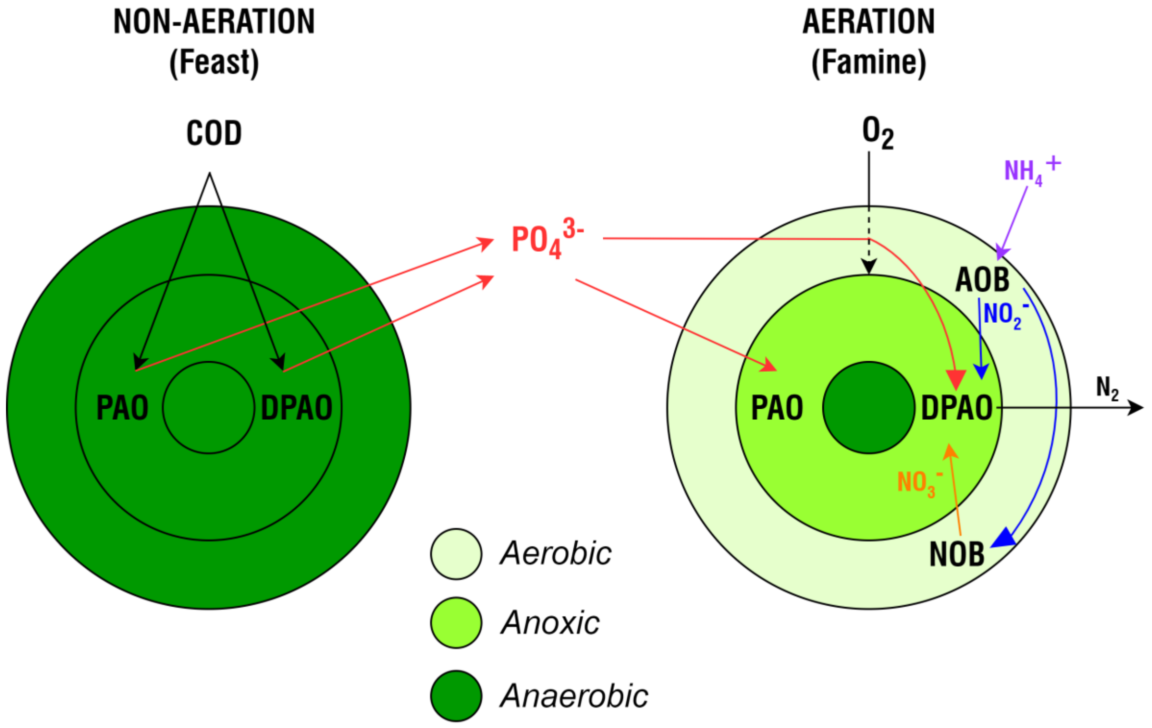


Figure 3.3. Main phosphorus, nitrogen and carbon transformations and layer distribution in an AGS granule during aeration and non-aeration phases.

Even though EBPR can occurs under complete aerobic conditions, the presence of an anaerobic phase could be necessary to produce VFA from complex organic matter typical of real wastewater. The levels of VFA in the feed of most laboratory-scale studies are not representative of those typically occurring in real WWTP influents ($< 100\ mg_{COD}/L$) (Barajas et al., 2002) and, so, is recommended to evaluate the effective P removal efficiency.

### *3.2.3. INTEGRATION OF MICROALGAE INTO WWTP TO ENHANCE P REMOVAL*

Through the development of microalgae-based P removal bioprocesses the use of P as a nutrient for photosynthetic organisms has been exploited. Microalgae, as well as PAO organisms, are able to absorb phosphorus that exceeds the need for growth (which can also be produced by solubilizing organic phosphorus through enzymatic phosphatase) and can store it inside the cell as polyphosphate granules (Bunce et al., 2018). The majority of microalgae-based systems applied at pilot and full scale for P removal consists in open suspended-growth systems, such as raceway open ponds (Chatterjee et al., 2019) and waste stabilization ponds (WSP) (Brown & Shilton, 2014). Using the microalgae for P removal from wastewater it is possible reach many advantages, compared with bacterial-based system. Indeed, microalgae led both to efficient P removal and recovery to $CO_2$ sequestration, in addition to energy generation (e.g. through production of biofuels) and production of organic fertilizer (Badgujar et al., 2020; Suleiman et al., 2020) but actually only a few full-scale microalgae-based system have been operated so far. The main challenges for the integration of microalgae-based systems in WWTP for nutrient removal refer to:

1) high operational costs associated to energy consumption for mixing, $CO_2$ supply and harvesting of microalgae, which are necessary for P removal and recovery (Gouveia et al., 2016)

2) climatic conditions, as cool temperatures ($\leq$ 15°C) can decrease P accumulation (especially as acid insoluble polyphosphate) within the cells (Powell et al., 2009).

To overcome these challenges, the latest research was focused on incorporating microalgae into bacterial systems typically operated in WWTPs. The main advantage of this algae-bacteria symbiosis is that microalgae can contribute to meet $O_2$ need of heterotrophic bacteria working in aeration basin for the degradation of the influent organic substrate, which can significantly reduce energy costs for aeration and mixing (M. Wang et al., 2015). On the other hand, microalgae can capture the $CO_2$ produced by bacterial oxidation of organic matter which turns into higher production of energy and P-rich algae biomass(Cai et al., 2019). Algae-bacteria systems do not require a transition between different operating environments for simultaneous removal of carbon and nutrients since they directly assimilate both N and P for cell growth and metabolic function, reducing the complexity of the treatment configuration. Direct N assimilation also results in lower $N_2O$ production which, combined with concomitant $CO_2$ capture, results in lower greenhouse gas emissions (Alcántara et al., 2015). The relationship between algae and bacteria can significantly decrease the costs related to the application of microalgae for wastewater treatments. For example, the costs for aeration can be reduced since $CO_2$ is supply by bacterial metabolism, in addition to the consequent reduction of $CO_2$ losses in the atmosphere. Mohsenpour et al., 2021 have shown that integration of integration of microalgae in a municipal WWTP leads to enhance to secondary treatment: indeed, the primary settling effluents feature a more balanced C/N/P ratio and higher nutrient concentrations to support microalgae growth compared to secondary treatment effluent. Microalgae culture and physical-chemical conditions should be accurately selected and maintained inside the system with the aim to establish a successful microalgae-bacteria symbiosis. Microalgae belonging to *Chlorella* and *Scenedesmus* have been successfully applied for P removal from municipal wastewater (3.8-7.5 mg P-$PO_4^{3-}$/L), resulting in removal efficiencies up to 100% for P and 98% for N in a pilot-scale photobioreactor, with respect to the effluent discharge standards of Directive 98/15/CE (Gouveia et al., 2016).

Illumination period and intensity should guarantee optimal growth of microalgae to avoid increase of the bacteria/algae ratio. Low light intensity may cause the proliferation of nitrifying bacteria, causing $NO_3^-$ and $NO_2^-$ accumulation in the system and reducing TN removal, although P removal seems less affected (González-Camejo et al., 2018). The optimal pH range to sustain growth of both microalgae and bacteria is between 7 and 9. Higher values may lead to $CO_2$ consumption by microalgae and could compromise bacterial growth that then provide less $CO_2$ supporting the growth of microalgae, reducing P removal from wastewater. With cultures of *Chlorella* and *Scenedesmus* could be reached significant P removal a temperature of, respectively, 15°C (Filippino et al., 2015) and 5°C (Chatterjee et al., 2019), that are lower than the optimal temperature (28-30°C) for the growth of microalgae, suggested by Park et al. (2009).

In order to reduce the operational costs and promote the application at real scale, recent studies are focussing on the optimization of microalgae-bacteria system. Microalgae separation and harvesting (generally performed via centrifugation, filtration, coagulant/flocculation, gravity sedimentation and flotation) is represents one of the main costs (Xia et al., 2017). To solve this issue, microalgae can be collected from the support material (as flat panels) or by harvesting the gel matrixes in which they are incorporated. Anyway, the support materials require high capital costs for their purchase and, in addition, the application of microalgae biofilm need a high surface for the development of biofilm (Mohsenpour et al., 2021).

An alternative strategy is to generate microalgae-bacteria granules. Cai et al. (2019) achieved stable granulation with microalgae in a SBR treating synthetic domestic wastewater after 60-day operation. Granule development seems particularly advantageous for P sequestration, as P content of the granules was as high as 33.4 $mg/g_{TSS}$, being 1.64 times higher than that of seed microalgae. In addition, the microalgae-bacterial granules showed a higher fraction (91.8%) of bioavailable P, i.e., organic P and non-apatite inorganic P, compared to that (89.2%) of the seed algae, showing great potential of harvested granules as agricultural fertilizer. Process scale-up is required to test the effect of real wastewater and fluctuation in the influent quality and flow rate on granule stability, as well as capital and operating costs of the algae-bacteria AGS system.

Full- and pilot-scale studies recently focussed on demonstrating the economic feasibility of applying microalgae-bacteria consortia in open systems for treatment of WWTP streams. Mantovani et al. (2020) showed that the application of an open raceway pond for the side-stream treatment of the centrate produced from a WWTP sludge streamline led to P and N removal both higher than 70% (on average) and nearly satisfied oxygen demand for nitrification.

Tua et al. (2021) indicated agricultural recovery of the produced biomass as a better option for nutrient reuse than incineration based on a comparative life cycle assessment (LCA) evaluating 15 environmental indicators.

# *CHAPTER 4. PHOSPHOROUS RECOVERY METHODS*

*This chapter has, in part, resulted in the review entitled "Phosphorous removal and recovery from urban wastewater: Current practices and new directions" by Di Capua,* ***de Sario****, Ferraro, Petrella, Race, Pirozzi, Fratino, Spasiano (Science of The Total Environment, 153750, 2022)* (Di Capua et al., 2022).

As previously stated, P removal from wastewater and WWTP sludge is crucial to avoid negative impact on the aquatic environment due to the occurrence of eutrophication phenomena. Besides, another fundamental aspect is the potential benefits that derive from the reuse of the removed P, through its recovery. In the literature many patented treatment systems for P recovery are reported, some of them also tested on the real municipal WWTP streams. These processes are distinguished by the treatments from which P is recovered (liquid or solid phase).

## *4.1. PHOSPHOROUS RECOVERY FROM THE LIQUID STREAMS*

P recovery from municipal WWTP can be performed both on liquid fraction of the sludge and on the sludge/sludge ash. Liquid fraction of anaerobically digested or hydrolyzed sewage sludge obtained post dewatering (e.g., centrate or filtrate) are generally P-loaded stream.

### *4.1.1. CRYSTALLIZATION TECHNOLOGIES*

Accounting for the P recovery from the liquid phase, one of the main processes among the available technologies is represented by the **crystallization** (Chrispim et al., 2019). An example is provided by the Crystalactor® water treatment technology of Royal HaskoningDHV (Figure 4.1). This system provides crystallization of a determined component through a fluidized-bed reactor (FBR). During the crystallization process, the size of the reactor filling material increased, and the resulting heavier material settles to the reactor bottom. With the aim to obtain P recovery in form of calcium/magnesium phosphate or struvite, an adequate reagent dosage (for example lime and $Mg(OH)_2$) must be provided for an adequate crystallization rate. Main advantages deriving from this technology are represented by the combination in one stage of the conventional steps constituting the precipitation process i.e., coagulation, flocculation, separation of the produced sludge and its dewatering. Water-free pellets can be produced leading to the elimination of dewatering treatment and related costs.

P recovery through Crystalactor® technology can reach values up to 40% while typical ranges for recovery systems from digester supernatant are from 10% to 25% of WWTP influent (Egle et al., 2016). However, the higher efficiency observed with the Crystalactor® technology can be achievable if EPBR process is expected in the WWTP. This technology is most suitable for treatment of flows with above 25 $mgPO_4^{3-}P$ /L.

Good recovery percentage up to 30% is also reported for a further crystallization system represented by the patented Ostara Pearl® technology, schematized in figure 4.2 (Chrispim et al., 2019). In this case, phosphorous is recovered solely as struvite through a FBR named as “Pearl” in which magnesium salts are added for struvite crystallization, in addition to sodium hydroxide for the pH adjust (if necessary). The struvite obtained has been commercialized under the name of Crystal Green®. In small WWTPs and farms are already applied the Multifom Harvest™ process in which a cone shaped FBR is used for the struvite crystallization, using the addition of sodium hydroxide and magnesium chloride.

Alternatively to the fluidized-bed systems, P-RoC® process carried out in both fixed-bed and stirred reactors also proved feasible P recovery from supernatant digester especially referring to the fixed-bed configuration (Berg et al., 2007). In this process, crystallization is achieved using calcium silicate hydrate (CSH) or synthesized pellets of tobermorite. The obtained product displayed a P total yield of 10-11% which was comparable to the common values for a commercial NPK 12-24-12 fertilizer (total P equal to 10.5%) as well as natural P-rocks (Berg et al., 2007; Green, 2015).

In alternative, the NuReSys® (figure 4.3) is carried out in two CSTRs, i.e., a stripper for pH and scaling control and a reactor with $MgCl_2$ addition to promote active formation of struvite pellets (Bio-Stru®). NuReSys® has been successfully applied at full-scale selectively on centrate and digested sludge (5–6% TS) of municipal WWTP as well as on both streams sequentially through a hybrid configuration, resulting in P recovery higher than 86% (Dewaele, 2015).

Combining biological COD removal to chemical P removal in an aerated CSTR, Pasques has developed the PHOSPAQ™ process (figure 4.4): aeration provides oxygen for biological COD oxidation to $CO_2$, leading to increase of pH up to 8.2-8.3, favoring the struvite formation through the magnesium oxide addition.

Further solution for phosphorous recovery from the liquid phase is provided by the REM-NUT® technology. In this case, the phosphate removed through a selective ion-exchange is then recovered from the spent regeneration liquid of the ion-exchange with chemical precipitation as struvite (Liberti et al., 2001). Despite the main hindrance of the process could be related to the selection of proper ion-exchangers for selective removal of phosphorus, P percentage in the precipitated still varies in values range (i.e. 10-12%) typically observed for the struvite (Egle et al., 2016; Petruzzelli et al., 2004). This technology has never been applied at full scale for the high costs linked to the ion-exchangers.

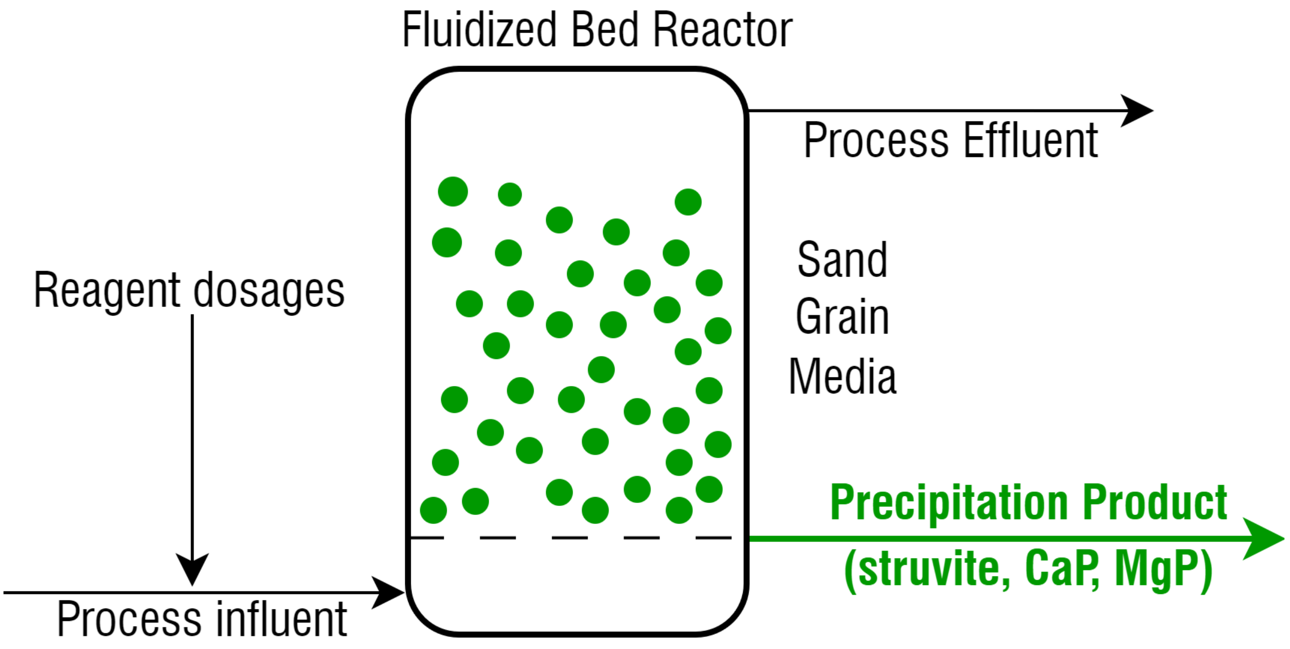


Figure 4.1. Diagram of the Crystalactor® process flow.

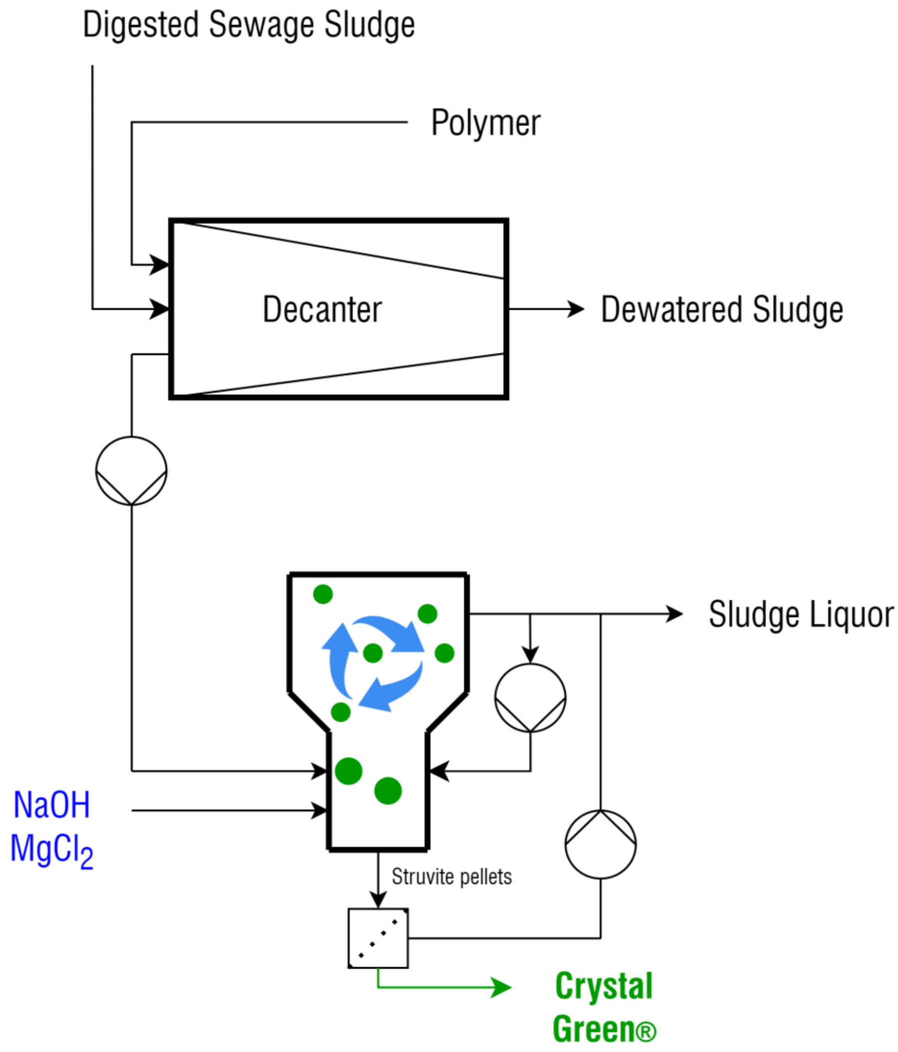


Figure 4.2. Diagram of the Ostara Pearl® technology.

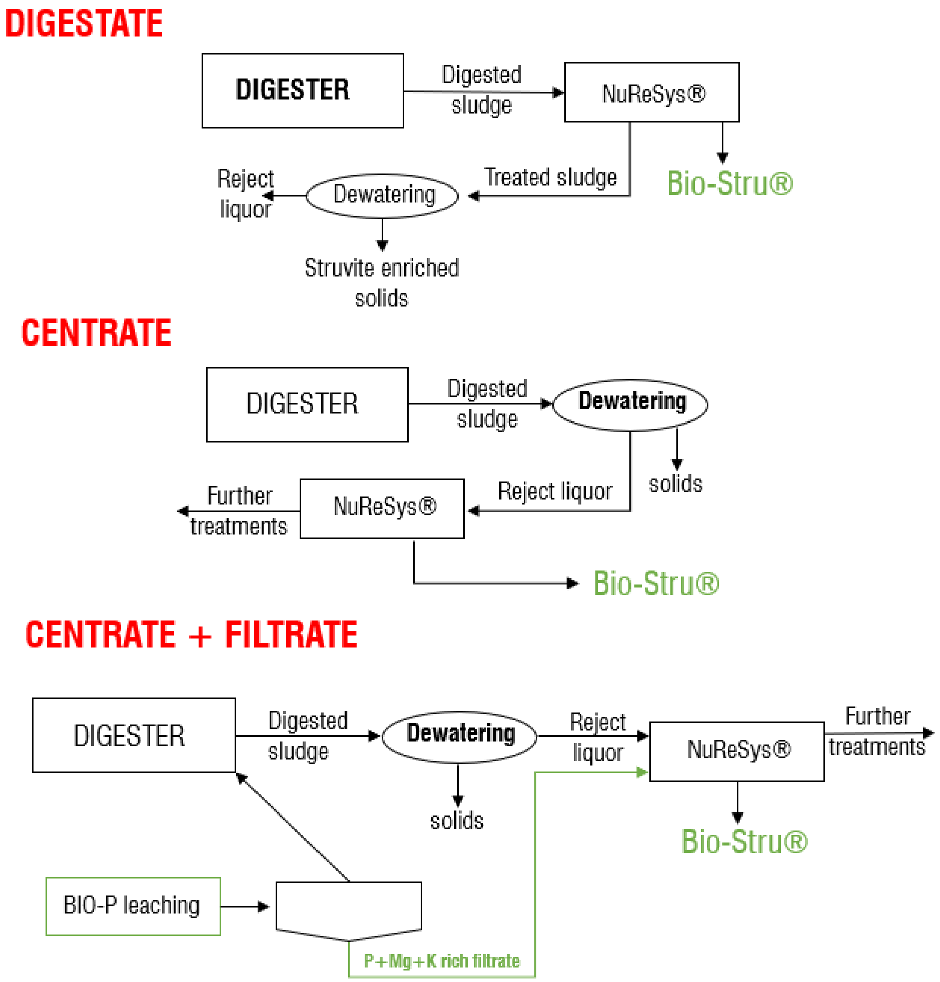


Figure 4.3. Application of NuReSys® technology on digestate, centrate and filtrate of WWTP.

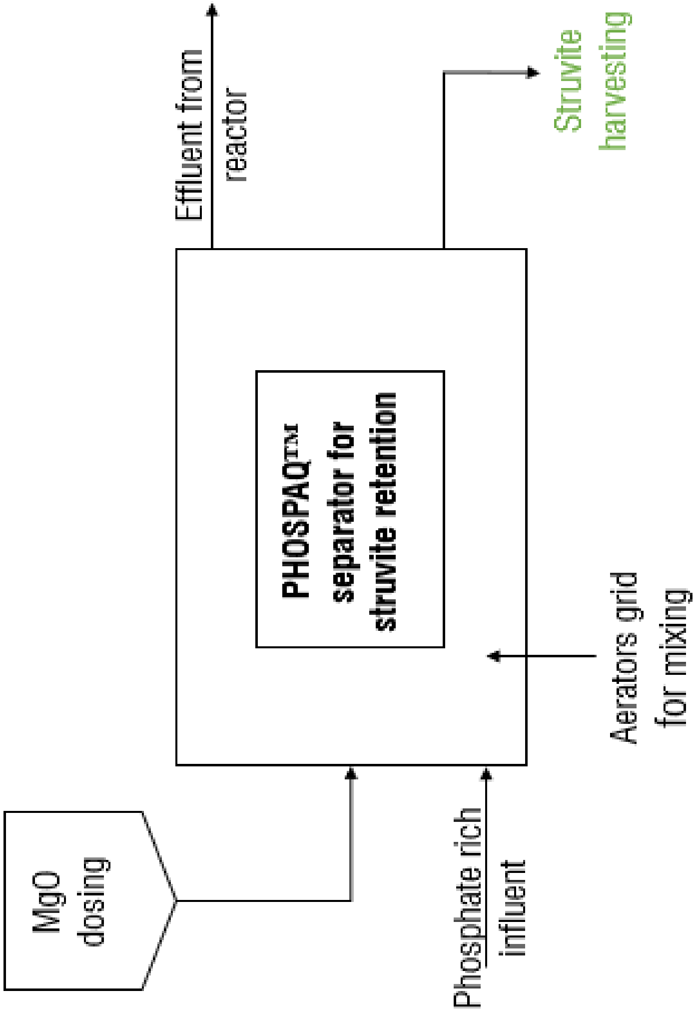


Figure 4.4. PHOSPAQ process.

### *4.1.2. SORPTION*

Sorption is another possible strategy to recover phosphorous from the liquid fraction of the sewage sludge. The sorption process represents a combination of chemical and physical mechanisms in which atoms, ions or molecules tend to adhere to a surface. It's a surface phenomenon characterized by the formation of an adsorbate film after interaction with the sorbent functional groups, the amount and position of which can influence the resulting bonds and type of sorption (McKay, 1996). The differences between chemical and physical sorption are illustrated in the Table 4.1.

| Chemical sorption | Physical sorption |
|---|---|
| Irreversible | Reversible |
| Requires high energy | Attributed to Van der Waals and electrostatic forces |
| Favored by low temperature | Favored by high temperature |

Table 4.1. Differences between chemical and physical sorption

Important parameters of the process are the pH of the solution which controls the sorption capacities, the contact time and the increase of sorbent dosage which was demonstrated to increase the phosphate removal until maximum values were reached (Ajmal et al., 2018; Ismail, 2012; Kumar & Viswanathan, 2017a, 2017b, 2018; Micháleková-Richveisová et al., 2017; Xu et al., 2009; Yue et al., 2010). Moreover, the phosphate concentration influences the uptake capacity which decreases with the increase of the contaminant in solution (Mezenner & Bensmaili, 2009; Xu et al., 2009), and the sorbent size influences the phosphate removal because smaller particles allow to reduce internal diffusional and mass transfer limitations (Eberhardt & Min, 2008). Finally, this process is affected by the increase of the temperature which increases the particle transport favored by a decrease of water viscosity (Kumar & Viswanathan, 2017a, 2017b, 2018; Mor et al., 2017; Nur et al., 2014). In addition, this process can be also affected by competing ions, such as sulphates rather than nitrates, which may limit the P removal efficiency (Sansalone & Ma, 2009; T. Wu & Sansalone, 2013).

High sorption capacities and low costs are required, together with easy desorption of the contaminants from the surface and regeneration of the reference materials.

P removal occur through double-step mechanism constituted by sorption and precipitation.

Phosphate sorption mechanism depends on the sorbent characteristics and on the operative conditions and can be represented by (i) ion exchange, (ii) ligand exchange, (iii) hydrogen bonding, (iv) surface precipitation and (v) diffusion of the contaminant into the sorbent (Loganathan et al., 2014).

Ion exchange is based on the exchange of mobile ions of a solid matrix with ions of the solution having similar electrical charge (outer-sphere surface complexation). The mechanism relies on electrostatic attractive forces between sorbent and ions which, after physical sorption, retain the inner hydration shell. The ion exchangers are made of high molecular weight polymers that does not give rise to the formation of homogeneous solutions with the different solvents. Ions of higher valency, higher concentration and smaller hydrated radius are preferentially sorbed by the ion exchangers (Helfferich, 1962). Characteristics of the ion exchange process is the reversibility of the process by which the solid ion exchanger can be regenerated.

The ligand exchange mechanism is based on a chemical bond at the sorbent surface between phosphate ions and a metal ion, with a release of other ions (i.e. $OH^-$) formerly bonded to the cation (inner sphere surface complexation) (Almasri et al., 2019; B. Zhang et al., 2018). The sorbents show high sorption efficiencies together with high anions selectivity, also in very dilute solutions.

Hydrogen bond is an intermolecular force which can explain the mechanism of phosphate sorption on metal oxides and organic molecules (B. Wu et al., 2020). It is stronger than Van der Waals interactions but weaker than covalent bonds. Specifically, a hydrogen atom is involved in a covalent bond with very electronegative elements (such as fluorine (F), oxygen (O), nitrogen (N)), which attract to themselves the valence electrons, acquiring a partial negative charge (δ-) and leaving the hydrogen with a partial positive charge (δ+). At the same time, hydrogen is bonded to an electronegative atom of a nearby molecule.

Phosphate anions can be removed from water and wastewater by metal phosphates precipitation onto the sorbent surface also with concentrations of the reactants lower than the precipitation values in solution. Phosphate precipitates containing metals, such as Ca, Fe, Al, and Zn, on the surface of specific sorbents were observed (Marshall et al., 2017; X. Wang et al., 2017).

Phosphate removal by intraparticle diffusion is characterized by a fast sorption which, after equilibrium at the liquid/solid interface (film diffusion), is followed by a slower process in which the contaminant moves into the internal pores of the sorbent (pore diffusion) (Pan et al., 2017; Zhong et al., 2019).

Sorbents are of natural origin as zeolites, clays, oxides and biopolymers or derive from industrial and activation processes which are more efficient because produced under controlled procedures and with more stable properties. Specifically, phosphate sorbents are classified as organic sorbents, industrial by-products and biological sorbents.

#### *4.1.2.1. ORGANIC SORBENTS*

Ion-exchange resins are widely used as phosphate sorbents. They are characterize by a polymeric matrix with a few mm granulometry (Helfferich, 1962). These resins are largely used in many chemical engineering applications, as in the water demineralization processes. There are numerous resins for ion exchange, most of which are based on polystyrene, generally cross-linked with divinylbenzene, to which are then added functional groups able of capturing or releasing ions. The resins can be cationic (able to exchange cations) with acidic functional constituents (commonly sulfonic or carboxylic) or anionics (able to exchange anions) with basic functional constituents (amine). The working cycle of a resin consists of the

- exercise phase, also called *exhaustion phase*, during which a replacement of the ions presents on the functional groups with those present in the solution occurs until exhaustion by saturation;
- recharge phase, also called *regeneration phase*, in which the functional groups are recharged with the original ions.

During this process, very low running costs and energy consumption are required, cheap chemicals are used, and resin beds show high durability before replacement.

To remove phosphates from wastewater different resins, as Purolite A500P, Purolite A520E, Purolite FerrIX A33E, Amberlite IRA910Cl and Amberjet 1200Na, Dowex 21K XLT (Nur et al., 2012, 2014; Paul Chen et al., 2002), or magnetic ion exchange (MIEX) and hybrid anion exchange (HAIX) resins, made of anion exchange resin beads and hydrated ferric oxide, could be used (Blaney et al., 2007; Ding et al., 2012; Johir et al., 2011; Nur et al., 2012; Sowmya & Meenakshi, 2013a). Exhausted material can be regenerated by NaCl, NaOH, $CaCl_2$, HCl, and $Na_2CO_3$ (Loganathan et al., 2014) or their mixtures. The subsequent precipitation with calcium/or magnesium salts allows to employ P as fertilizer (Midorikawa et al., 2008; Tsuji et al., 2011).

As an alternative to ion exchange resins, activated carbons (AC) represent a wide range of amorphous carbon-based materials which exhibit low cost, easy availability, high porosity, high specific surface area (from 500 to 2500 $m^2/g$), different functional groups which are very useful for a wide range of processes such as filtration, purification, deodorization and discoloration (Dias et al., 2007; Ioannidou & Zabaniotou, 2007) and, so, these types of sorbents can be used for phosphate removal from water and wastewater (Khalil et al., 2017; W. Xiong et al., 2017; Yao et al., 2018).

Specifically, Khalil et al. (2017) reached a removal efficiency of P from aqueous solution equal to 100% , with a thermal treatment of AC. Xiong et al. (2017) synthesized a novel sorbent by loading zirconium oxide and iron oxide onto activated carbon nanofiber (ACF-ZrFe) simultaneously, estimating a maximum P sorption capacity of 26.3 mg P/g at 25°C. Yao et al. (2018) showed that removal of phosphate from aqueous solution by sewage sludge-based AC loaded with pyrolusite can reach up about 90% of removal rate in a pH range of 4-8.

AC can be produced from almost any organic substances with high carbon content, including wood, peat, coconut shell, etc. by a carbonization process at 600-900°C in an inert atmosphere followed by calcining in oxidizing environment at 600-1200°C, or by chemical impregnation followed by 450-900°C heating (Dias et al., 2007; Gupta et al., 2009; Ioannidou & Zabaniotou, 2007).

The complex internal area of ACs is usually formed of micropores with a diameter lower than 2 nm, mesopores with a diameter in the 2-50 nm range and macropores with a diameter higher than 50 nm. Basically, activated carbon can be found in two forms:

1) a granular activated carbon (GAC) consisting of particles with diameter in the range of 0.2-5 mm;
2) a powdered activated carbon (PAC) with smaller particles ($<0.045$ mm), not easy to be separated from solution.

The AC surface is characterized by the presence of carbonyl, carboxylic, phenolic (hydroxylic), ether, and lactones groups (Chubar, 2010; Faust & Aly, 1987) with type and number which can be modified by thermal and chemical treatments and with positive or negative charges influenced by the pH of the solution (Faust & Aly, 1987; Mahmudov & Huang, 2011).

#### *4.1.2.2. INDUSTRIAL BY-PRODUCT*

The advantage of using industrial by-products for the P recovery by sorption is that a waste is reused as secondary raw material for these specific environmental applications (Bhatnagar & Sillanpää, 2011; Gupta et al., 2009; Mohan & Pittman, 2007; Pratt et al., 2007; Westholm, 2006). These sorbents are chemically constituted by oxides, hydroxides, Si, Fe, Al, Mg, Ca, and Ti carbonates and derived from i.e. power plant, mining and steel industry (Goscianska et al., 2018; Guo et al., 2018; Kim et al., 2020):

▪ **Red mud** is obtained during the alumina production process after the caustic digestion of bauxite, where aluminum oxide is extracted under high temperature and pressure (de Souza et al., 2013). The chemical composition of red mud is based on aluminum oxide, iron oxide, titanium oxide, silicon oxide and calcium oxide (Pontikes & Angelopoulos, 2013). The phosphate sorption capacities of this material can be obtained by activation before use as a sorbent. Methods for the activation of red mud are acidification, neutralization, and thermal treatment (Howe et al., 2011).

- **Slags** are industrial wastes derived from the steel factory and used for phosphate removal from wastewater thanks to the presence of Ca, Fe, Al, Mg, and Mn oxides (Bowden et al., 2009; Westholm, 2006; Xue et al., 2009). These materials are produced in a basic oxygen furnace, blast furnace slag or electric arc furnace. Recently, a lot of studies have used slag as an alternative sorbent for phosphate removal with different findings depending on the methods of production, on the chemical and physical characteristics of the reference waste as surface area and surface structure, on the different sorbent treatments (milling, acid treatments) and modification (lime, Ti/Al modified slags), on pH and temperature (Blanco et al., 2016; Bowden et al., 2009; Gong et al., 2009; Han et al., 2016; Johansson, 1999; Kostura et al., 2005; Oguz, 2004; J. H. Park et al., 2017; Pradhan et al., 1998; J. Xiong et al., 2008; Xue et al., 2009; Yu et al., 2015).
- **Fly ash** is a by-product of coal-fired power plants and is the lighter part of coal ash, characterized by particles in the range of microns and showing pozzolanic properties (S. Gu et al., 2021). The use of fly ash in wastewater treatments has been extensively studied in recent years (Goscianska et al., 2018; Hermassi et al., 2017; Kim et al., 2020; S. Li et al., 2017) and it was concluded that this material is a good phosphate sorbent by a combined mechanism of sorption and precipitation of i.e. hydroxyapatite due to Ca dissolved from fly ash (Cheung & Venkitachalam, 2000; Lu et al., 2009; Oguz, 2005; Ugurlu & Salman, 1998), also improved by acid and thermal treatments which increase the sorbent surface area (Y. Li et al., 2006; Lu et al., 2009), but also of insoluble Al and Fe phosphates (Grubb et al., 2000).

Ligand exchange and surface precipitation are the predominant mechanism and removal capacity depends on the material compositions and their granulometry and porosity, as well as the methodology adopted.

#### *4.1.2.3. BIOLOGICAL SORBENTS*

Agricultural wastes are low-cost biological sorbents able to remove phosphate from wastewater. The surface properties and the porosity of these materials can be improved after activated carbon conversion or chemical modification of the structure. Specifically, efficient anion exchangers are obtained by grafting amine groups onto wheat straw (Xu et al., 2010), whereas chemical treatments may increase the porosity and the number of functional groups as in the case of saw dust from woodworking operations (Benyoucef & Amrani, 2011). Organic wastes with quantitative presence of iron showed good retention capacities of the phosphates (Field et al., 2019; Zou et al., 2017). The European Biochar Certificate defines biochar as "[…] a heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of sustainably obtained biomass under controlled conditions with clean technology and is used for any purpose that does not involve its rapid mineralization to $CO_2$ and may eventually become a soil amendment […]" (Schmidt, 2015). The negative surface charge of this sorbent has been modified with functional additives, such as $AlCl_3$, $MgCl_2$, and $Fe_3O_4$, in order to obtain efficient phosphate removal (Z. Wang et al., 2015; M. Zhang & Gao, 2013). Efficient organic pollutants and phosphate removal can be observed in the case of sorbents made of iron oxide and biochar and obtained from orange peel powder by $Fe^{3+}/Fe^{2+}$ co-precipitation followed by pyrolysis (B. Chen et al., 2011). Other biological wastes are chitosan beads (Kumar & Viswanathan, 2017b; Liu & Zhang, 2015; Sowmya & Meenakshi, 2013b) mussel shells (Paradelo et al., 2016), egg shells (D. Chen et al., 2016) and oyster shells (Martins et al., 2017).

### 4.2. PHOSPHOROUS RECOVERY FROM SLUDGE

Since 95% of P removed from the influent is estimated to be transferred to the sewage sludge (Cornel & Schaum, 2009), higher P recovery from sludge can be expected compared to the liquid phases. This could promote the strategy of direct sewage sludge spread for land fertilization purposes. However, the main drawback about this practice is indeed represented by the concurrent high amount of other chemicals, such as heavy metals, within the sludge (Pradel & Aissani, 2019). Accordingly, strategies for P recovery from sludge also aim at decreasing the heavy metals content to provide a product feasible for reuse in agriculture without secondary contamination. Gifhorn process (Figure 4.5), for instance, is carried out by a first extraction of phosphorous from solid phase with $H_2SO_4$ addition. Metal precipitation, as sulfides after pH adjustment with NaOH, allows their content reduction and addition of $Mg(OH)_2$ leads to P precipitation and recovery as struvite and calcium phosphate mixed (Rashid et al., 2020). The wet-chemical extraction step observed for the previous process is a general key-point for strategies involved in the P recovery from sewage sludge.

The Stuttgart process (Figure 4.6) is performed through a first acidification step of the sludge similarly to the Gifhorn approach but metal ion separation is achieved with a cation exchange membrane (Güney et al., 2008). The whole process efficiency depends on the chemicals involved and pH conditions for P dissolution. In fact, initial acid leaching step at pH equal to 3 can lead to final P recovery from Stuttgart process higher than 65% in struvite form with low heavy metal content (Meyer et al., 2019).

A different approach is displayed by the Aqua Reci® process in which a supercritical water oxidation step is employed before the acid or alkaline leaching phase. This phase provides total organic matter oxidation simultaneously oxidizing heavy metals to their maximum valency and phosphorus to $P_2O_5$ (Stendahl & Jäfverström, 2004). The resulting ash from the oxidation can further undergo to alkaline leaching to extract phosphorous as sodium phosphate that can be easily precipitated as calcium phosphate by lime addition. Alternatively, acid leaching may be involved, and precipitation may occurs through three neutralization steps that gradually increase pH and recover ferric phosphate, aluminum, iron and heavy metals (Stendahl & Jäfverström, 2004). Although the overall system may lead to a reduction in the volume of sludge which is beneficial for operating costs, it should also be taken into account that previous life cycle analyses have shown significant energy consumption related to the process (Amann et al., 2018). Low pressure wet oxidation at temperature ranging between

160 and 220 °C, pressure of 11.8-27.6 atm and acidic condition (pH=1.5) can be used for sludge oxidation in presence of pure oxygen. This oxidation treatment is identified as the LOPROX system (Hug et al., 1998). LOPROX system followed by two membrane filtration phases has been tested for P recovery from sludge (Blöcher et al., 2012). The first membrane step (ultrafiltration) aims at removing suspended solids from the LOPROX effluent while second nanofiltration leads to P recovery in the membrane permeate. Indeed, in this case, the rate of recovery is strictly related to the ion rejection effects of the nanofiltration membrane on the phosphorous. Then, higher phosphorus recovery is expected with decreasing rejection which can be achieved through diluted acidic solution wash of the nanofiltration (Blöcher et al., 2012). Finally, MEPHREC® metallurgic process (Figure 4.7) allows, among the other processes applied on the sludge, the highest recovery percentage in terms of WWTP-influent (up to 75%) in a final P-rich slag where P is present as calcium silicon phosphates. Nonetheless, during the process, some differences can be present in terms of depollution due to possible variations in the behavior of metals (Egle et al., 2016).

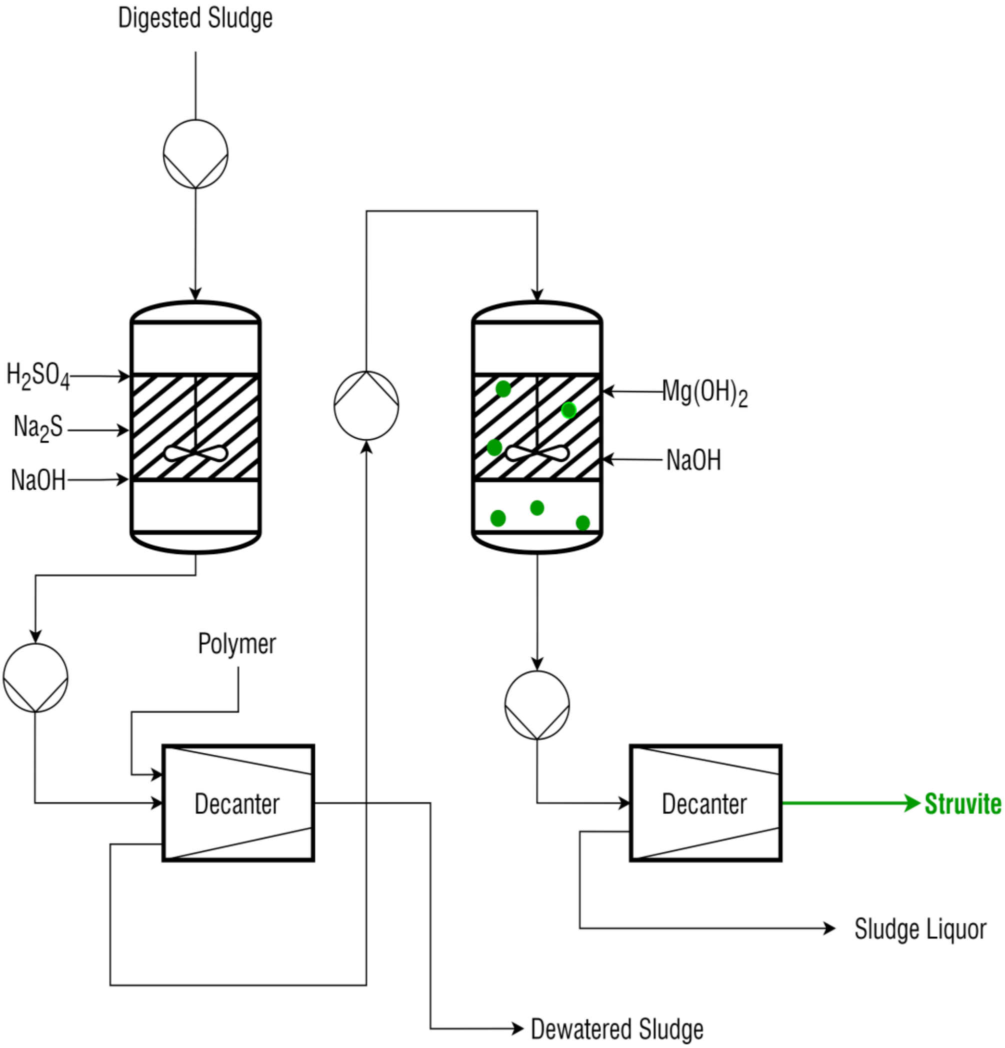


Figure 4.5. Gifhorn process.

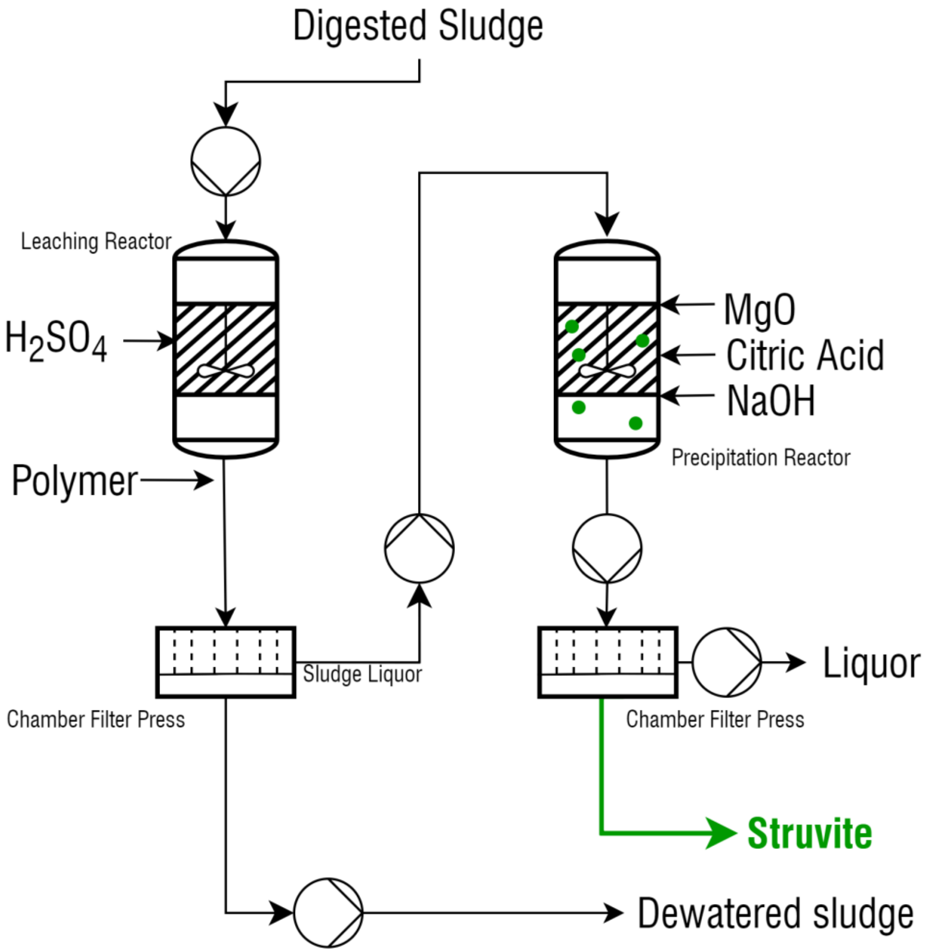


Figure 4.6. Stuttgart process.

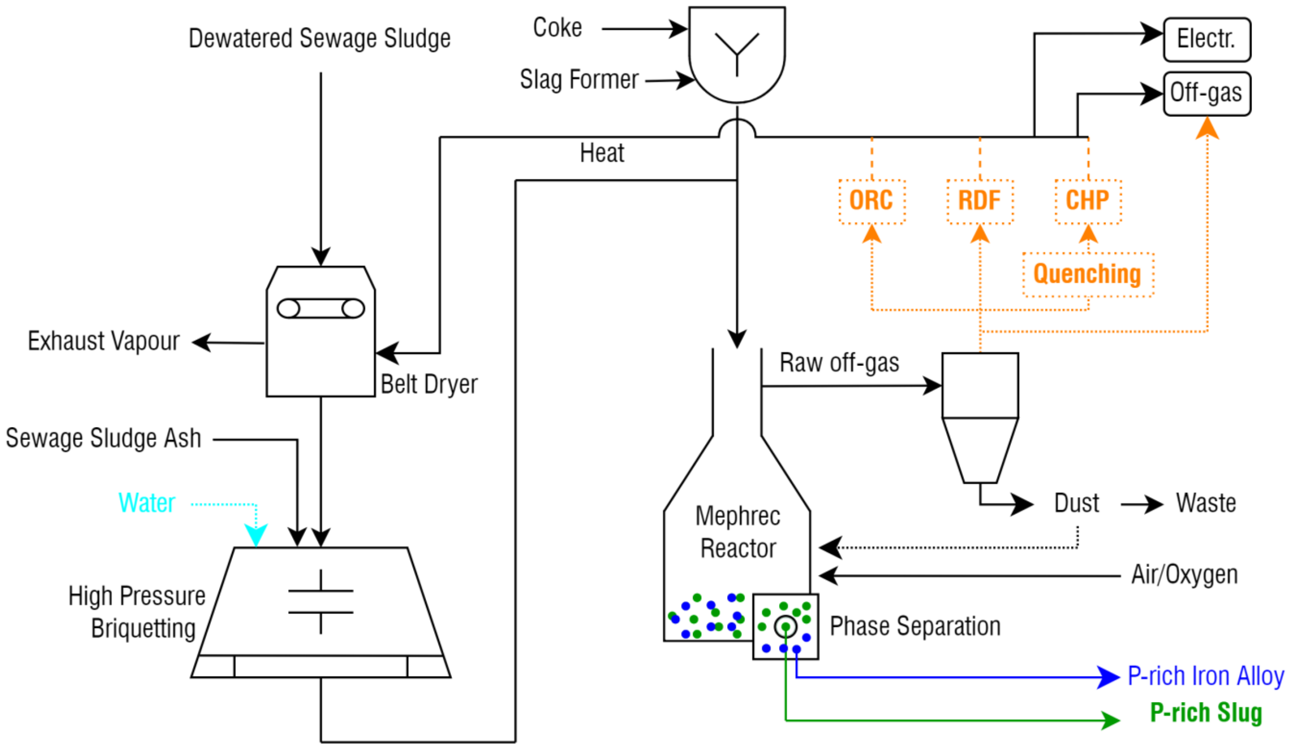


Figure 4.7. MEPHREC® metallurgic process.

## 4.3. PHOSPHOROUS RECOVERY FROM SLUDGE ASH

For the P recovery from the sludge ash, some technologies, including wet-chemical extraction, wet-chemical leaching and thermos-chemical treatments, were proposed. With the use of these technologies, it can be possible to reach a P recovery up to 70-89% related to the WWTP influent.

Acidic wet leaching has been widely applied for P recovery from sludge ashes and corresponds to the main steps of several systems involved in this field (taking care to first separate heavy metals from phosphorus for its safe use in agriculture). Examples are provided by PASCH e LEACHPHOS® (Figure 4.8) processes which aims at re-solubilizing the P in the ashes after the incineration process. For PASH, a liquid-liquid heavy metals removal step is also performed in order to achieve a higher purification of the recovered P.

In RecoPhos® and Fertilizer Industry processes it is possible to recover P in form of mineral fertilizer through acid-wet chemical extraction, reaching 85% of P recovered from WWTP influent. Although no selective extraction of heavy metals has been carried out, the production of a fertilizer derived by RecoPhos® process has demonstrated compliance both with the German Fertiliser Ordinance and conventional fertilizers in terms of heavy metals content (Weigand et al., 2013).

Different final recovered products is instead achieved from the EcoPhos®. In this case, the technology is involved for production of fertilizer-grade phosphoric acid. Basically, after a first acid digestion step, phosphate in the leachate is purified by chemical precipitation for dicalcium phosphate removal or ion exchange. However, the whole technology has been developed in modular units  to provide a more adjustable systems for the recovery of different products (Takhim et al., 2019).

A further approach for the P recovery from sludge ash is provided by thermal processes. The AshDec® system (Figure 4.9), that has been tested in a pilot-scale, represents a well-assessed solution in which the sludge ashes are treated through a thermochemical process in a rotary kiln. Then, inorganic calcined phosphates are produced at temperature value higher than 900 °C with the addition of potassium and/or sodium alkaline compounds. At the same time, heavy metals are removed by evaporation and further treated in the gaseous phase through air pollution control systems (Hermann & Schaaf, 2019).

Finally, in the Thermphos® process it is possible to recover P as elemental white phosphorus ($P_4$) at high temperatures (1500-1600 °C) achieved through electric heating. This method involves high energy costs, although it allows the recovery of products that can be reused in the production of several P-based chemicals (such as $P_2O_5$, $NaH_2PO_2$, $PCl_3$, $PH_3$, etc.) (Jupp et al., 2021).

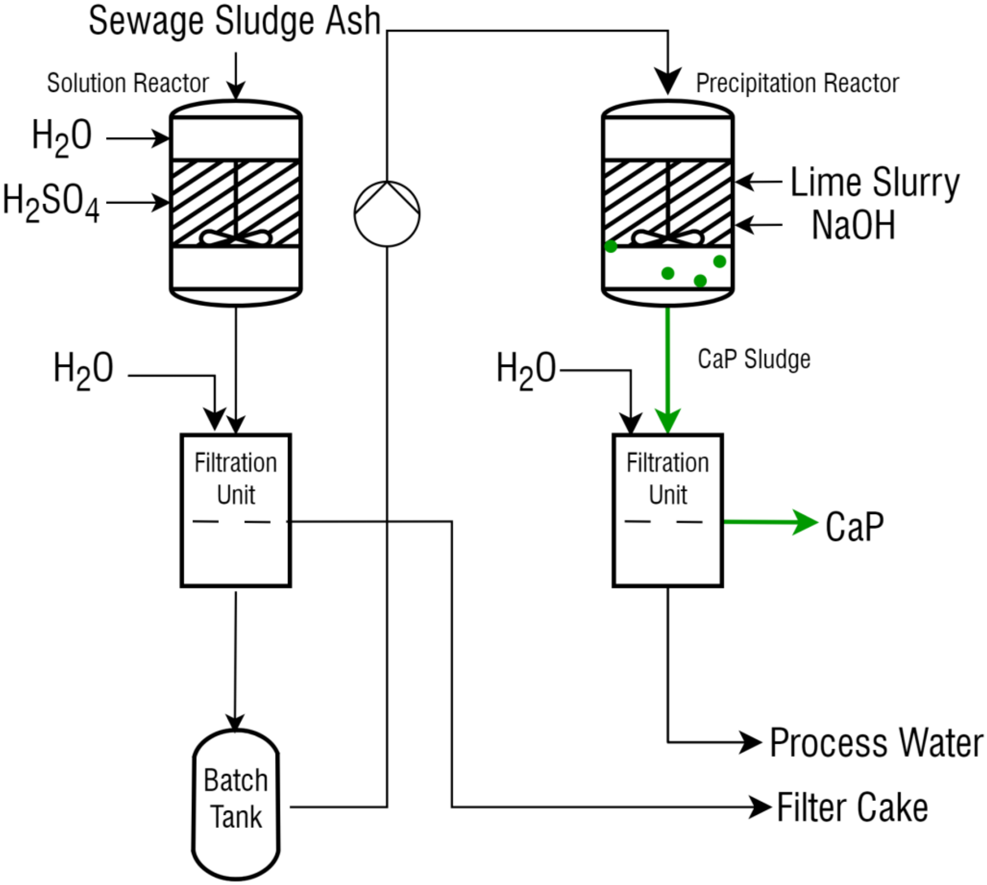


Figure 4.8. LEACHPHOS® process.

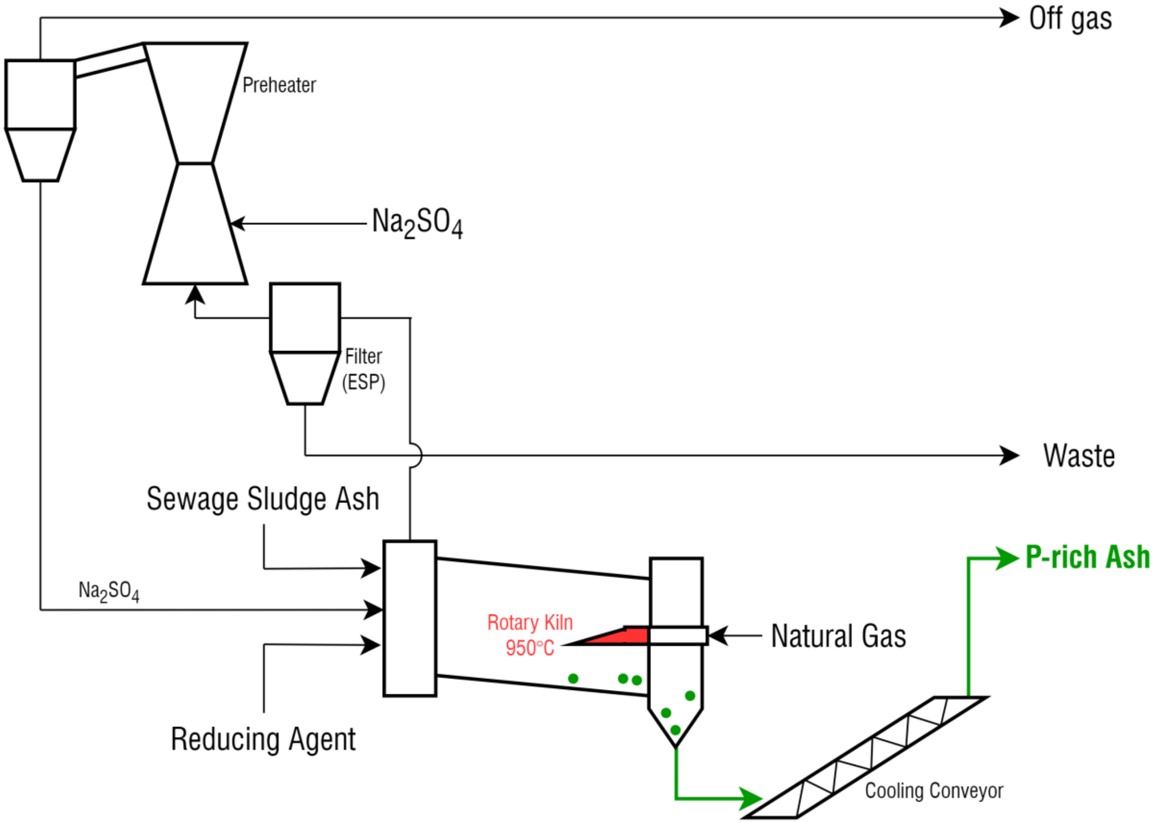


Figure 4.9. AshDec® system.

# CHAPTER 5. PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE OF MWTTP OF ANDRIA

*This chapter has, in part, resulted in the technical report entitled "Phosphorus recovery as struvite and hydroxyapatite from the liquid fraction of municipal sewage sludge with limited magnesium addition" by Ferraro, **de Sario**, Attanasio, Di Capua, Gorgoglione, Fratino, Mascolo, Pirozzi, Trancone, Spasiano (Journal of Environmental Quality, 2022)* (Ferraro et al., 2022)

At the end of the investigation of the P removal and recovery methods available in scientific literature, an experimental campaign was carried out in order to test a method for recovering P from municipal WWTP to obtain products that could be reused in agriculture. The municipal WWTP chosen is located in Andria (Italy) and the tested recovery method is the chemical precipitation, in order to obtain struvite and hydroxyapatite. Tests was carried out at laboratory scale, with different reagent doses at three pH value. In particular, low doses of magnesium have been tested in order to reduce the costs associated with it. The laboratory analysis on the liquid phase obtain was compared with analysis performed on precipitate. In the following subparagraphs will be described the municipal WWTP of Andria, the laboratory set-up and the analytic methods adopted. Finally, the results obtained are discussed.

## 5.1. MATERIAL AND METHODS

The digestate centrate used for the precipitation tests was collected from the dewatering unit of a municipal WWTP located in Andria (Italy), which treats approximately 14,300 m$^3$/d of domestic and industrial wastewaters from a municipality of 149,050 population equivalent. The wastewater streamline comprises pre-treatments, equalization basin, primary settlement, Modified Ludzac-Ettinger (MLE) cycle, and disinfection. The secondary sludge is sent to a static thickener and then, together with the primary sludge, to anaerobic digester. The last treatment of the sludge streamline is a centrifugation operating 72 hours/week, in which a sludge flow rate of about 132 $m^3$/d is conveyed together with a flocculant flow rate (25% of the sludge flow) characterized by a dry solid concentration of 0.5%. The TP concentration in the WWTP influent and effluent during 2020-2021 averaged 15.6(±7) and 2.1(±2) mg/L, respectively, resulting in a mean TP removal efficiency of 83(±22%). A detailed scheme of Andria municipal WWTP is illustrated in Figures 5.1 and 5.2. Moreover, in Annexes section (Figure S1-S12) are reported pictures that show some section of the treatment plant.

The chosen method for P recovery is its precipitation in form of struvite and/or hydroxyapatite, both reusable as slow-release fertilizer. Precipitation tests were carried out on samples of centrate recirculated from the sludge dewatering unit to the equalization tank of the WWTP (Figure 5.1). The centrate used for the tests was composed of 436 mg/L of $P\text{-}PO_4^{3-}$, 80 mg/L of $Mg^{2+}$, 290 mg/L of $Ca^{+}$, 152 mg/L of $N\text{-}NH_4^{+}$, and 870 mg/L (as $CaCO_3$) alkalinity. Other chemical elements (including heavy metals) composing the centrate and their concentrations were as follows: arsenic (0.01 mg/L), boron (0.2 mg/L), iron (0.7 mg/L), manganese (0.1 mg/L), nickel (0.01 mg/L), copper (0.01 mg/L), selenium (0.002 mg/L), and zinc (0.1 mg/L). The pH of the centrate was 7.03. The centrate was poured in 50 mL Falcon tubes (Corning Incorporated, USA) (working volume = 40 mL) to study the effect of different alkalinizing agents and $Ca^{2+}$ and $Mg^{2+}$ sources on P precipitation. Sodium hydroxide (NaOH) (>99.0%), magnesium chloride ($MgCl_2$) (>99.0%), calcium chloride ($CaCl_2$) (>99.0%) and calcium hydroxide ($Ca(OH)_2$) (>99.0%) were purchased from Sigma-Aldrich (USA) and used as received. $Ca(OH)_2$ and NaOH were added as alkalizing agents at selected dosages to obtain different initial pH conditions (pH 8, 9 and 10), while $MgCl_2$ was added as $Mg^{2+}$ source at concentrations ranging from 0 to 656 mg/L. Specifically, by considering the $Mg^{2+}$ already present in the solution, after the $MgCl_2$ additions the molar $Mg/P\text{-}PO_4^{3-}$ and $Mg/N\text{-}NH_4^{+}$ ratios were in the ranges of 0.24-0.74 and 0.31-0.95, respectively, being below the stoichiometric requirement for struvite precipitation according to reaction 3.2.

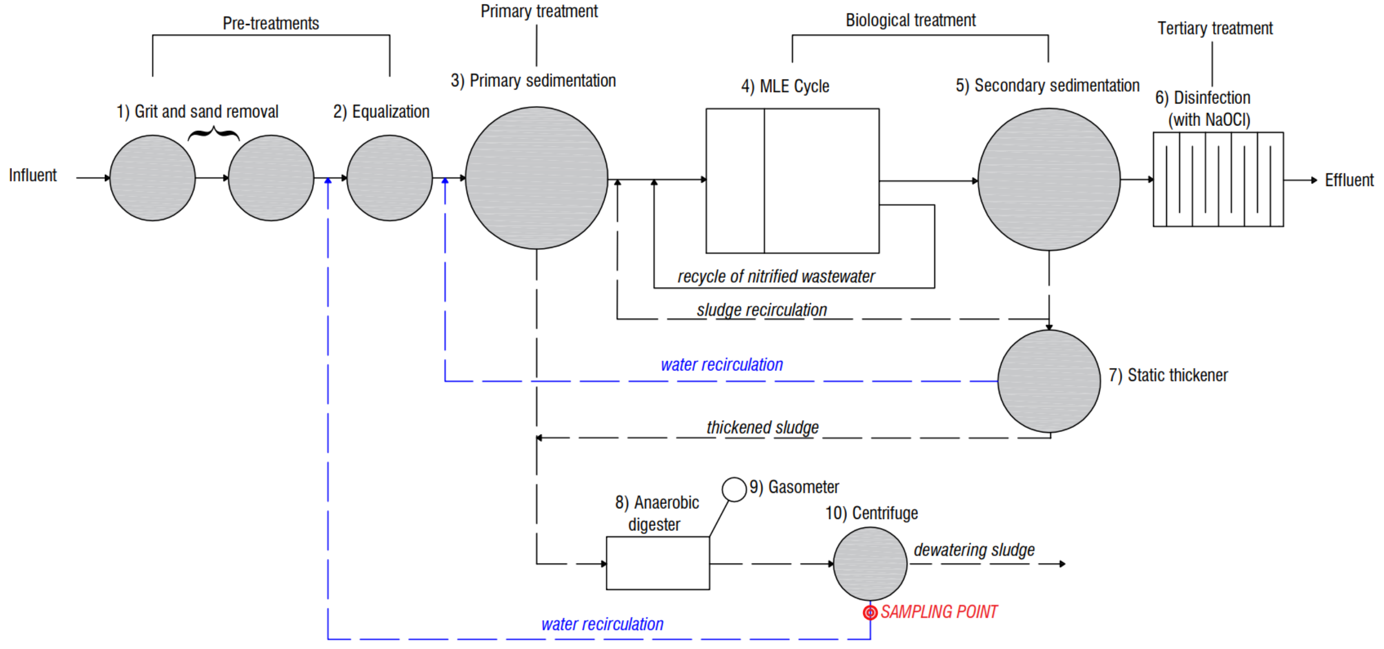


Figure 5.1. Diagram of the Andria sewage treatment plant.

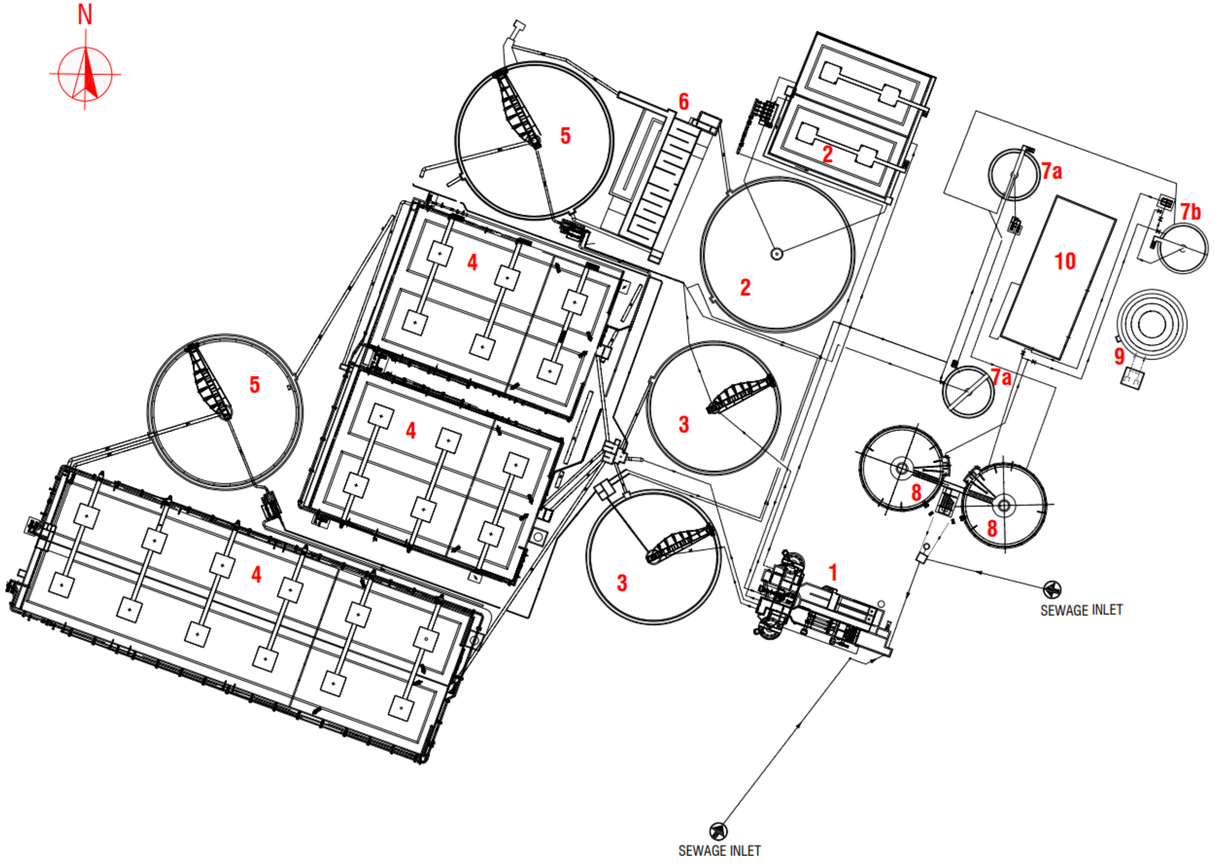


Figure 5.2. View of the Andria sewage treatment plant (1=Grit and sand removal; 2=Equalization; 3=Primary sedimentation; 4=MLE Cycle; 5=Secondary sedimentation; 6=Disinfection; 7a=Static pre-thickener; 7b=Static post-thickener; 8=Anaerobic digester; 9=Gasometer; 10=Centrifuge.

In the first experimental campaign, NaOH (*test 1*) or $Ca(OH)_2$ (*test 2*) were used for pH adjustment to study the effects of pH increase and concomitant $Ca^{2+}$ addition on P precipitation. The experimental designs of *test 1* and *test 2* are reported in Table 5.1. To discriminate between the influence of pH increase and $Ca^{2+}$ addition, a third experimental test (*test 3*) was carried out by initially adjusting the pH with NaOH and then separately adding $Ca^{2+}$ (as $CaCl_2$) at dosages equimolar to $Ca(OH)_2$ in *test 2* (Table 5.2).

| **Test tubes** | **pH** | **Dose of $MgCl_2$ (mg/L)** | **Mg/ P-$PO_4^{3}$ molar ratio** | **Mg/N-$NH_4^+$ molar ratio** |
|---|---|---|---|---|
| 1.1, 2.1 | 8 | 0 | 0.24 | 0.31 |
| 1.2, 2.2 | 9 | | | |
| 1.3, 2.3 | 10 | | | |
| 1.4, 2.4 | 8 | 109 | 0.32 | 0.41 |
| 1.5, 2.5 | 9 | | | |
| 1.6, 2.6 | 10 | | | |
| 1.7, 2.7 | 8 | 219 | 0.41 | 0.52 |
| 1.8, 2.8 | 9 | | | |
| 1.9, 2.9 | 10 | | | |
| 1.10, 2.10 | 8 | 437 | 0.57 | 0.73 |
| 1.11, 2.11 | 9 | | | |
| 1.12, 2.12 | 10 | | | |
| 1.13, 2.13 | 8 | 656 | 0.74 | 0.95 |
| 1.14, 2.14 | 9 | | | |
| 1.15, 2.15 | 10 | | | |

Table 5.1. Experimental conditions of batch tests 1 and test 2 performed with NaOH (tests 1.1-1.15) or $Ca(OH)_2$ (tests 2.1-2.15) for pH adjustment.

| Test tubes | Dose of $CaCl_2$ (mg/L) | pH | Dose of $MgCl_2$ (mg/L) |
|---|---|---|---|
| 3.1 | 749 | 8 | 109 |
| 3.2 | 1498 | | |
| 3.3 | 2247 | | |
| 3.4 | 749 | 9 | |
| 3.5 | 1498 | | |
| 3.6 | 2247 | | |
| 3.7 | 749 | 10 | |
| 3.8 | 1498 | | |
| 3.9 | 2247 | | |
| 3.10 | 749 | 8 | 219 |
| 3.11 | 1498 | | |
| 3.12 | 2247 | | |
| 3.13 | 749 | 9 | |
| 3.14 | 1498 | | |
| 3.15 | 2247 | | |
| 3.16 | 749 | 10 | |
| 3.17 | 1498 | | |
| 3.18 | 2247 | | |
| 3.19 | 749 | 8 | 437 |
| 3.20 | 1498 | | |
| 3.21 | 2247 | | |
| 3.22 | 749 | 9 | |
| 3.23 | 1498 | | |
| 3.24 | 2247 | | |
| 3.25 | 749 | 10 | |
| 3.26 | 1498 | | |
| 3.27 | 2247 | | |
| 3.28 | 749 | 8 | 656 |
| 3.29 | 1498 | | |
| 3.30 | 2247 | | |
| 3.31 | 749 | 9 | |
| 3.32 | 1498 | | |
| 3.33 | 2247 | | |
| 3.34 | 749 | 10 | |
| 3.35 | 1498 | | |
| 3.36 | 2247 | | |

Table 5.2. Experimental conditions of batch tests 3 performed with NaOH for pH adjustment and $CaCl_2$ as $Ca^{2+}$ source.

To minimize the volume change in the tubes, $MgCl_2$, NaOH and $CaCl_2$ has been added as 0.5-2 M solutions, while $Ca(OH)_2$ (which has a low solubility of 1.7 g/L at 293 K) was added as a powder directly in the tubes. At the end of the additions, the tubes were vortexed for 1 min to allow the complete mixing of centrate and reagents and set to rest for 2 h to achieve precipitates settling. At the end of the settling period, the tubes were classified according to i) the appearance of the liquid phase, ii) the volume of detectable precipitate, and iii) the appearance of the precipitate (Table 5.3).

| Test tubes | Appearance of the liquid phase | Appearance of the precipitate / mL |
|---|---|---|
| **1.1** | 0 | G / 1 |
| **1.2** | 0 | G / 2.5 |
| **1.3** | L | F / 2.5 |
| **1.4** | 0 | G / 1 |
| **1.5** | 0 | F / 2 |
| **1.6** | 0 | F / 2.5 |
| **1.7** | 0 | G / 1 |
| **1.8** | 0 | G / 2 |
| **1.9** | L | F / 2.5 |
| **1.10** | 0 | G / 1 |
| **1.11** | L | G / 2 |
| **1.12** | L | F / 5 |
| **1.13** | 0 | G / 2 |
| **1.14** | 0/L | G / 2.5 |
| **1.15** | L | F / 7.5 |
| **2.1** | 0 | F / 1.5 |
| **2.2** | 0 | F / 2 |
| **2.3** | L | G / 3 |
| **2.4** | 0 | G / 2 |
| **2.5** | 0 | G / 2.5 |
| **2.6** | 0 | G / 5 |
| **2.7** | 0 | G / 2 |
| **2.8** | 0 | G / 2.5 |
| **2.9** | 0/L | G / 7.5 |
| **2.10** | 0 | G / 1.5 |
| **2.11** | 0 | G / 3 |
| **2.12** | L | G / 7.5 |
| **2.13** | 0 | G / 2.5 |
| **2.14** | 0 | G / 2.5 |
| **2.15** | L | F / 7.5 |
| **3.1** | L | G / 2.5 |
| **3.2** | L | G / 2.5 |

| Test tubes | Appearance of the liquid phase | Appearance of the precipitate / mL |
|---|---|---|
| **3.3** | L | G / 5 |
| **3.4** | O | G / 2.5 |
| **3.5** | O | G / 2.5 |
| **3.6** | O | F / 10 |
| **3.7** | O | F / 5 |
| **3.8** | L | G / 5 |
| **3.9** | L | F / 10 |
| **3.10** | L | G / 2.5 |
| **3.11** | L | G / 5 |
| **3.12** | L | F / 7.5 |
| **3.13** | L | G / 5 |
| **3.14** | L | G / 5 |
| **3.15** | L | F / 10 |
| **3.16** | O/L | F / 5 |
| **3.17** | L | F / 5 |
| **3.18** | L | F / 10 |
| **3.19** | L | F / 5 |
| **3.20** | L | F / 5 |
| **3.21** | L | F / 6 |
| **3.22** | L | F / 5 |
| **3.23** | L | F / 6 |
| **3.24** | L | F / 7.5 |
| **3.25** | L | F / 7.5 |
| **3.26** | L | F / 10 |
| **3.27** | L | F / 10 |
| **3.28** | L | F / 5 |
| **3.29** | L | F / 7.5 |
| **3.30** | L | F / 7.5 |
| **3.31** | L | F / 5 |
| **3.32** | L | F / 7.5 |
| **3.33** | L | F / 7.5 |
| **3.34** | L | F / 7.5 |
| **3.35** | L | F / 10 |
| **3.36** | L | F / 10 |

Table 5.3. Classification of samples at the end of the precipitation tests; for the appearance of the liquid phase, L refers to “Limpid” and O refers to “Opalescent”, while for the appearance of the precipitate, G refers to “Granular” and F refers to “Flaky” (the number indicates the volume of detectable precipitate in mL).

Afterwards, the samples were centrifuged for 10 minutes at 4500 rpm and the liquid phase was filtered with 0.45 µm Sartorius filters (Fisher Scientific, Italy) in 15 mL falcon tubes (Corning Incorporated, USA) for further analysis and characterization. All the tests were carried out in triplicate. Two-way and three-way analysis of variance (ANOVA) were performed through XLSTAT on the results of the experimental set-up reported in Tables 5.1 and 5.2, respectively. Post-hoc Turkey tests were carried out to identify the statistical differences for each experimental set-up. The statistical significance was set at $p < 0.05$.

For the analysis of the liquid-phase, 10 mL of each filtered samples was used to determine $PO_4^{3-}$, $Mg^{2+}$, $Ca^{2+}$ e $NH_4^+$ concentrations. All analyses were carried out in triplicate. The precipitates were dried at 105°C until constant mass was achieved and subsequently ground for 30 min in a ball mill prior to solid-phase analysis.

The formation of solid precipitates and the amount of precipitated ions within the 12 selected samples was predicted by thermodynamic modelling via Visual MINTEQ software. The initial concentrations of the analyzed chemical species composing the centrate and alkalinity as well as the pH of each test tube were used as input parameters for the model. Moreover, the simulation temperature was set at 20°C and the precipitation of oversaturated solids was allowed.

The concentrations of $Ca^{2+}$ e $Mg^{2+}$ in the solutions were evaluated through AAS using a Varian Model 55B SpectrAA (Agilent Technologies, USA) F-AAS equipped with a nitrous oxide-acetylene flame and a deuterium lamp for background correction. The concentrations of other metals and selenium in the centrate was obtained via analysis with a NexION 2000 inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer, USA) according to methods UNI EN ISO 17294-2:2016 and UNI EN ISO 15587-2:2002. $NH_4^+$ concentration has been determined spectrophotometrically using the indophenol blue method (APAT ISRA-CNR, 2003). $PO_4^{3-}$ concentration was measured with a Metrohm 883 Basic IC Plus system equipped with a Metrosep A Supp 5–150/4.0 column and chemically-suppressed conductivity (Metrohm, Switzerland). The pH of the solution was monitored with a HI 98190 pH/ORP pH-meter (Hanna Instruments, USA). The alkalinity of the centrate was measured by potentiometric titration (APHA, 2005). The precipitate samples were analysed for their mineralogy using a powder X-ray diffractometer (PANalytical X'Pert Pro), at 40 kV and 40 mA, using Cu K$\alpha$ radiation, with divergence slit of 0.5, spinner revolution 1 mm/s. The apparatus was equipped with a solid-state detector (X'Celerator) covering an angle of 2.1° and integrates the diffracted intensity as it scans. The powders were scanned in the range $2\theta = 5–80°$. Specifically, the JCPDS (Joint Committee on Powder Diffraction Standards -International Centre for Diffraction Data) database was used to identify the crystalline precipitates through XRD analysis.

## 5.2. RESULTS AND DISCUSSION

### 5.2.1. EFFECT OF PH AND $Mg^{2+}$ AND $Ca^{2+}$ DOSES ON P PRECIPITATION

Figure 5.3 shows the percentage of P recovery at the different pH values and $MgCl_2$ dosages during *test 1*. The effect of $Mg^{2+}$ dose on P precipitation was significant since an increase of P recovery was observed when comparing experiments with same pH values but increasing Mg dose. Indeed, the highest P recovery efficiency for each pH tested was observed at the highest $MgCl_2$ dose of 656 mg/L (corresponding to a total Mg concentration of 247 mg/L). At this dose, P recovery was 72.02% at pH=8, 87.3% at pH=9 and 88.9% at pH=10. These results are in line with previous reports showing that increasing Mg dose enhances P precipitation (Lee et al., 2015; Siciliano et al., 2020). The influence of pH on P precipitation was less linear, as P precipitation efficiencies at pH 9 and 10 and different $MgCl_2$ doses were quite similar in agreement with previous observations (Shaddel et al., 2019).

Figure 5.4 shows P recovery at different pH values obtained by adding $Ca(OH)_2$ (*test 2*). $Ca^{2+}$ addition had a strong impact on P precipitation. Compared to the results of *test 1*, P recovery with $Ca(OH)_2$ was higher at all investigated pH values. Moreover, a more linear effect due to the pH increase was observed. P recovery efficiencies at pH 10 (all $\geq$85%) were always higher than those at lower pH values.

The significant influence of $Ca^{2+}$ on P precipitation was confirmed also when $CaCl_2$ was used as $Ca^{2+}$ source and the pH adjusted with NaOH (*test 3*). In fact, higher precipitation efficiencies were observed as compared to the *test 1* (Figure 5.3). Comparing the results of *test 2* (Figure 5.4) and *test 3* (Figure 5.5) at pH 8 and equimolar $Ca^{2+}$ concentrations, lower P recovery efficiencies were displayed with $CaCl_2$ compared to $Ca(OH)_2$ at the different $MgCl_2$ doses tested (except at 109 mg/L). A similar result was observed at pH 9 and equimolar $Ca^{2+}$ dose. In contrast, P precipitation efficiencies obtained at pH 10 with $Ca(OH)_2$ were lower than those obtained with $CaCl_2$. As a result, adding $Ca(OH)_2$ instead of $CaCl_2$ in the centrate led to higher P precipitation up to pH 9. Efficient P precipitation at pH 8 would allow to limit the dose of alkalizing agent. By adding NaOH (*test 1*), efficient P precipitation (>70%) at pH 8 was achieved only with $MgCl_2$ doses of 437 and 656 mg/L (Figure 5.3). At the same pH and $MgCl_2$ concentrations in *test 2*, P precipitation efficiencies ≥80% were obtained (Figure 5.4). Notably, abatement percentages with $Ca^{2+}$ addition (*test 2* and *test 3*) were always ≥70% even at the lowest pH and $MgCl_2$ dose tested. It should be highlighted that these results were obtained by using $Mg^{2+}/P\text{-}PO_4^{3-}$ molar ratios always below 1.0, while the values typically applied are higher than 1.05 (Jaffer et al., 2002).

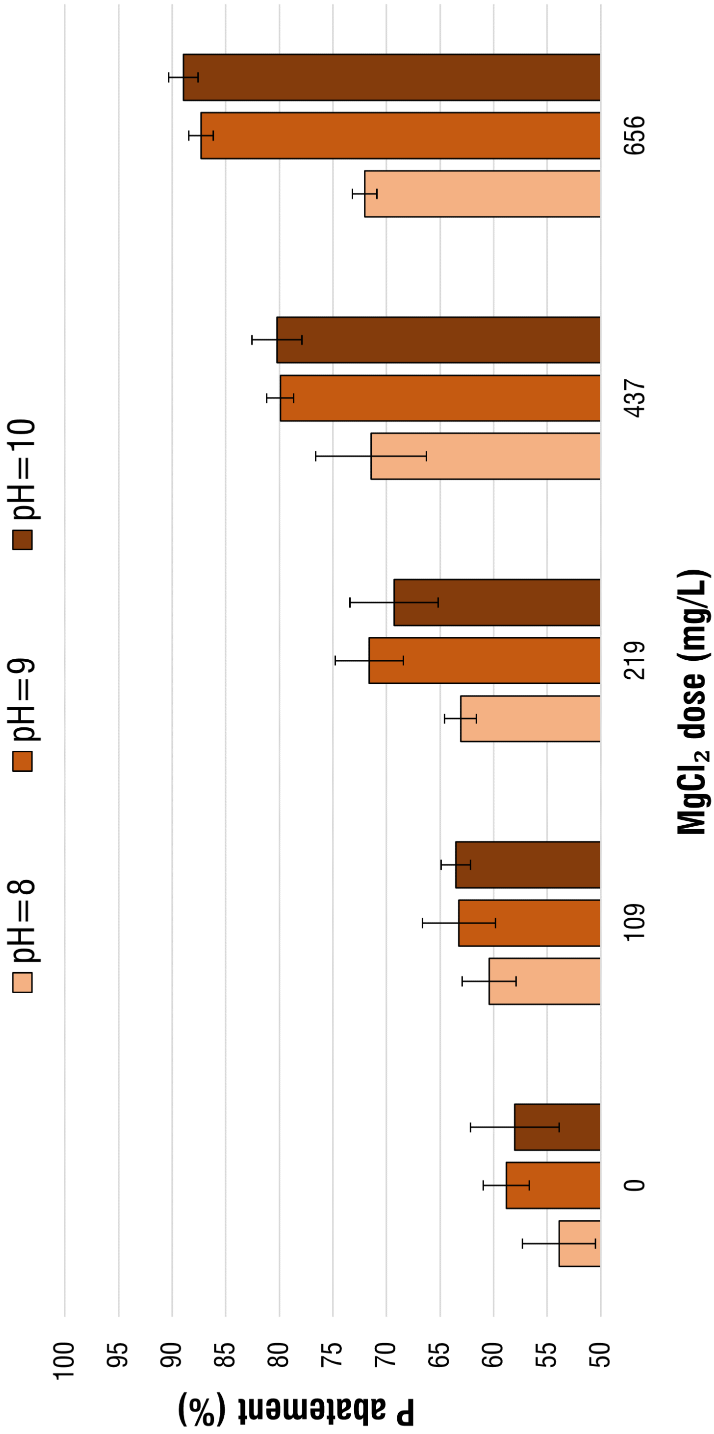


Figure 5.3. Effect of MgCl$_2$ and NaOH dosage on P recovery at different pH (test 1).

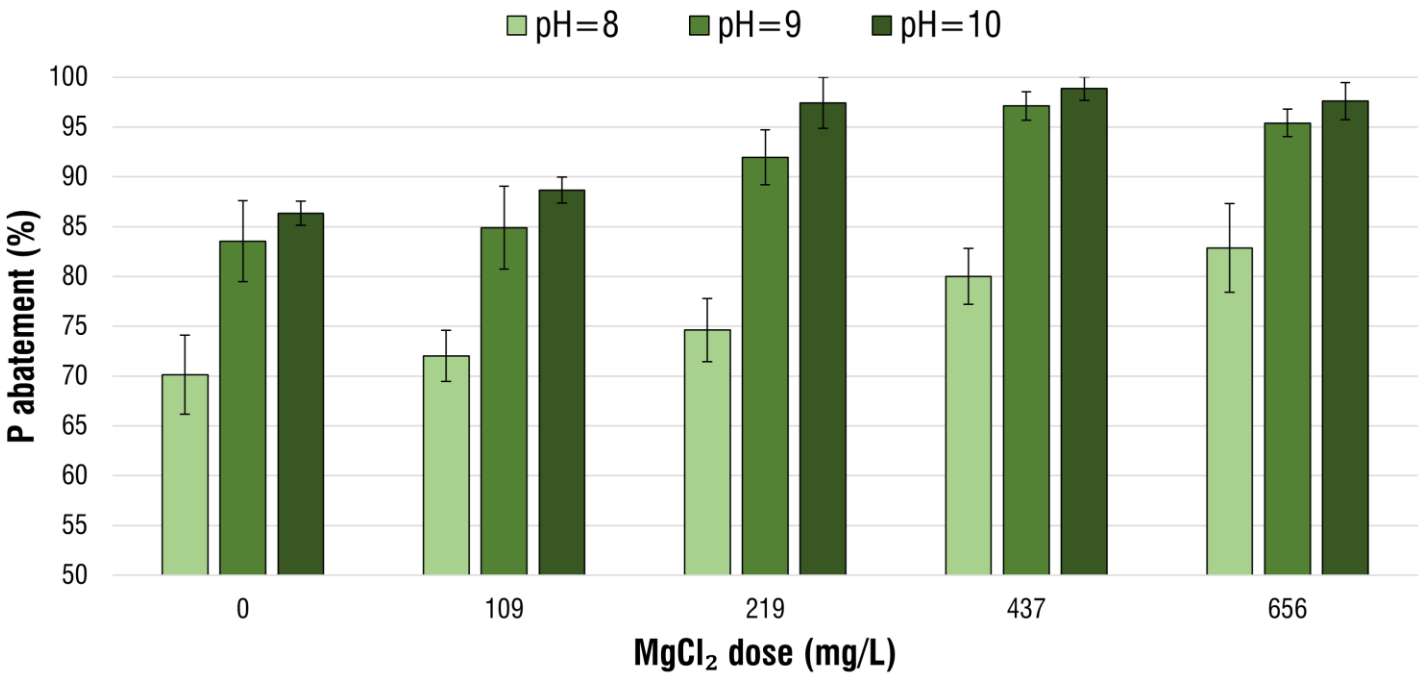


Figure 5 4. Effect of $MgCl_2$ and $Ca(OH)_2$ dosage on P recovery at different pH (test 2).

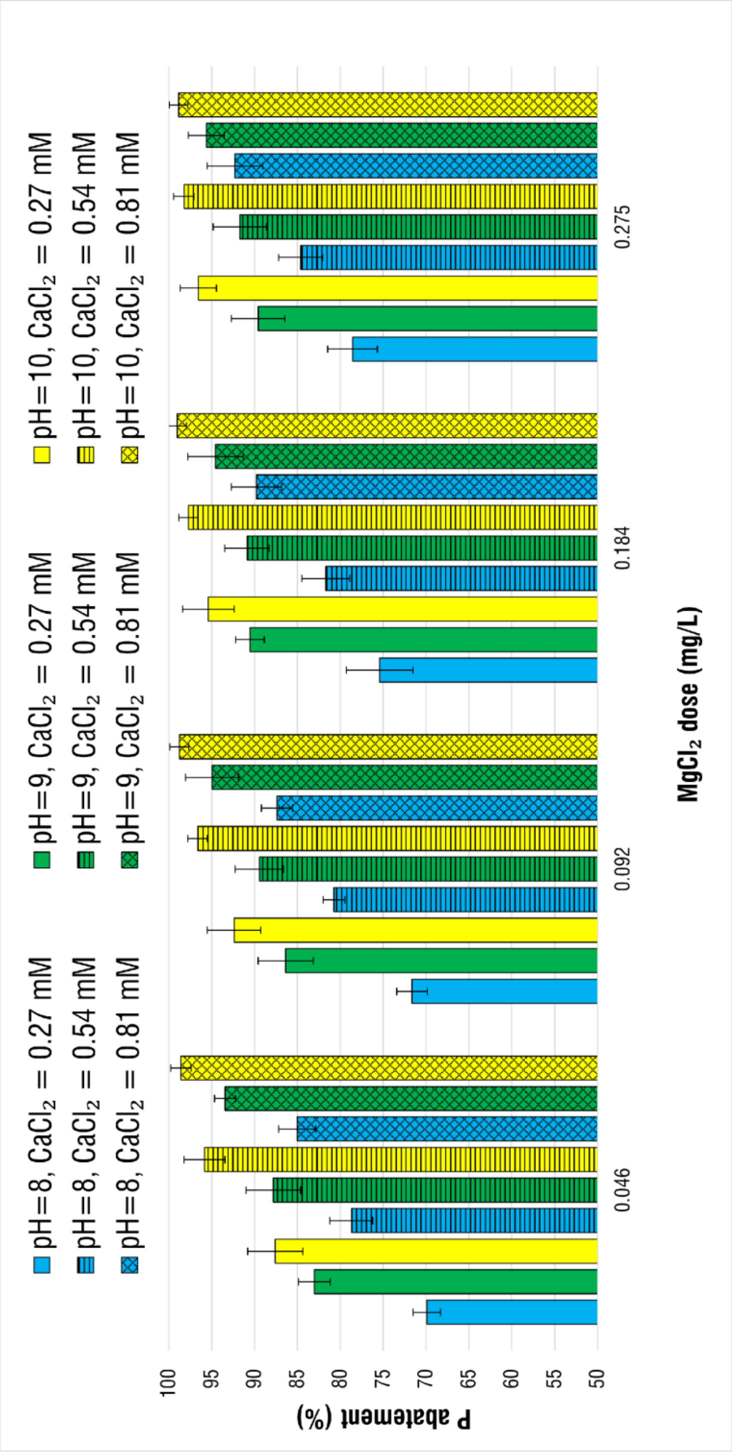


Figure 5. 5. Effect of $MgCl_2$ and NaOH dosage on P recovery at different pH with three different dosages of $CaCl_2$ (test 3). Full texture columns refer to $CaCl_2$=749 mg/L, horizontal texture columns to $CaCl_2$=1498 mg/L and grid texture columns to $CaCl_2$=2247 mg/L.

### *5.2.2. EFFECT OF PH AND REAGENT DOSES ON $Mg^{2+}$, $Ca^{2+}$ AND $NH_4^+$ PRECIPITATION*

Based on the results of the P precipitation experiments, 12 tests were selected to further characterize the liquid and solid phases to understand the impact of the different experimental conditions on the formation of struvite and hydroxyapatite. The samples selection from each test group (*test 1, 2* and *3*) was made in accordance with the operating conditions, which allowed the achievement of an optimal compromise between the lowest possible reagent dosage and the highest P recovery percentage. In particular, the selected samples were characterized by 1) P recovery efficiency ≥70% (*tests 1-3*), 2) lower precipitate formation at similar P recovery efficiency and Mg dose (*tests 1-3*), suggesting the presence of more struvite and hydroxyapatite, and 3) lower $MgCl_2$ doses (*test 3*), being more economical.

$Mg^{2+}$, $Ca^{2+}$ and $NH_4^+$ precipitation as well as precipitate composition were evaluated for the 12 selected tests.

The experimental conditions of these tests are detailed in Table 5.4, which also reports the concentrations and percentages of precipitated $PO_4^{3-}$, $Mg^{2+}$, $Ca^{2+}$ and $NH_4^+$.

Regarding $Mg^{2+}$, for the samples in which $MgCl_2$ was added, the highest removal (210 mg/L, 84.4%) was obtained for test n°1.14. The highest $Mg^{2+}$ abatement (93.9%) was observed for the test n°2.2 (with no $MgCl_2$ addition and $Ca(OH)_2$ as alkalinizing agent). The lowest $Mg^{2+}$ abatements were found in the samples characterized by $CaCl_2$ addition. In this case, the percentage values (35.1-40.6 %) appear independent from the $Ca^{2+}$ dosage.

$Ca^{2+}$ precipitation in the tests with $Ca(OH)_2$ was higher than 90%, with removal efficiencies being very similar at different pH and $MgCl_2$ doses. Lower $Ca^{2+}$ abatement efficiencies were observed in presence of $CaCl_2$, with a minimum value of 61.7% for the test at 219 mg/L $MgCl_2$, 2247 mg/L $CaCl_2$ and pH=8 (n°3.12). However, the conditions of test tube n°3.3 led to the highest amount of $Ca^{2+}$ precipitate, being equal to 1023 mg/L (92.9%).

| Tests | Test details | $PO_4^{3-}$ recovery (mg/L / %) | $Mg^{2+}$ abatement (mg/L / %) | $Ca^{2+}$ abatement (mg/L / %) | $NH_4^+$ recovery (mg/L / %) |
|---|---|---|---|---|---|
| 1.13 | $MgCl_2$=656 mg/L,<br>pH=8 (NaOH) | 942 / 72.0 | 169 / 68.8 | 288 / 99.2 | 58 / 29.8 |
| 1.14 | $MgCl_2$=656 mg/L,<br>pH=9 (NaOH) | 1142 / 87.3 | 210 / 84.4 | 288 / 99.3 | 93 / 47.6 |
| 2.1 | $MgCl_2$=0 mg/L,<br>pH=8 ($Ca(OH)_2$) | 937 / 70.1 | 74 / 91.8 | 558 / 99.6 | 23 / 11.9 |
| 2.2 | $MgCl_2$=0 mg/L,<br>pH=9 ($Ca(OH)_2$) | 1101 / 83.5 | 75 / 93.9 | 830 / 99.9 | 1 / 0.3 |
| 2.10 | $MgCl_2$=437 mg/L,<br>pH=8 ($Ca(OH)_2$) | 1106 / 80.0 | 154 / 80.6 | 554 / 98.9 | 33 / 17.1 |
| 2.11 | $MgCl_2$=437 mg/L,<br>pH=9 ($Ca(OH)_2$) | 1270 / 97.1 | 153 / 80.0 | 825 / 99.2 | 19 / 10.0 |
| 2.13 | $MgCl_2$=656 mg/L,<br>pH=8 ($Ca(OH)_2$) | 1084 / 82.9 | 188 / 75.7 | 552 / 98.5 | 17 / 8.8 |
| 2.14 | $MgCl_2$=656 mg/L,<br>pH=9 ($Ca(OH)_2$) | 1248/ 95.4 | 189 / 75.8 | 816 / 98.2 | 31 / 15.9 |
| 3.2 | $MgCl_2$=109 mg/L,<br>$CaCl_2$=1498 mg/L<br>pH=8 (NaOH) | 1130 / 78.7 | 42 / 39.5 | 750 / 90.3 | 8 / 3.9 |
| 3.3 | $MgCl_2$=109 mg/L,<br>$CaCl_2$=2247 mg/L<br>pH=8 (NaOH) | 1212 / 85.0 | 39 / 35.1 | 1023 / 92.9 | 66 / 34.0 |
| 3.11 | $MgCl_2$=219 mg/L,<br>$CaCl_2$=1498 mg/L<br>pH=8 (NaOH) | 1084 / 80.7 | 50 / 36.8 | 709 / 85.3 | 13 / 6.5 |
| 3.12 | $MgCl_2$=219 mg/L,<br>$CaCl_2$=2247 mg/L<br>pH=8 (NaOH) | 1206 / 87.4 | 55 / 40.6 | 680 / 61.7 | 24 / 12.3 |

Table 5.4. Percentage decrease of dissolved $PO_4^{3-}$, $Mg^{2+}$, $Ca^{2+}$ and $NH_4^+$ and their concentrations in the precipitate for different selected tests.

$NH_4^+$ recovery was lower than 50% in all 12 tests. A maximum $NH_4^+$ removal of 93 mg/L was obtained with a $MgCl_2$ dose of 656 mg/L and pH 9 using NaOH as alkalizing agent (n°1.14). The experimental test n°1.14 was characterized also by high removal of the other dissolved ions, which suggests that struvite precipitate might have formed in considerable amounts. Unlike $Ca^{2+}$ and $Mg^{2+}$, a significant correlation between the $CaCl_2$ addition and $NH_4^+$ removal was observed. The increase of $CaCl_2$ dosage from 1498 to 2247 mg/L increased $NH_4^+$ removal by 30.1% at a $MgCl_2$ dose of 109 mg/L (tests 3.2 and 3.3) and by 5.8% at a $MgCl_2$ dose of 219 mg/L (tests 3.11 and 3.12). Only a 0.3% $NH_4^+$ removal was obtained in absence of $MgCl_2$ at pH 9 with $Ca(OH)_2$ corresponding to the lowest value observed during the experiments. Finally, it was observed that in tests without $CaCl_2$ addition and $MgCl_2$ dose <656 mg/L (pH=9), the removal percentage of $NH_4^+$, mainly involved in the formation of struvite, was lower than the one at pH 8. In fact, $NH_4^+$ removal decreased from 17.1% for test n°2.10 (pH=8) to 10.0% for test n°2.11 (pH=9) and from 11.9% for test n°2.1 (pH=8) to 0.3% for test n°2.2 (pH=9). In general, these results suggested a lower struvite precipitation occurrence at pH 9.

### *5.2.3. ANOVA COMPARISON OF TESTS-1-3 DATA*

According to the two-way ANOVA results for *test 1* and *test 2*, both pH and $MgCl_2$ dose showed higher statistical significance ($p < 0.0001$) in influencing the P removal percentage compared to their interaction ($pH*MgCl_2$). From the post-hoc Turkey test, different outcomes could be observed for *test 1* and *test 2*. For *test 1* a significant statistical difference was highlighted only for the pH 8 compared to the pH 9 and 10 while all the pH values displayed differences for *test 2* (Table 5.5). On the other side, the addition of $MgCl_2$ resulted in statistical differences among all the doses for the *test 1*. As for *test 2*, instead, similarities were observed between the two higher dose values (437 and 656 mg/L) as well as between the null and 109 mg/L doses, while the 219 mg/L dose showed statistical difference compared to all the conditions (Table 5.5).

Accounting for the parameter interaction (Table 5.6), the post-hoc Turkey test highlighted a more complex outcomes in terms of similarities/differences among the experimental conditions. Despite this, it is worth noticing that similarities were mainly occurring as a function of the $MgCl_2$ doses involved for t*est 1*. As regards *test 2*, more statistical similarities were observed between experiments involving pH 9 and 10. The three-way ANOVA performed on results of *test 3* highlighted that all the investigated parameters (pH, $CaCl_2$ dose, and $MgCl_2$ dose) and their interactions had significant effect on the P removal percentage. However, the highest statistical significance ($p < 0.0001$) was observed for each single parameter and the interaction between pH and $CaCl_2$ dose (pH*$CaCl_2$). More in detail, by comparing results of the post-hoc Turkey test on parameters interaction, different statistical similarities/differences could be noticed according to the parameter values and the interaction types (Table 5.7). In fact, accounting for the interaction between pH and $CaCl_2$ dose, main statistical differences compared to the other experimental groups were observed by considering the interactions with pH 8 and 749 mg $CaCl_2$/L as well as pH 8 and 1498 mg $CaCl_2$/L. Instead, for pH 9 and 10 more statistical similarities were observed among interactions with same pH value and various $CaCl_2$ doses. Higher number of statistical similarities were observed for interactions between pH and $MgCl_2$ doses. However, it is worth highlighting that clear statistical differences were still noticeable when comparing the lowest and highest pH value at any $MgCl_2$ dose. Finally, also for the interactions between doses of both $CaCl_2$ and $MgCl_2$, several similarities were observed especially at $CaCl_2$ doses of 1498 and 2247 mg/L. On the contrary, the only group statistically different from the other experimental conditions resulting for two interactions both characterized by lowest $CaCl_2$ dose (749 mg/L) and the lower $MgCl_2$ doses (109 and 219 mg/L, respectively).

| Parameter | Groups | | | | |
|---|---|---|---|---|---|
| | | | *test 1* | | |
| pH 8 | A | | | | |
| pH 9 | | B | | | |
| pH 10 | | B | | | |
| | | | | | |
| $MgCl_2$ (0 mg/L) | $A^{\wedge}$ | | | | |
| $MgCl_2$ (109 mg/L) | | $B^{\wedge}$ | | | |
| $MgCl_2$ (219 mg/L) | | | $C^{\wedge}$ | | |
| $MgCl_2$ (437 mg/L) | | | | $D^{\wedge}$ | |
| $MgCl_2$ (656 mg/L) | | | | | $E^{\wedge}$ |
| | | | *test 2* | | |
| pH 8 | F | | | | |
| pH 9 | | G | | | |
| pH 10 | | | H | | |
| | | | | | |
| $MgCl_2$ (0 mg/L) | $F^{\wedge}$ | | | | |
| $MgCl_2$ (109 mg/L) | $F^{\wedge}$ | | | | |
| $MgCl_2$ (219 mg/L) | | $G^{\wedge}$ | | | |
| $MgCl_2$ (437 mg/L) | | | $H^{\wedge}$ | | |
| $MgCl_2$ (656 mg/L) | | | $H^{\wedge}$ | | |

Table 5.5. Post-hoc Turkey test results for test 1 and test 2 on similarities/differences related to pH and $MgCl_2$ dose. Letters without and with “ ^ ” superscripts distinguish the groups identified for pH and $MgCl_2$, respectively.

| Parameters interaction | Groups | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| pH*$MgCl_2$ (mg/L) | | | | | | | | |
| | | | *test 1* | | | | | |
| pH 8*$MgCl_2$ (0) | $A^{\wedge}$ | | | | | | | |
| pH 8*$MgCl_2$ (109) | $A^{\wedge}$ | $B^{\wedge}$ | | | | | | |
| pH 8*$MgCl_2$ (219) | | $B^{\wedge}$ | $C^{\wedge}$ | | | | | |
| pH 8*$MgCl_2$ (437) | | | $C^{\wedge}$ | $D^{\wedge}$ | $E^{\wedge}$ | | | |
| pH 8*$MgCl_2$ (656) | | | | $D^{\wedge}$ | $E^{\wedge}$ | $F^{\wedge}$ | | |
| pH 9*$MgCl_2$ (0) | $A^{\wedge}$ | $B^{\wedge}$ | | | | | | |
| pH 9*$MgCl_2$ (109) | | $B^{\wedge}$ | $C^{\wedge}$ | | | | | |
| pH 9*$MgCl_2$ (219) | | | $C^{\wedge}$ | $D^{\wedge}$ | $E^{\wedge}$ | | | |
| pH 9*$MgCl_2$ (437) | | | | | $E^{\wedge}$ | $F^{\wedge}$ | $G^{\wedge}$ | |
| pH 9*$MgCl_2$ (656) | | | | | | | $G^{\wedge}$ | $H^{\wedge}$ |
| pH 10*$MgCl_2$ (0) | $A^{\wedge}$ | $B^{\wedge}$ | | | | | | |
| pH 10*$MgCl_2$ (109) | | $B^{\wedge}$ | $C^{\wedge}$ | $D^{\wedge}$ | | | | |
| pH 10*$MgCl_2$ (219) | | | $C^{\wedge}$ | $D^{\wedge}$ | | | | |
| pH 10*$MgCl_2$ (437) | | | | | | $F^{\wedge}$ | $G^{\wedge}$ | |
| pH 10*$MgCl_2$ (656) | | | | | | | | $H^{\wedge}$ |
| | | | *test 2* | | | | | |
| pH 8*$MgCl_2$ (0) | $A^{+}$ | | | | | | | |
| pH 8*$MgCl_2$ (109) | $A^{+}$ | $B^{+}$ | | | | | | |
| pH 8*$MgCl_2$ (219) | $A^{+}$ | $B^{+}$ | $C^{+}$ | | | | | |
| pH 8*$MgCl_2$ (437) | | $B^{+}$ | $C^{+}$ | $D^{+}$ | | | | |
| pH 8*$MgCl_2$ (656) | | | $C^{+}$ | $D^{+}$ | $E^{+}$ | | | |
| pH 9*$MgCl_2$ (0) | | | | $D^{+}$ | $E^{+}$ | $F^{+}$ | | |
| pH 9*$MgCl_2$ (109) | | | | $D^{+}$ | $E^{+}$ | $F^{+}$ | | |
| pH 9*$MgCl_2$ (219) | | | | | | $F^{+}$ | $G^{+}$ | $H^{+}$ |
| pH 9*$MgCl_2$ (437) | | | | | | | $G^{+}$ | $H^{+}$ |
| pH 9*$MgCl_2$ (656) | | | | | | | $G^{+}$ | $H^{+}$ |
| pH 10*$MgCl_2$ (0) | | | | $D^{+}$ | $E^{+}$ | $F^{+}$ | | |
| pH 10*$MgCl_2$ (109) | | | | | $E^{+}$ | $F^{+}$ | $G^{+}$ | |
| pH 10*$MgCl_2$ (219) | | | | | | | | $H^{+}$ |
| pH 10*$MgCl_2$ (437) | | | | | | | | $H^{+}$ |

Table 5. 6. Post-hoc Turkey test results for test 1 and test 2 on similarities/differences in the comparison of interactions among pH and $MgCl_2$ dose. “ ^ ” and “ + ” superscripts following the letters distinguish the groups identified for test 1 and test 2, respectively.

| **Parameters interaction** | **Groups** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **pH*$CaCl_2$ (mg/L)** | | | | | | | | | | |
| pH 8*$CaCl_2$ (749) | $A^-$ | | | | | | | | | |
| pH 8*$CaCl_2$ (1498) | | $B^-$ | | | | | | | | |
| pH 8*$CaCl_2$ (2247) | | | $C^-$ | | | | | | | |
| pH 9*$CaCl_2$ (749) | | | $C^-$ | | | | | | | |
| pH 9*$CaCl_2$ (1498) | | | $C^-$ | | | | | | | |
| pH 9*$CaCl_2$ (2247) | | | | $D^-$ | $E^-$ | | | | | |
| pH 10*$CaCl_2$ (749) | | | | | $E^-$ | | | | | |
| pH 10*$CaCl_2$ (1498) | | | | $D^-$ | | $F^-$ | | | | |
| pH 10*$CaCl_2$ (2247) | | | | | | $F^-$ | | | | |
| **pH*$MgCl_2$ (mg/L)** | | | | | | | | | | |
| pH 8*$MgCl_2$ (109) | $A^+$ | | | | | | | | | |
| pH 8*$MgCl_2$ (219) | $A^+$ | $B^+$ | | | | | | | | |
| pH 8*$MgCl_2$ (437) | | $B^+$ | $C^+$ | | | | | | | |
| pH 8*$MgCl_2$ (656) | | | $C^+$ | $D^+$ | | | | | | |
| pH 9*$MgCl_2$ (109) | | | | $D^+$ | $E^+$ | | | | | |
| pH 9*$MgCl_2$ (219) | | | | | $E^+$ | $F^+$ | | | | |
| pH 9*$MgCl_2$ (437) | | | | | | $F^+$ | $G^+$ | | | |
| pH 9*$MgCl_2$ (656) | | | | | | $F^+$ | $G^+$ | $H^+$ | | |
| pH 10*$MgCl_2$ (109) | | | | | | | $G^+$ | $H^+$ | $I^+$ | |
| pH 10*$MgCl_2$ (219) | | | | | | | | $H^+$ | $I^+$ | $J^+$ |
| pH 10*$MgCl_2$ (437) | | | | | | | | | $I^+$ | $J^+$ |
| pH 10*$MgCl_2$ (656) | | | | | | | | | | $J^+$ |
| **$CaCl_2$ (mg/L)*$MgCl_2$ (mg/L)** | | | | | | | | | | |
| $CaCl_2$ (749)*$MgCl_2$ (109) | $A^{\wedge}$ | | | | | | | | | |
| $CaCl_2$ (749)*$MgCl_2$ (219) | $A^{\wedge}$ | | | | | | | | | |
| $CaCl_2$ (749)*$MgCl_2$ (437) | | $B^{\wedge}$ | | | | | | | | |
| $CaCl_2$ (749)*$MgCl_2$ (656) | | $B^{\wedge}$ | $C^{\wedge}$ | | | | | | | |
| $CaCl_2$ (1498)*$MgCl_2$ (109) | | $B^{\wedge}$ | | | | | | | | |
| $CaCl_2$ (1498)*$MgCl_2$ (219) | | $B^{\wedge}$ | $C^{\wedge}$ | $D^{\wedge}$ | | | | | | |
| $CaCl_2$ (1498)*$MgCl_2$ (437) | | $B^{\wedge}$ | $C^{\wedge}$ | $D^{\wedge}$ | $E^{\wedge}$ | | | | | |
| $CaCl_2$ (1498)*$MgCl_2$ (656) | | | $C^{\wedge}$ | $D^{\wedge}$ | $E^{\wedge}$ | $F^{\wedge}$ | | | | |
| $CaCl_2$ (2247)*$MgCl_2$ (109) | | | | $D^{\wedge}$ | $E^{\wedge}$ | $F^{\wedge}$ | $G^{\wedge}$ | | | |
| $CaCl_2$ (2247)*$MgCl_2$ (219) | | | | | $E^{\wedge}$ | $F^{\wedge}$ | $G^{\wedge}$ | | | |
| $CaCl_2$ (2247)*$MgCl_2$ (437) | | | | | | $F^{\wedge}$ | $G^{\wedge}$ | | | |
| $CaCl_2$ (2247)*$MgCl_2$ (656) | | | | | | | $G^{\wedge}$ | | | |

Table 5.7. Post-hoc Turkey test results on similarities/differences in the interactions among pH, $CaCl_2$ dose and $MgCl_2$ dose. “-”, “+”, and “ ^ ” superscripts following the letters distinguish the groups identified for each parameters interaction.

### *5.2.4. SOLID-PHASE IDENTIFICATION*

Struvite crystallization is influenced by foreign compounds (e.g., potassium, calcium, zinc, chloride, carbonates) that can be absorbed on the crystal surface and perturb struvite formation (Koutsoukos et al., 2003). The presence of $Ca^{2+}$ or carbonate ($CO_3^{2-}$) can influence struvite formation either by competing for $PO_4^{3-}$ or by interfering with struvite crystallization (Kofina & Koutsoukos, 2004; Koutsoukos et al., 2003). Indeed, $Ca^{2+}$ can interact with $PO_4^{3-}$ or $CO_3^{2-}$ to form calcium phosphates (e.g., poorly crystallized hydroxyapatite) or calcium carbonate according to the following reactions (R. 5.1 and 5.2):

$$5Ca^{2+} + 3PO_4^{3-} + H_2O \rightarrow Ca_5(PO_4)_3OH + H^+ \qquad \text{(R. 5.1)}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad \text{(R. 5.2)}$$

Figure 5.6 shows the XRD patterns of the precipitate samples collected from tests n°1.13, 1.14, 2.1, 2.2, 2.10, 2.11, 2.13 and 2.14 where struvite peaks can be mainly observed (JCPDS card n° 00-015-0762). From the XRD patterns of tests n°2.1, 2.2, 2.10, 2.11, 2.13 and 2.14, calcite ($CaCO_3$, JCPDS card n° 00-005-0586) peaks have also been detected as a secondary phase. The latter can be mainly ascribed to the previous reaction (Eq. 5.2).

Tests n°1.13 and n°1.14 are characterized by struvite as the main crystalline phase, since XRD peaks are of higher intensities indicating bigger struvite crystals compared to other samples. Furthermore, it can be noted that for each sample from tests with $MgCl_2$ and pH=9 (tests n°2.2, 2.11 and 2.14), struvite peaks decrease in intensity compared to corresponding samples with equal $MgCl_2$ concentration and pH=8 (tests n°2.1, 2.10 and 2.13). This could be ascribable to the higher $Ca^{2+}$ addition in tests at pH=9 which led to the reduction of crystal size. The high $Mg^{2+}$, $PO_4^{3-}$ and $NH_4^+$ abatement and recovery in test tube 1.14 compared to 1.13 suggest that the former led to a greater presence of struvite.

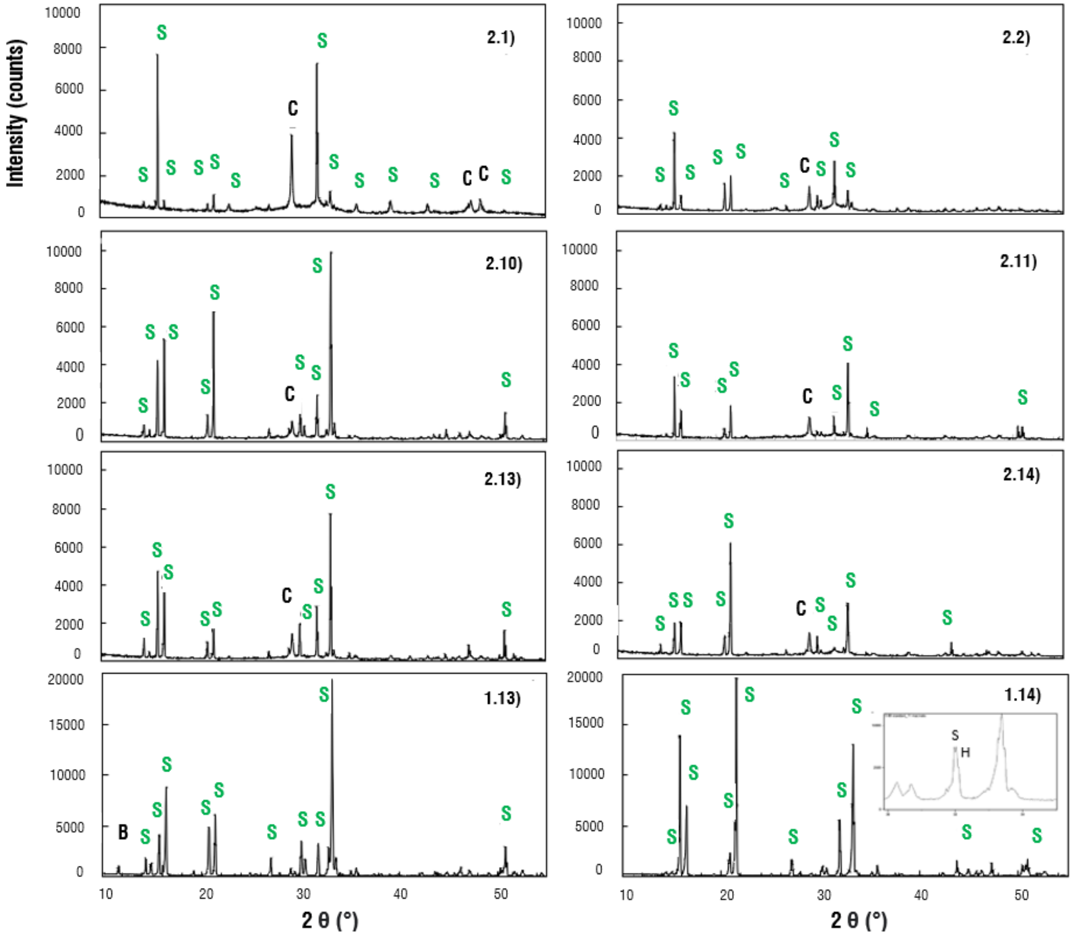


Figure 5.6. XRD Patterns of the precipitate samples collected from tests n° 1.13, 1.14, 2.1, 2.2, 2.10, 2.11, 2.13, 2.14 (S = Struvite, JCPDS card n° 00-015-0762; C = Calcite, JCPDS card n° 00-005-0586; B = Brushite, JCPDS card n° 00-009-0077; H = Hydroxyapatite, JCPDS card n° 00-001-1008).

$Mg^{2+}$, unlike $Ca^{2+}$, promotes the formation of struvite, so the morphology of the crystals is influenced by the initial concentration of $Mg^{2+}$ (Netshidzivhe, 2020). Specifically, when $Mg^{2+}$ concentration increases, the crystal size is bigger. In fact, in the tests n°2.1 (pH=8) and n°2.2 (pH=9), with no $MgCl_2$ addition, the peaks of the struvite are slightly lower in intensity, which suggests that the average size of the crystals is smaller than the corresponding samples with the same pH but higher $MgCl_2$ concentrations (tests n° 2.11 and 2.14). Furthermore, in tests n°1.13 and n°1.14, traces of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, JCPDS card n° 00-001-1008) have been also detected, while brushite ($CaHPO_4 \cdot 2(H_2O)$, JCPDS card n° 00-009-0077) peaks are present for test n°1.13 (Table 5.8). The strong $Ca^{2+}$ abatement for both tests shown in Table 5.4 is related to the precipitation of calcium phosphates in the form of hydroxyapatite and brushite or amorphous phases that precipitate on struvite crystal surfaces, thus interfering with its formation (Le Corre et al., 2005). Table 5.8 also shows an estimate of the expected concentrations of struvite and hydroxyapatite in the precipitate obtained by simulation with Visual MINTEQ. The tests n°1.13 and n°1.14 were predicted to have the highest concentration of struvite, which agrees with the XRD analysis. P removal predicted by Visual MINTEQ is generally higher than those experimentally observed (Table 5.4), probably due to the shorter duration of the settling phase during the experiments (2 h) compared to the time needed to reach the thermodynamical equilibrium. Thermodynamic modelling allowed to estimate the precipitation of other compounds within the 12 selected test tubes (Table 5.9).

|  | Solid phases detected by XRD analysis |  |  |  |  |  | Predicted phases precipitation with Visual MINTEQ at 20°C |  |  |
|---|---|---|---|---|---|---|---|---|---|
| **Test** | **S** | **H** | **$Ca_{2.86}Mg_{0.14}(PO_4)_2$** | **B** | **Ch** | **C** | **S (mg/L)** | **H (mg/L)** | **P recovery (%)** |
| **1.13** | X | • |  | • |  |  | 1944 | 727 | 89.1 |
| **1.14** | X | • |  |  |  |  | 2015 | 727 | 91.2 |
| **2.1** | X |  |  |  |  | Y | 710 | 1405 | 82.0 |
| **2.2** | X |  |  |  |  | Y | 257 | 2083 | 98.0 |
| **2.10** | X |  |  |  |  | Y | 1164 | 1404 | 95.4 |
| **2.11** | X |  |  |  |  | Y | 295 | 2083 | 99.1 |
| **2.13** | X |  |  |  |  | Y | 1183 | 1404 | 96.0 |
| **2.14** | X |  |  |  |  | Y | 310 | 2083 | 99.6 |
| **3.2** |  | • | X |  |  |  | 235 | 2082 | 97.32 |
| **3.3** |  | X | • |  | • |  | 0 | 2306 | 100.0 |
| **3.11** |  |  | X |  |  |  | 241 | 2082 | 97.5 |
| **3.12** |  | X | X | • | • |  | 0 | 2306 | 99.99 |

Table 5.8. Compounds detected by XRD analysis (X = primary phase; Y = secondary phase, • = phase in traces) and predicted struvite and hydroxyapatite precipitation with Visual MINTEQ at 20°C. S: struvite; H: hydroxyapatite; B: brushite; Ch: Chlorapatite; C: Calcite.

| Tests | Magnesite (mg/L) | Dolomite (mg/L) | Siderite (mg/L) | Vivianite (mg/L) | Manganese hydrogen phosphate (mg/L) | Hopeite (mg/L) | Hdrozincite (mg/L) | Nickel selenide (mg/L) |
|---|---|---|---|---|---|---|---|---|
| **1.13** | 5.8 |  |  | 1.68 | 0.27 | 0.083 |  | 0.0035 |
| **1.14** | 141.2 |  |  | 1.69 | 0.27 |  | 0.047 | 0.0035 |
| **2.1** |  |  |  | 1.68 | 0.27 | 0.122 |  | 0.0035 |
| **2.2** | 169.9 |  |  | 1.69 | 0.27 |  | 0.122 | 0.0035 |
| **2.10** | 85.5 |  |  | 1.68 | 0.27 | 0.013 |  | 0.0035 |
| **2.11** | 515.3 |  |  | 1.69 | 0.27 |  | 0.047 | 0.0035 |
| **2.13** | 220.3 |  |  | 1.68 | 0.27 | 0.003 |  | 0.0035 |
| **2.14** | 638.4 |  |  | 1.68 | 0.27 |  | 0.022 | 0.0035 |
| **3.2** | 117.5 |  |  | 1.67 | 0.27 |  |  | 0.0035 |
| **3.3** |  | 657.2 | 0.56 |  |  |  |  |  |
| **3.11** | 186.7 |  |  | 1.67 | 0.27 |  |  | 0.0035 |
| **3.12** |  | 687.1 | 0.26 |  |  |  |  | 0.0035 |

Table 5 9. Concentrations of other precipitates (besides struvite and hydroxyapatite) estimated through modelling with Visual MINTEQ.

Magnesite ($MgCO_3$) was estimated to form in all tests except 2.1, 3.3, and 3.12 at concentrations up to 638.4 mg/L. Dolomite ($CaMg(CO_3)_2$) and siderite ($FeCO_3$) were predicted to form only in tests 3.3 and 3.12 at concentrations of 657.2-687.1 mg/L and 0.3-0.6 mg/L, respectively. Conversely, vivianite ($Fe(PO_4)_2{\cdot}8H_2O$) and manganese hydrogen phosphate ($MnHPO_4$) were predicted to form in all tests except 3.3 and 3.12 at concentrations around 1.7 and 0.3 mg/L, respectively. Small amounts ($\leq$0.1 mg/L) of hopeite ($Zn_3(PO_4)_2{\cdot}4H_2O$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) can precipitate both in *tests 1* and *test 2* at pH 8 and 9, respectively. The predicted formation of nickel selenide (NiSe) was negligible ($<5\ \mu$g/L).

Figure 5.7 shows a XRD patterns enlargement of tests n°2.1, 2.2, 2.10, 2.11, 2.13 and 2.14. For these tests, the higher concentration of $Ca^{2+}$, due to the use of $Ca(OH)_2$ as alkalizing agent, inhibited the formation of struvite. However, XRD patterns also show an amorphous band in the range $2\theta=25$-35°, whose position corresponds to that of the characteristic peaks of struvite and hydroxyapatite. This suggests that phosphate-based compounds may have partly precipitated as amorphous phase. Furthermore, when comparing the amorphous band in the range $2\theta=25$-35° at the same $MgCl_2$ concentration, the greater presence of $Ca(OH)_2$ (i.e., at pH=9) (tests n° 2.2, 2.11 and 2.14) determines a slightly more pronounced amorphous band than at lower $Ca(OH)_2$ concentrations (pH=8) (tests n° 2.1, 2.10 and 2.13). Therefore, $Ca^{2+}$ addition promoted the formation of an amorphous phase instead of struvite.

Figure 5.8 shows the XRD patterns of tests n°3.2, 3.3, 3.11 and 3.12. Tests n°3.2, 3.3 and 3.12 are characterized by hydroxyapatite and calcium magnesium phosphate (CMP) ($Ca_{2.86}Mg_{0.14}(PO_4)_2$, JCPDS card n° 01-070-0681). In some of them, chlorapatite ($Ca_5(PO_4)_3Cl$, JCPDS card n° 00-001-1011) and brushite was also detected (Table 5.8).  Test 3.11 exhibits only the XRD diffraction peaks of CMP. In these tests, obtained with NaOH (pH=8) as alkalizing agent, the addition of $CaCl_2$ and the low concentrations of $MgCl_2$ inhibited the formation of struvite. At a dose of 109 mg/L of $MgCl_2$ (tests n°3.2 and n°3.3), a concentration of $CaCl_2$ of 1498 mg/L (test n°3.2) determined the formation of CMP as the main crystalline phase and traces of hydroxyapatite.

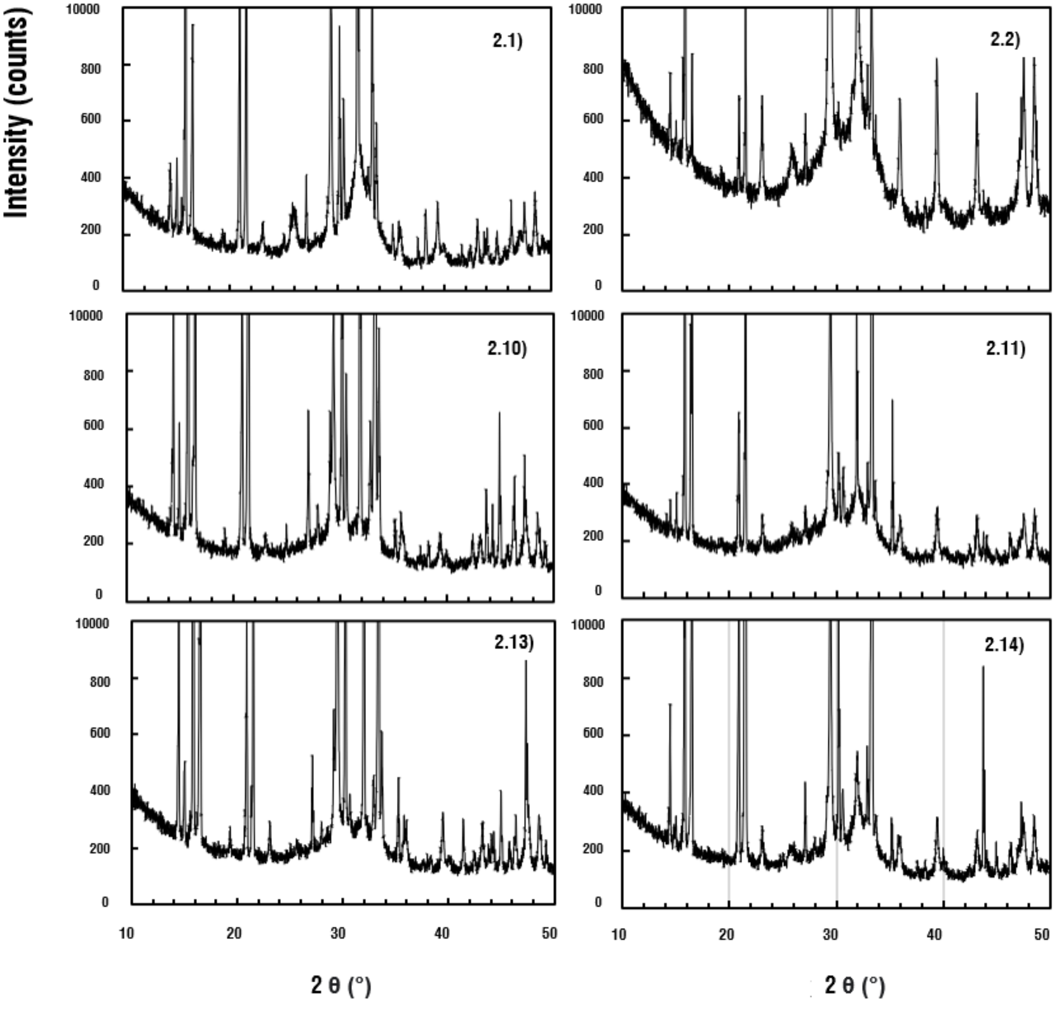


Figure 5.7. Enlargement in the range 2θ =10-50 ° and I= 0 -1000 counts of XRD pattern of tests n° 2.1, 2.2, 2.10, 2.11, 2.13, 2.14.

On the contrary, with $CaCl_2$ dose of 2247 mg/L (test n°3.3), hydroxyapatite was the main crystalline phase and CMP and chlorapatite were also detected in traces (Table 5.8). These results justify the greater reduction of $Mg^{2+}$ percentage in test n°3.2 compared to test n°3.3 and the greater reduction of $Ca^{2+}$ percentage in test n°3.3 compared to n°3.2 (Table 5.4), being the $Ca/PO_4$ molar ratios in hydroxyapatite and CMP respectively equal to 1.67 and 1.43. In test n°3.11, only CMP was detected (Figure 5.8) with more intense diffraction peaks, indicating higher crystallinity, compared to those detected for test n °3.2 with lower values of $MgCl_2$. Instead, the XRD pattern of test n°3.12, performed at higher $CaCl_2$ dose (2247 mg/L) than test n°3.11, presents both peaks of CMP and hydroxyapatite, as well as traces of brushite and chlorapatite, due to $Ca^{2+}$ interaction with $PO_4^{3-}$ or $CO_3^{2-}$ to form poorly crystallized calcium phosphates. Moreover, in test n°3.12, the greater dose of $MgCl_2$ (219 mg/L) determined the presence of CMP peaks compared to test n°3.3 (109 mg/L), characterized by the same amount of $CaCl_2$, in which CMP is present in traces.

Focusing on P-based precipitates, brushite features a higher solubility constant than struvite ($2.7 \cdot 10^{-7}$ and $5.51 \cdot 10^{-14}$ at 25°C, respectively) and, therefore, its formation should have not significantly impacted struvite crystallization. In contrast, hydroxyapatite has a lower solubility ($\sim 10^{-59}$ at 25°C) than struvite, so its formation may have occurred prior to that of struvite. However, none of the ions participating to struvite formation was completely precipitated at the end of the test. On the other hand, the small amount of amorphous precipitate in tests n°1.13 and n°1.14, probably due to the use of a $Ca^{2+}$-free base, suggests a lower hydroxyapatite generation that may have favored struvite crystallization.

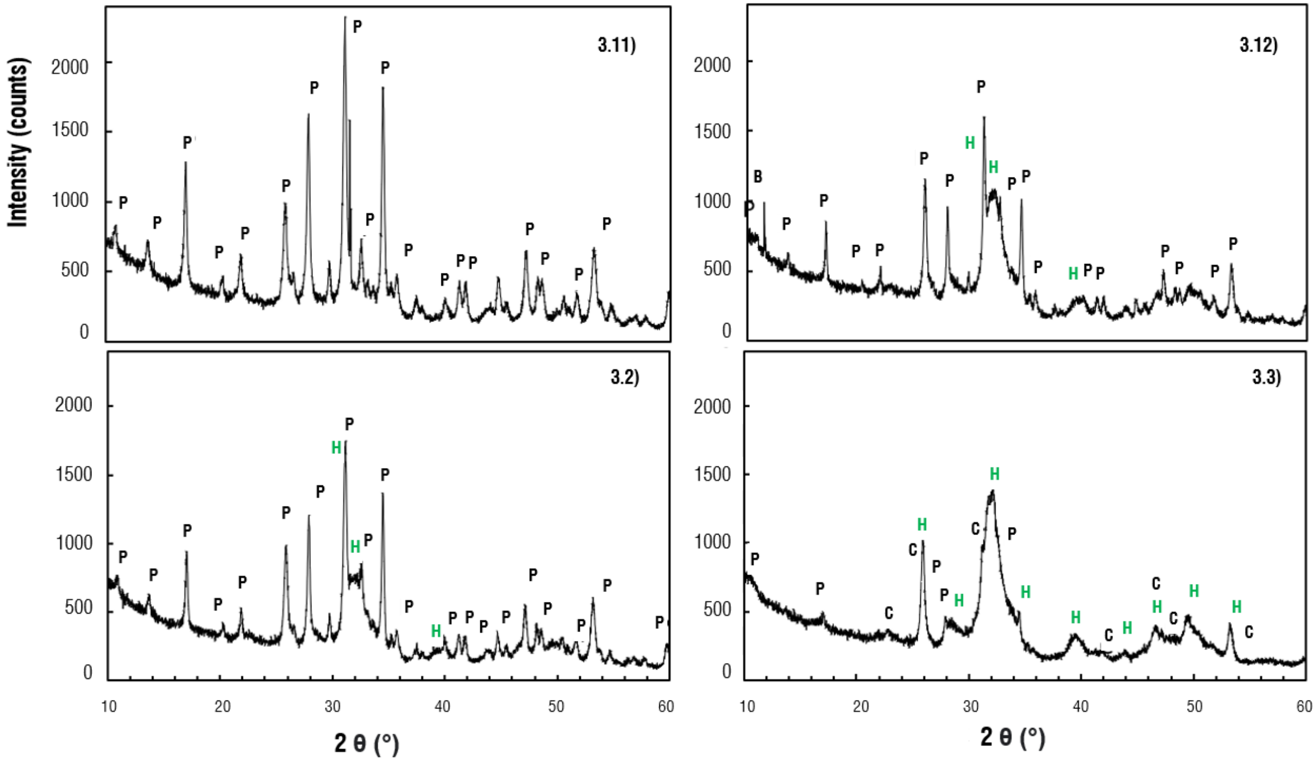


Figure 5.8. XRD patterns of tests n° 3.2, 3.3, 3.11 and 3.12 (P = calcium-magnesium phosphate ($Ca_{2.86}Mg_{0.14}(PO_4)_2$, JCPDS card n° 01-070-0681; H = hydroxyapatite, JCPDS card n° 00-001-1008; C = Calcite, JCPDS card n° 00-005-0586; B = Brushite, JCPDS card n° 00-009-0077).

# CHAPTER 6. ECONOMIC AND ENVIRONMENTAL EVALUATIONS AND PRACTICAL IMPLICATIONS

*This chapter has, in part, resulted in the technical report entitled "Phosphorus recovery as struvite and hydroxyapatite from the liquid fraction of municipal sewage sludge with limited magnesium addition" by Ferraro,* ***de Sario****, Attanasio, Di Capua, Gorgoglione, Fratino, Mascolo, Pirozzi, Trancone, Spasiano (Journal of Environmental Quality, 2022)* (Ferraro et al., 2022)

## 6.1. ENVIRONMENTAL IMPACT OF PHOSPHOROUS RECOVERY TECHNOLOGY APPLIED TO WWTPs

Through a LCA (Life Cycle Assessment) and considering the impact of energy production and waste disposal of each technology, Amann et al. (2018) has been carried out an environmental assessment, on the basis of three indicators:

- CED (cumulative energy demand), expressed as kWh, that is an indicator to determine the energy requirements during the entire life cycle of a product (VDI, 2012);
- GWP (global warming potential), gaseous emissions of $CO_2$, $CH_4$ and $N_2O$, expressed as $CO_2$ equivalents ($CO_2e$);
- AP (acidification potential) gaseous emissions of $SO_2$, $NO_x$, HCl and $NH_3$ expressed as $SO_2$ equivalents ($SO_2e$) that is crucial for soil acidity and, so, linked both to agriculture and P fertilizers.

Regarding the recovery technologies from the liquid fraction of the sewage sludge, have been indicated low environmental impact, except for Crystalactor® that has high energy demand. Moreover, these technologies allow to recover materials with low content of heavy metals, micropollutants and pathogens.

Also, P recovery technologies from sewage sludge ash can be present negative value of the three indicators, even though its high energy demand of incineration, thanks to P-rich recovery product such as $H_3PO_4$, but the products obtained can contains high level of heavy metals and the process can generate toxic contaminants.

In contrast, technologies that recover P from sewage sludge contains low levels of heavy metals but, due to high demand of high energetic intensity chemicals, these processes feature positive values of three indicators.

## *6.2. ECONOMIC EVALUATION OF PHOSPHOROUS RECOVERY TECHNOLOGY APPLIED IN WWTPS*

Annual costs for technologies aimed at P recovery from postdigestion supernatants resulting in annual costs of 5-8 €/kg$_{\text{P recovered}}$ for Crystalactor® and 9-10 €/kg$_{\text{P recovered}}$ for Ostara Pearl®. The NuReSys® technology is the lowest-priced technology on the market, with an operational cost of 1.31-3 €/kg$_{\text{P}}$ (Dewaele, 2015). Other details of full-scale technologies for P recovery from solid/liquid fraction of WWTP streams are reported in Table 6.1.

| **Technology** | **Application** | **Type of reactor** | **Number of active plants** | **Annual costs (€/kg$_{\text{P recovered}}$)** |
|---|---|---|---|---|
| Crystalactor® | Wastewater/supernatant | FBR | 4 | 5-8 |
| Ostara Pearl® | Digester and thickener supernatants | FBR | 8 | 9-10 |
| Multiform Harvest™ | Digester supernatant | Cone-shaped FBR | 2 | n.a. |
| NuReSys® | Digestate, filtrate and centrate of WWTP | CSTR | 7 | 1.31-3 |
| PHOSPHAQ™ | Municipal sludge reject liquors | CSTR | 11 | n.a. |
| MagPrex® | Digestate | Air-lift | 7 | 7-8 |

Table 6.1. Details and annual costs of full-scale technologies for P recovery from solid/liquid fraction of WWTP streams.

It must be considered that the implementation of these technologies can led to a reduction in maintenance costs, through the removal of struvite that can cause problems on the piping and pumping systems for the incrustation. Also, P-recovery allows to reduce the P-load in the backflow.

The REM-NUT® technology has annual costs up to 28 €/kg$_{\text{P recovered}}$ for the high cost linked to the reagents and resins (Egle et al., 2016) and the obtained product needed to further granulation and classification step to be made suitable for marketing. Regarding to P recovery from sewage sludge ash, can be expected high costs and energetic consumption especially linked to thermodynamical treatments, as in the case of AshDec® system.

Through commercialization of P-rich product obtained and heat recovery from thermal P-recovery processes, it can be possible reduce the capital and operational costs and the optimal solution is characterized by significant process efficiency, economic advantage and environmental sustainability.

## *6.3. FLOW/MASS BALANCE AND PRELIMINARY ECONOMIC EVALUATION OF THE PERFORMED TESTS LABORATORY*

Ammonia concentration in the WWTP centrate of Andria was significantly lower than the initial phosphate concentration, resulting in a $NH_4^+/PO_4^{3-}$ molar ratio of 0.77. This ratio would limit P recovery to a maximum of 77% regardless of Mg dosage. In this case, the addition of $Ca^{2+}$ in the form of calcium phosphates instead of struvite represents an alternative solution to precipitate and recover P. Even if calcium phosphates are generally recognized as a lower economically valuable product than struvite, their composition is similar to PR and could be used as raw material for fertilizer production (Hao et al., 2013; Lei et al., 2019). Moreover, the use of calcium phosphates can be also extended to the production of other goods, such as detergents and food additives, which improves the economic sustainability of P recovery (M. Chen & Graedel, 2016a)

A mass flow balance was carried out with the data provided by the Andria municipal WWTP to estimate the tons/year of struvite and hydroxyapatite that could be recovered from the centrate based on the conditions of tests n°1.13 and 1.14, leading to the highest predicted concentrations of struvite (Table 5.8). Based on the scheme represented in Figure 6.1 and on flow and mass balances reported in the equations 6.1 and 6.2, neglecting the concentration of dry solids in the centrate ($D_{S\%H2O} \sim 0$), it was possible to calculate a centrate flow rate equal to 12.68 $m^3/h$. This value, coupled to the concentrations of struvite and hydroxyapatite predicted by Visual MINTEQ (Table 5.8), normalized with respect to the P recovery values measured in the lab tests, allowed to estimate a production of struvite and hydroxyapatite respectively of 74.9 and 28.0 tons/year (from the WWTP of Andria) based on the operating conditions of test n°1.13 and of 92.0 and 33.2 tons/year based on test n°1.14.

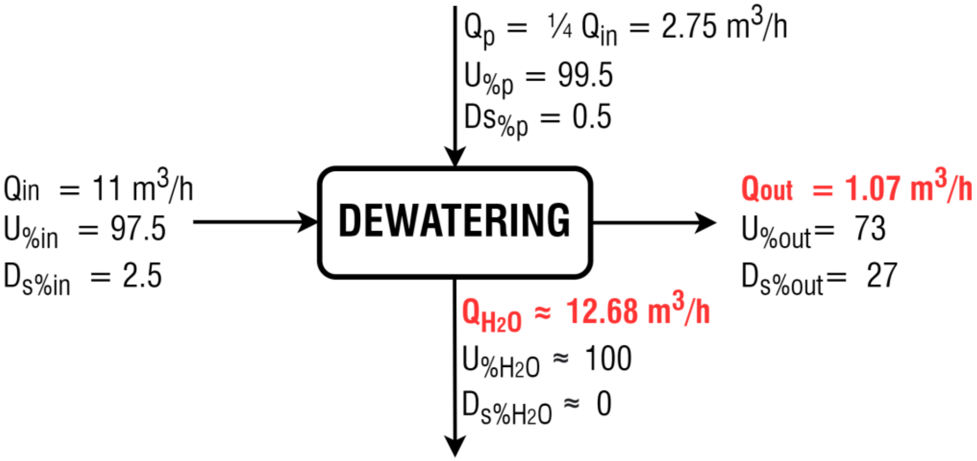


Figure 6.1. Scheme of flow and mass balances for the calculation of the recirculation flow. U% and Ds% indicate the weight percentages of water content and dry solids within the different volumetric flow rates Q, respectively. The subscript “in” refers to the influent digestate, “p” to polyelectrolytes, “H2O” to centrate, and “out” to dewatered sludge.

$$Q_{in} + Q_p - Q_{H2O} - Q_{out} = 0 \qquad \text{(Eq. 6.1)}$$

$$Q_{in} \cdot Ds_{\%in} + Q_p \cdot Ds_{\%p} - Q_{H2O} \cdot Ds_{\%H2O} - Q_{out} \cdot Ds_{\%out} = 0 \qquad \text{(Eq. 6.2)}$$

According to previous literature works, P has a market value of 1.7±0.5 €/kg (Egle et al., 2016), while the average annual cost for P recovered (usually as struvite) with known technologies from post-digestion supernatants is typically in the range of 8-10 €/kg P, how it is reported in Table 6.1. Considering market prices of $MgCl_2$ and NaOH (based on an e-commerce survey) equal to 115 and 530 €/ton, respectively, the cost of the reagents required for P recovery in test conditions n°1.13 and n°1.14 was estimated as 0.79 €/kg P and 0.93 €/kg P, respectively. However, a more precise cost-benefit assessment for phosphorus recovery with the tested method should include maintenance, operation, and personnel costs as well as the recovery of valuable elements (Mg, Ca, and N) from P precipitates. Performing an LCA analysis on the presented method, could be possible to know the potential environmental impact deriving by the application of the method on the industrial scale.

The low concentrations of heavy metals or even the absence of some of them such as cadmium, mercury or lead, in the centrate used for this study led to the production of a marketable P-rich fertilizers in compliance with recent regulations, e.g., the Regulation (EU) No 2019/1009 (Regulation (EC) No 2019/1009 of the European Parliament and of the Council, 2019). Moreover, the presence of small amounts of the minerals reported in Table 5.9 may exert a positive effect on crops due to the presence in the precipitates of micronutrients, such as Fe and Zn, together with P and N (Di Capua et al., 2020).

# *FUTURE PERSPECTIVES*

Although the experimental campaign has led to satisfactory results in terms of removed P and economic estimation, it is necessary to make some important considerations.

The whole test set has been performed at laboratory scale and considering the centrate of a single municipal WWTP. For a more trusted result is important:

1) To rerun the experimental campaign considering the centrate of other WWTP, with different operating conditions and different centrate compositions, thus expanding the data set available. This would allow to identify a methodology for P recovery applicable on several WWTP.
2) To switch from the laboratory scale to a pilot plant. Indeed, a pilot plant has a behavior closer to that of an industrial plant, compared to the results obtained during laboratory tests. This could reduce the uncertainty linked to laboratory-scale.

At the end of the experimental phase, the precipitate obtained must then be tested in agriculture. This step is crucial to assess the improvement that this type of application can bring in the field. Obviously, it is also necessary to consider the comparison between the cost to obtain struvite and hydroxyapatite with that of common fertilizers.
So, another step that must be considered is the LCA, for analysis of the environmental aspect and potential impacts throughout the obtain product's life cycle, including production, use and disposal (ISO 14040:2006) (how is reported in Chapter 6.3.).

# CONCLUSIONS

Phosphorous recovery is one goal for the sustainable development. The incentives of national governments to promote the use of P-based fertilizers derived from WWTP would significantly encourage this practice. This can lead both to increasing the availability of a non-renewable resource and P reduction load in the effluent (and the consequent fight against eutrophication). Among the various method that allow to recover phosphorous from the liquid (crystallization, adsorption) or solid (from sludge and sludge ash) phases of the municipal WWTP, there are many differences in terms of costs and efficiency (percentage of P removal). However, the product obtained from these processes is not always suitable for agricultural reuse.

In this experimental study, P precipitation tests have been performed on municipal WWTP centrate to evaluate the recovery of struvite and hydroxyapatite with limiting Mg doses at different pH (8-10), alkalizing agent (NaOH and $Ca(OH)_2$), as well as $MgCl_2$ and $CaCl_2$ additions. The experiments led to P removal efficiencies in the range of 53-99%. Specifically, the optimal condition for struvite and hydroxyapatite formation (pH=9 with NaOH e 656 mg/L of $MgCl_2$, with consequent P removal equal to 87,3%) has been identified. In this condition, 92.0 and 33.2 tons/year of struvite and hydroxyapatite could be recovered, respectively, from the WWTP of Andria. By a preliminary economic evaluation, the costs for the reagent consumption obtained was found to be almost half of the mean P market value. It is noteworthy to highlight that substantial quantity of heavy metal in the precipitates is absent, as it was shown by the thermodynamic simulation.

Iterating the experimental procedure described on other WWTP, together with a detailed economic assessment, would certainly lead to the refinement of the method which could then be applied on a large scale.

# *ACKNOWLEDGEMENTS*

I thank the DICATECH and all the teachers and researchers I have been lucky enough to meet in my scientific-professional journey for having contributed to my growth and for the support I received. I also thank Dr Antonella Attanasio of the Acquedotto Pugliese S.p.A. for her constant support in laboratory and research activities.

Moreover, I want to thank the Italian Ministry of University and Research (MUR) which provided, through the National Operational Programme "Research and Innovation 2014- 2020", financial support for my PhD fellowship (grant number DOT130UZWT n. 2) in the frame of the research project entitled "Phosphorous And Nitrogen. Their Recovery from Urban Sewage Treatment (PAN-TRUST)" (CUP - D94I20000110006) of the PhD course in "Environmental, Territorial and Building Risk and Development" at the Polytechnic University of Bari.

Simona de Sario

# *REFERENCES*

Ajmal, Z., Muhmood, A., Usman, M., Kizito, S., Lu, J., Dong, R., & Wu, S. (2018). Phosphate removal from aqueous solution using iron oxides: Adsorption, desorption and regeneration characteristics. *Journal of Colloid and Interface Science*, *528*, 145–155. https://doi.org/10.1016/j.jcis.2018.05.084

Alcántara, C., Domínguez, J. M., García, D., Blanco, S., Pérez, R., García-Encina, P. A., & Muñoz, R. (2015). Evaluation of wastewater treatment in a novel anoxic-aerobic algal-bacterial photobioreactor with biomass recycling through carbon and nitrogen mass balances. *Bioresource Technology*, *191*, 173–186. https://doi.org/10.1016/j.biortech.2015.04.125

Almasri, D. A., Saleh, N. B., Atieh, M. A., McKay, G., & Ahzi, S. (2019). Adsorption of phosphate on iron oxide doped halloysite nanotubes. *Scientific Reports*, *9*(1), 3232. https://doi.org/10.1038/s41598-019-39035-2

Amann, A., Zoboli, O., Krampe, J., Rechberger, H., Zessner, M., & Egle, L. (2018). Environmental impacts of phosphorus recovery from municipal wastewater. *Resources, Conservation and Recycling*, *130*, 127–139. https://doi.org/10.1016/j.resconrec.2017.11.002

Badgujar, N. R., Di Capua, F., Papirio, S., Pirozzi, F., Lens, P. N. L., & Esposito, G. (2020). CO2 biofixation by Chlamydomonas reinhardtii using different CO2 dosing strategies. *Advances in Science, Technology and Innovation*, 321–324. https://doi.org/10.1007/978-3-030-13068-8_80

Bai, Y., Zhang, Y., Quan, X., & Chen, S. (2016). Nutrient removal performance and microbial characteristics of a full-scale IFAS-EBPR process treating municipal wastewater. *Water Science and Technology*, *73*(6), 1261–1268. https://doi.org/10.2166/wst.2015.604

Ball Coelho, B., Murray, R., Lapen, D., Topp, E., & Bruin, A. (2012). Phosphorus and sediment loading to surface waters from liquid swine manure application under different drainage and tillage practices. *Agricultural Water Management*, *104*, 51–61. https://doi.org/10.1016/j.agwat.2011.10.020

Barajas, M. G., Escalas, A., & Mujeriego, R. (2002). Fermentation of a low VFA wastewater in an activated primary tank. *Water SA*, *28*(1), 89–98. https://doi.org/10.4314/wsa.v28i1.4872

Barnard, J. L. (1974). Cut P and N without chemicals. *Water and Wastes Engineering*, *11*, 41–44.

Beccari, M., Passino, R., Ramadori, R., & Vismara, R. (1993). *Rimozione di azoto e fosforo dai liquami*. Hoepli.

Beer, M., Stratton, H. M., Griffiths, P. C., & Seviour, R. J. (2006). Which are the polyphosphate accumulating organisms in full-scale activated sludge enhanced biological phosphate removal systems in Australia? *Journal of Applied Microbiology*, *100*(2), 233–243. https://doi.org/10.1111/j.1365-2672.2005.02784.x

Benyoucef, S., & Amrani, M. (2011). Adsorption of phosphate ions onto low cost Aleppo pine adsorbent. In *Desalination* (Vol. 275, Issues 1–3, pp. 231–236). Elsevier B.V. https://doi.org/10.1016/j.desal.2011.03.004

Berg, U., Knoll, G., Kaschka, E., Kreutzer, V., Donnert, D., Weidler, P. G., & Nüesch, R. (2007). P-RoC – Phosphorus recovery from wastewater by crystallisation of calcium phosphate compounds. *Journal of Residuals Science and Technology*, *4*, 121–126.

Bhatnagar, A., & Sillanpää, M. (2011). A review of emerging adsorbents for nitrate removal from water. In *Chemical Engineering Journal* (Vol. 168, Issue 2, pp. 493–504). Elsevier. https://doi.org/10.1016/j.cej.2011.01.103

Bi, W., Li, Y., & Hu, Y. (2014). Recovery of phosphorus and nitrogen from alkaline hydrolysis supernatant of excess sludge by magnesium ammonium phosphate. *Bioresource Technology*, *166*, 1–8. https://doi.org/10.1016/j.biortech.2014.04.092

Blanco, I., Molle, P., Sáenz de Miera, L. E., & Ansola, G. (2016). Basic Oxygen Furnace steel slag aggregates for phosphorus treatment: Evaluation of its potential use as a substrate in constructed wetlands. *Water Research*, *89*, 355–365. https://doi.org/10.1016/j.watres.2015.11.064

Blaney, L. M., Cinar, S., & SenGupta, A. K. (2007). Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Research*, *41*(7), 1603–1613. https://doi.org/10.1016/j.watres.2007.01.008

Blöcher, C., Niewersch, C., & Melin, T. (2012). Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration. *Water Research*, *46*(6), 2009–2019. https://doi.org/10.1016/j.watres.2012.01.022

Bompan, E., & Brambilla, I. N. (2016). *Che cosa è l'economia circolare*. Edizioni Ambiente.

Bowden, L. I., Jarvis, A. P., Younger, P. L., & Johnson, K. L. (2009). Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag. *Environmental Science & Technology*, *43*(7), 2476–2481. https://doi.org/10.1021/es801626d

Brown, N., & Shilton, A. (2014). Luxury uptake of phosphorus by microalgae in waste stabilisation ponds: current understanding and future direction. *Reviews in Environmental Science and Biotechnology*, *13*(3), 321–328. https://doi.org/10.1007/s11157-014-9337-3

Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A., & Graham, D. W. (2018). A review of phosphorus removal technologies and their applicability to small-scale domestic wastewater treatment systems. *Frontiers in Environmental Science*, *6*, 8. https://doi.org/10.3389/fenvs.2018.00008

Burton, F., & Stensey, H. (2003). *Wastewater Engineering, Treatment and Reuse* (4th ed.). McGraw Hill.

Cai, W., Zhao, Z., Li, D., Lei, Z., Zhang, Z., & Lee, D. J. (2019). Algae granulation for nutrients uptake and algae harvesting during wastewater treatment. *Chemosphere*, *214*, 55–59. https://doi.org/10.1016/j.chemosphere.2018.09.107

Campo, R., Sguanci, S., Caffaz, S., Mazzoli, L., Lubello, C., & Lotti, T. (2020). Efficient carbon, nitrogen and phosphorus removal from low C/N real domestic wastewater with aerobic granular sludge. *Bioresource Technology*, *305*, 122961. https://doi.org/10.1016/j.biortech.2020.122961

Canziani, R., & Di Cosmo, R. (2018). STATO DELL'ARTE E POTENZIALITÀ DELLE TECNOLOGIE DI RECUPERO DEL FOSFORO DAI FANGHI DI DEPURAZIONE. *Ingegneria Dell'ambiente*, *5*(3), 149–170. https://doi.org/doi.org/10.32024/ida.v5i3.p01

Chai, H., Xiang, Y., Chen, R., Shao, Z., Gu, L., Li, L., & He, Q. (2019). Enhanced simultaneous nitrification and denitrification in treating low carbon-to-nitrogen ratio wastewater: treatment performance and nitrogen removal pathway. *Bioresource Technology*, *280*(November 2018), 51–58. https://doi.org/10.1016/j.biortech.2019.02.022

Chatterjee, P., Granatier, M., Ramasamy, P., Kokko, M., Lakaniemi, A. M., & Rintala, J. (2019). Microalgae grow on source separated human urine in Nordic climate: Outdoor pilot-scale cultivation. *Journal of Environmental Management*, *237*, 119–127. https://doi.org/10.1016/j.jenvman.2019.02.074

Chen, B., Chen, Z., & Lv, S. (2011). A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresource Technology*, *102*(2), 716–723. https://doi.org/10.1016/j.biortech.2010.08.067

Chen, D., Xiao, X., & Yang, K. (2016). Removal of phosphate and hexavalent chromium from aqueous solutions by engineered waste eggshell. *RSC Advances*, *6*(42), 35332–35339. https://doi.org/10.1039/C6RA05034D

Chen, M., & Graedel, T. E. (2016a). A half-century of global phosphorus flows, stocks, production, consumption, recycling, and environmental impacts. *Global Environmental Change*, *36*, 139–152. https://doi.org/10.1016/j.gloenvcha.2015.12.005

Chen, M., & Graedel, T. E. (2016b). A half-century of global phosphorus flows, stocks, production, consumption, recycling, and environmental impacts. *Global Environmental Change*, *36*, 139–152. https://doi.org/10.1016/J.GLOENVCHA.2015.12.005

Chen, X., Kong, H., Wu, D., Wang, X., & Lin, Y. (2009). Phosphate removal and recovery through crystallization of hydroxyapatite using xonotlite as seed crystal. *Journal of Environmental Sciences*, *21*(5), 575–580. https://doi.org/10.1016/S1001-0742(08)62310-4

Cheung, K. C., & Venkitachalam, T. H. (2000). Improving phosphate removal of sand infiltration system using alkaline fly ash. *Chemosphere*, *41*(1–2), 243–249. https://doi.org/10.1016/S0045-6535(99)00417-8

Chrispim, M. C., Scholz, M., & Nolasco, M. A. (2019). Phosphorus recovery from municipal wastewater treatment: Critical review of challenges and opportunities for developing countries. *Journal of Environmental Management*, *248*, 109268. https://doi.org/10.1016/j.jenvman.2019.109268

Chubar, N. (2010). Physico-chemical treatment of micropollutants: adsorption and ion exchange. In J. Virkutyte, R. S. Varma, & V. Jegatheesan (Eds.), *Treatment of Micropollutants in Water and Wastewater* (pp. 165–203). IWA Publishing.

Coats, E. R., Brinkman, C. K., & Lee, S. (2017). Characterizing and contrasting the microbial ecology of laboratory and full-scale EBPR systems cultured on synthetic and real wastewaters. *Water Research*, *108*, 124–136. https://doi.org/10.1016/j.watres.2016.10.069

Cooper, J., Lombardi, R., Boardman, D., & Carliell-Marquet, C. (2011). The future distribution and production of global phosphate rock reserves. *Resources, Conservation and Recycling*, *57*, 78–86. https://doi.org/10.1016/j.resconrec.2011.09.009

Cornel, P., & Schaum, C. (2009). Phosphorus recovery from wastewater: needs, technologies and costs. *Water Science and Technology*, *59*(6), 1069–1076. https://doi.org/10.2166/wst.2009.045

Costa, R. H. R., Villafranca, B. M., Voltolini, C. A., Guimarães, L. B., Hoffmann, H., Velho, V. F., & Mohedano, R. A. (2019). EFFECTIVENESS OF PHOSPHORUS REMOVAL IN AN SBR USING CO-PRECIPITATION WITH FERRIC CHLORIDE, AND ITS EFFECTS ON MICROBIAL ACTIVITY. *Brazilian Journal of Chemical Engineering*, *36*(2), 785–795. https://doi.org/10.1590/0104-6632.20190362s20180378

Cydzik-Kwiatkowska, A., & Zielińska, M. (2016). Bacterial communities in full-scale wastewater treatment systems. *World Journal of Microbiology and Biotechnology*, *32*, 66.

De-Bashan, L. E., & Bashan, Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997-2003). *Water Research*, *38*(19), 4222–4246. https://doi.org/10.1016/j.watres.2004.07.014

de Souza, K. C., Antunes, M. L. P., Couperthwaite, S. J., da Conceição, F. T., de Barros, T. R., & Frost, R. (2013). Adsorption of reactive dye on seawater-neutralised bauxite refinery residue. *Journal of Colloid and Interface Science*, *396*, 210–214. https://doi.org/10.1016/j.jcis.2013.01.011

Deselnicu, D. C., Militaru, G., Deselnicu, V., Zăinescu, G., & Albu, L. (2018). Towards a circular economy– a zero waste programme for europe. *ICAMS Proceedings of the International Conference on Advanced Materials and Systems*, 563–568. https://doi.org/10.24264/icams-2018.XI.4

Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Bruggen, B. Van der, Verstraete, W., Rabaey, K., & Meesschaert, B. (2015). Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review. *Critical Reviews in Environmental Science and Technology*, *45*(4), 336–384. https://doi.org/10.1080/10643389.2013.866531

Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., Verstraete, W., Rabaey, K., & Meesschaert, B. (2015). Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review. *Critical Reviews in Environmental Science and Technology*, *45*(4), 336–384. https://doi.org/10.1080/10643389.2013.866531

Dewaele, C. (2015). NuReSys–from P recovery to fertilizer production. *Eurpoean Sustainable Phosphorus Conference. Berlin*.

Di Capua, F., de Sario, S., Ferraro, A., Petrella, A., Race, M., Pirozzi, F., Fratino, U., & Spasiano, D. (2022). Phosphorous removal and recovery from urban wastewater: Current practices and new directions. *Science of The Total Environment*, *823*, 153750. https://doi.org/10.1016/j.scitotenv.2022.153750

Di Capua, F., Spasiano, D., Giordano, A., Adani, F., Fratino, U., Pirozzi, F., & Esposito, G. (2020). High-solid anaerobic digestion of sewage sludge: challenges and opportunities. *Applied Energy*, *278*, 115608. https://doi.org/10.1016/j.apenergy.2020.115608

Di Costanzo, N., Cesaro, A., Di Capua, F., & Esposito, G. (2021). Exploiting the Nutrient Potential of Anaerobically Digested Sewage Sludge: A Review. *Energies*, *14*(23), 8149. https://doi.org/10.3390/en14238149

Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Rivera-Utrilla, J., & Sánchez-Polo, M. (2007). Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. In *Journal of Environmental Management* (Vol. 85, Issue 4, pp. 833–846). Academic Press. https://doi.org/10.1016/j.jenvman.2007.07.031

Ding, L., Wu, C., Deng, H., & Zhang, X. (2012). Adsorptive characteristics of phosphate from aqueous solutions by MIEX resin. *Journal of Colloid and Interface Science*, *376*(1), 224–232. https://doi.org/10.1016/j.jcis.2012.03.002

Doyle, J. D., & Parsons, S. A. (2002). Struvite formation, control and recovery. *Water Research*, *36*(16), 3925–3940. https://doi.org/10.1016/S0043-1354(02)00126-4

Eberhardt, T. L., & Min, S. H. (2008). Biosorbents prepared from wood particles treated with anionic polymer and iron salt: Effect of particle size on phosphate adsorption. *Bioresource Technology*, *99*(3), 626–630. https://doi.org/10.1016/j.biortech.2006.12.037

Regulation (EC) No 2019/1009 of the European Parliament and of the Council, 114 (2019).

Egle, L., Rechberger, H., Krampe, J., & Zessner, M. (2016). Phosphorus recovery from municipal wastewater: An integrated comparative technological, environmental and economic assessment of P recovery technologies. *Science of the Total Environment*, *571*, 522–542. https://doi.org/10.1016/j.scitotenv.2016.07.019

El Hamouri, B. (2009). Rethinking natural, extensive systems for tertiary treatment purposes: The high-rate algae pond as an example. *Desalination and Water Treatment*, *4*(1–3), 128–134. https://doi.org/10.5004/dwt.2009.367

European Chemicals Agency. (2017). Guidance for identification and naming of substances under REACH and CLP. In *Ver 2.1* (Issue May). https://echa.europa.eu/documents/10162/23036412/substance_id_en.pdf/ee696bad-49f6-4fec-b8b7-2c3706113c7d

European Parliament. (2016). *Proposal for a regulation of the European Parliament and of the Council laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009*.

Fattah, K. P. (2012). Assessing Struvite Formation Potential at Wastewater Treatment Plants. *International Journal of Environmental Science and Development*, 548–552. https://doi.org/10.7763/IJESD.2012.V3.284

Faust, S. D., & Aly, O. M. (1987). *Adsorption Processes for Water Treatment*. Butterworths. https://doi.org/10.1016/B978-0-409-90000-2.50003-0

Fernando, E. Y., McIlroy, S. J., Nierychlo, M., Herbst, F. A., Petriglieri, F., Schmid, M. C., Wagner, M., Nielsen, J. L., & Nielsen, P. H. (2019). Resolving the individual contribution of key microbial populations to enhanced biological phosphorus removal with Raman–FISH. *ISME Journal*, *13*(8), 1933–1946. https://doi.org/10.1038/s41396-019-0399-7

Ferraro, A., de Sario, S., Attanasio, A., Capua, F. Di, Gorgoglione, A., Fratino, U., Mascolo, M. C., Pirozzi, F., Trancone, G., & Spasiano, D. (2022). Phosphorus recovery as struvite and hydroxyapatite from the liquid fraction of municipal sewage sludge with limited magnesium addition. *Journal of Environmental Quality*. https://doi.org/10.1002/jeq2.20446

Field, H. R., Whitaker, A. H., Henson, J. A., & Duckworth, O. W. (2019). Sorption of copper and phosphate to diverse biogenic iron (oxyhydr)oxide deposits. *Science of The Total Environment*, *697*, 134111. https://doi.org/10.1016/j.scitotenv.2019.134111

Filali-Meknassi, Y., Auriol, M., Tyagi, R. D., Comeau, Y., & Surampalli, R. Y. (2005).

Phosphorus Co-Precipitation in the Biological Treatment of Slaughterhouse Wastewater in a Sequencing Batch Reactor. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, *9*(3), 179–192. https://doi.org/10.1061/(ASCE)1090-025X(2005)9:3(179)

Filippino, K. C., Mulholland, M. R., & Bott, C. B. (2015). Phycoremediation strategies for rapid tertiary nutrient removal in a waste stream. *Algal Research*, *11*, 125–133. https://doi.org/10.1016/j.algal.2015.06.011

Garske, B., Stubenrauch, J., & Ekardt, F. (2020). Sustainable phosphorus management in European agricultural and environmental law. *Review of European, Comparative & International Environmental Law*, *29*(1), 107–117. https://doi.org/10.1111/reel.12318

Gibbons, M. K., & Gagnon, G. A. (2011). Understanding removal of phosphate or arsenate onto water treatment residual solids. *Journal of Hazardous Materials*, *186*(2–3), 1916–1923. https://doi.org/10.1016/j.jhazmat.2010.12.085

Giesen, A., de Bruin, L. M. M., Niermans, R. P., & van der Roest, H. F. (2013). Advancements in the application of aerobic granular biomass technology for sustainable treatment of wastewater. *Water Practice and Technology*, *8*(1), 47–54. https://doi.org/10.2166/wpt.2013.007

Giesen, A., Loosdrecht, M. van, Pronk, M., Robertson, S., & Thompson, A. (2016). Aerobic Granular Biomass Technology: recent performance data, lessons learnt and retrofitting conventional treatment infrastructure. *Proceedings of the Water Environment Federation*, *2016*(11), 1913–1923. https://doi.org/10.2175/193864716819707139

Gong, G., Ye, S., Tian, Y., Wang, Q., Ni, J., & Chen, Y. (2009). Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution. *Journal of Hazardous Materials*, *166*(2–3), 714–719. https://doi.org/10.1016/j.jhazmat.2008.11.077

González-Camejo, J., Barat, R., Pachés, M., Murgui, M., Seco, A., & Ferrer, J. (2018). Wastewater nutrient removal in a mixed microalgae–bacteria culture: effect of light and temperature on the microalgae–bacteria competition. *Environmental*

*Technology (United Kingdom)*, *39*(4), 503–515. https://doi.org/10.1080/09593330.2017.1305001

González-Morales, C., Fernández, B., Molina, F. J., Naranjo-Fernández, D., Matamoros-Veloza, A., & Camargo-Valero, M. A. (2021). Influence of pH and Temperature on Struvite Purity and Recovery from Anaerobic Digestate. *Sustainability*, *13*(19), 10730. https://doi.org/10.3390/su131910730

Goscianska, J., Ptaszkowska-Koniarz, M., Frankowski, M., Franus, M., Panek, R., & Franus, W. (2018). Removal of phosphate from water by lanthanum-modified zeolites obtained from fly ash. *Journal of Colloid and Interface Science*, *513*, 72–81. https://doi.org/10.1016/j.jcis.2017.11.003

Gouveia, L., Graça, S., Sousa, C., Ambrosano, L., Ribeiro, B., Botrel, E. P., Neto, P. C., Ferreira, A. F., & Silva, C. M. (2016). Microalgae biomass production using wastewater: Treatment and costs. Scale-up considerations. *Algal Research*, *16*, 167–176. https://doi.org/10.1016/j.algal.2016.03.010

Green, B. W. (2015). Fertilizers in aquaculture. In D. A. Davis (Ed.), *Feed and Feeding Practices in Aquaculture* (pp. 27–52). Elsevier. https://doi.org/10.1016/b978-0-08-100506-4.00002-7

Grubb, D. G., Guimaraes, M. S., & Valencia, R. (2000). Phosphate immobilization using an acidic type F fly ash. *Journal of Hazardous Materials*, *76*(2–3), 217–236. https://doi.org/10.1016/S0304-3894(00)00200-4

Gu, A. Z., Saunders, A., Neethling, J. B., Stensel, H. D., & Blackall, L. L. (2008). Functionally Relevant Microorganisms to Enhanced Biological Phosphorus Removal Performance at Full-Scale Wastewater Treatment Plants in the United States. *Water Environment Research*, *80*(8), 688–698. https://doi.org/10.2175/106143008X276741

Gu, S., Fu, B., Ahn, J.-W., & Fang, B. (2021). Mechanism for phosphorus removal from wastewater with fly ash of municipal solid waste incineration, Seoul, Korea. *Journal of Cleaner Production*, *280*, 124430. https://doi.org/10.1016/j.jclepro.2020.124430

Güney, K., Weidelener, A., & Krampe, J. (2008). Phosphorus recovery from digested sewage sludge as MAP by the help of metal ion separation. *Water Research*, *42*(18), 4692–4698. https://doi.org/10.1016/j.watres.2008.08.016

Guo, T., Yang, H., Liu, Q., Gu, H., Wang, N., Yu, W., & Dai, Y. (2018). Adsorptive removal of phosphate from aqueous solutions using different types of red mud. *Water Science & Technology*, *2017*(2), 570–577. https://doi.org/10.2166/wst.2018.182

Gupta, V. K., Carrott, P. J. M., Carrott, M. M. L. R., & Suhas. (2009). Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review. *Critical Reviews in Environmental Science and Technology*, *39*(10), 783–842. https://doi.org/10.1080/10643380801977610

Han, C., Wang, Z., Yang, W., Wu, Q., Yang, H., & Xue, X. (2016). Effects of pH on phosphorus removal capacities of basic oxygen furnace slag. *Ecological Engineering*, *89*, 1–6. https://doi.org/10.1016/j.ecoleng.2016.01.004

Hao, X., Wang, C., Van Loosdrecht, M. C. M., & Hu, Y. (2013). Looking beyond struvite for P-recovery. *Environmental Science and Technology*, *47*(10), 4965–4966. https://doi.org/10.1021/ES401140S/ASSET/IMAGES/LARGE/ES-2013-01140S_0001.JPEG

He, S., Gu, A. Z., & McMahon, K. D. (2008). Progress Toward Understanding the Distribution of Accumulibacter Among Full-Scale Enhanced Biological Phosphorus Removal Systems. *Microbial Ecology*, *55*, 229–236. https://doi.org/10.1007/s00248-007-9270-x

He, S., & McMahon, K. D. (2011). Microbiology of “Candidatus Accumulibacter” in activated sludge. *Microbial Biotechnology*, *4*(5), 603–619. https://doi.org/10.1111/j.1751-7915.2011.00248.x

Helfferich, F. (1962). *Ion-Exchange*. McGraw-Hill.

Helness, H., & Ødegaard, H. (2001). Biological phosphorus and nitrogen removal in a sequencing batch moving bed biofilm reactor. *Water Science and Technology*, *43*(1), 233–240. https://doi.org/10.2166/wst.2001.0053

Henze, M., Harremoes, P., la Cour Jansen, J., & Arvin, E. (1997). *Wastewater Treatment: Biological and Chemical Processes* (2nd ed.). Springer.

Henze, M., van Loosdrecht, M. C. M., Ekama, G. A., & Brdjanovic, D. (2008). Biological Wastewater Treatment: Principles, Modelling and Design. In *Biological Wastewater Treatment: Principles, Modelling and Design*. IWA Publishing. https://doi.org/10.2166/9781780401867

Hermann, L., & Schaaf, T. (2019). Outotec (AshDec®) Process for P Fertilizers from Sludge Ash. In H. Ohtake & S. Tsuneda (Eds.), *Phosphorus Recovery and Recycling* (pp. 221–233). Springer. https://doi.org/10.1007/978-981-10-8031-9_15

Hermassi, M., Valderrama, C., Moreno, N., Font, O., Querol, X., Batis, N. H., & Cortina, J. L. (2017). Fly ash as reactive sorbent for phosphate removal from treated waste water as a potential slow release fertilizer. *Journal of Environmental Chemical Engineering*, *5*(1), 160–169. https://doi.org/10.1016/j.jece.2016.11.027

Howe, P. L., Clark, M. W., Reichelt-Brushett, A., & Johnston, M. (2011). Toxicity of raw and neutralized bauxite refinery residue liquors to the freshwater cladoceran Ceriodaphnia dubia and the marine amphipod Paracalliope australis. *Environmental Toxicology and Chemistry*, *30*(12), 2817–2824. https://doi.org/10.1002/etc.692

Huang, H., Liu, J., & Ding, L. (2015). Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation. *Journal of Cleaner Production*, *102*, 437–446. https://doi.org/10.1016/j.jclepro.2015.04.117

Huang, H., Xu, C., & Zhang, W. (2011). Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology. *Bioresource Technology*, *102*(3), 2523–2528. https://doi.org/10.1016/j.biortech.2010.11.054

Huang, W., Zhang, Y., & Li, D. (2017). Adsorptive removal of phosphate from water using mesoporous materials: A review. In *Journal of Environmental Management* (Vol. 193, pp. 470–482). Academic Press. https://doi.org/10.1016/j.jenvman.2017.02.030

Hug, A., Harf, J., Vogel, F., & Rohr, P. R. von. (1998). Deactivation of Sewage Sludge by Wet Oxidation (WO) Using the LOPROX Process: A Complete Wastewater Plant/WO System with an Analysis of Wet Oxidation Products. *Chemical Engineering Technology*, *21*(11), 880–885. https://doi.org/10.1002/(SICI)1521-4125(199811)21:11<880::AID-CEAT880>3.0.CO;2-2

Iannacone, F., Di Capua, F., Granata, F., Gargano, R., & Esposito, G. (2020). Simultaneous nitrification, denitrification and phosphorus removal in a continuous-flow moving bed biofilm reactor alternating microaerobic and aerobic conditions. *Bioresource Technology*, *310*, 123453. https://doi.org/10.1016/j.biortech.2020.123453

Iannacone, F., Di Capua, F., Granata, F., Gargano, R., & Esposito, G. (2021). Shortcut nitrification-denitrification and biological phosphorus removal in acetate- and ethanol-fed moving bed biofilm reactors under microaerobic/aerobic conditions. *Bioresource Technology*, 124958. https://doi.org/10.1016/j.biortech.2021.124958

Iannacone, F., Di Capua, F., Granata, F., Gargano, R., Pirozzi, F., & Esposito, G. (2019). Effect of carbon-to-nitrogen ratio on simultaneous nitrification denitrification and phosphorus removal in a microaerobic moving bed biofilm reactor. *Journal of Environmental Management*, *250*, 109518. https://doi.org/10.1016/J.JENVMAN.2019.109518

Ibrahim, M., Iqbal, M., Tang, Y.-T., Khan, S., Guan, D.-X., & Li, G. (2022). Phosphorus Mobilization in Plant–Soil Environments and Inspired Strategies for Managing Phosphorus: A Review. *Agronomy*, *12*(10), 2539. https://doi.org/10.3390/agronomy12102539

Ioannidou, O., & Zabaniotou, A. (2007). Agricultural residues as precursors for activated carbon production-A review. In *Renewable and Sustainable Energy Reviews* (Vol. 11, Issue 9, pp. 1966–2005). Pergamon. https://doi.org/10.1016/j.rser.2006.03.013

Ismail, Z. Z. (2012). Kinetic study for phosphate removal from water by recycled date-palm wastes as agricultural by-products. *International Journal of Environmental*

*Studies*, *69*(1), 135–149. https://doi.org/10.1080/00207233.2012.656975

Jaffer, Y., Clark, T. ., Pearce, P., & Parsons, S. . (2002). Potential phosphorus recovery by struvite formation. *Water Research*, *36*(7), 1834–1842. https://doi.org/10.1016/S0043-1354(01)00391-8

Jenkins, D., Ferguson, J. F., & Menar, A. B. (1971). Chemical processes for phosphate removal. In *Water Research* (Vol. 5, Issue 7, pp. 369–389). Pergamon. https://doi.org/10.1016/0043-1354(71)90001-7

Johansson, L. (1999). Industrial By-Products and Natural Substrata as Phosphorus Sorbents. *Environmental Technology*, *20*(3), 309–316. https://doi.org/10.1080/09593332008616822

Johir, M. A. H., George, J., Vigneswaran, S., Kandasamy, J., & Grasmick, A. (2011). Removal and recovery of nutrients by ion exchange from high rate membrane bio-reactor (MBR) effluent. *Desalination*, *275*(1–3), 197–202. https://doi.org/10.1016/j.desal.2011.02.054

Jørgensen, S. K., & Pauli, A. S. L. (1995). Polyphosphate accumulation among denitrifying bacteria in activated sludge. *Anaerobe*, *1*, 161–168.

Joyce, S. (2000). The dead zones: oxygen-starved coastal waters. *Environmental Health Perspectives*, *108*(3). https://doi.org/10.1289/ehp.108-a120

Jupp, A. R., Beijer, S., Narain, G. C., Schipperc, W., & Slootweg, J. C. (2021). Phosphorus recovery and recycling – closing the loop. *Chemical Society Reviews*, *50*(1), 87–101. https://doi.org/10.1039/D0CS01150A

Kataki, S., West, H., Clarke, M., & Baruah, D. C. (2016). Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. *Resources, Conservation and Recycling*, *107*, 142–156. https://doi.org/10.1016/j.resconrec.2015.12.009

Khalil, A. M. E., Eljamal, O., Amen, T. W. M., Sugihara, Y., & Matsunaga, N. (2017). Optimized nano-scale zero-valent iron supported on treated activated carbon for enhanced nitrate and phosphate removal from water. *Chemical Engineering Journal*, *309*, 349–365. https://doi.org/10.1016/j.cej.2016.10.080

Kim, K., Kim, K., Asaoka, S., Lee, I.-C., Kim, D.-S., & Hayakawa, S. (2020).

Quantitative Measurement on Removal Mechanisms of Phosphate by Class–F Fly Ash. *International Journal of Coal Preparation and Utilization*, *40*(12), 892–903. https://doi.org/10.1080/19392699.2018.1428192

Kofina, A. N., & Koutsoukos, P. G. (2004). Nucleation and growth of struvite from synthetic wastewater. *Proceeding of the International Conference on Struvite: Its Role in Phosphorus Recovery and Reuse, Cranfield (UK)*.

Koppelaar, R. H. E. M., & Weikard, H. P. (2013). Assessing phosphate rock depletion and phosphorus recycling options. *Global Environmental Change*, *23*(6), 1454–1466. https://doi.org/10.1016/j.gloenvcha.2013.09.002

Kostura, B., Kulveitová, H., & Leško, J. (2005). Blast furnace slags as sorbents of phosphate from water solutions. *Water Research*, *39*(9), 1795–1802. https://doi.org/10.1016/j.watres.2005.03.010

Koutsoukos, P., Kofina, A., & Klepetsanis, P. (2003). Exploration of alternatives for phosphorus recovery from wastewater by crystallisation. *WASIC Workshop, Istanbul*.

Kristiansen, R., Nguyen, H. T. T., Saunders, A. M., Nielsen, J. L., Wimmer, R., Le, V. Q., McIlroy, S. J., Petrovski, S., Seviour, R. J., Calteau, A., Nielsen, K. L., & Nielsen, P. H. (2013). A metabolic model for members of the genus Tetrasphaera involved in enhanced biological phosphorus removal. *The ISME Journal*, *7*, 543–554. https://doi.org/10.1038/ismej.2012.136

Kumar, I. A., & Viswanathan, N. (2017a). Fabrication of metal ions cross-linked alginate assisted biocomposite beads for selective phosphate removal. *Journal of Environmental Chemical Engineering*, *5*(2), 1438–1446. https://doi.org/10.1016/j.jece.2017.02.005

Kumar, I. A., & Viswanathan, N. (2017b). Development of multivalent metal ions imprinted chitosan biocomposites for phosphate sorption. *International Journal of Biological Macromolecules*, *104*, 1539–1547. https://doi.org/10.1016/j.ijbiomac.2017.02.100

Kumar, I. A., & Viswanathan, N. (2018). A facile synthesis of magnetic particles sprayed gelatin embedded hydrotalcite composite for effective phosphate sorption. *Journal of Environmental Chemical Engineering*, *6*(1), 208–217. https://doi.org/10.1016/j.jece.2017.11.042

Kwon, S., Kim, T.-S., Yu, G. H., Jung, J.-H., & Park, H.-D. (2010). Bacterial community composition and diversity of a full-scale integrated fixed-film activated sludge system as investigated by pyrosequencing. *Journal of Microbiology and Biotechnology*, *20*(12), 1717–1723.

Lanham, A. B., Oehmen, A., Saunders, A. M., Carvalho, G., Nielsen, P. H., & Reis, M. A. M. (2013). Metabolic versatility in full-scale wastewater treatment plants performing enhanced biological phosphorus removal. *Water Research*, *47*(19), 7032–7041. https://doi.org/10.1016/j.watres.2013.08.042

Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2005). Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth*, *283*(3–4), 514–522. https://doi.org/10.1016/j.jcrysgro.2005.06.012

Lee, E. Y., Oh, M. H., Yang, S.-H., & Yoon, T. H. (2015). Struvite Crystallization of Anaerobic Digestive Fluid of Swine Manure Containing Highly Concentrated Nitrogen. *Asian-Australasian Journal of Animal Sciences*, *28*(7), 1053–1060. https://doi.org/10.5713/ajas.14.0679

Lei, Y., Du, M., Kuntke, P., Saakes, M., Van Der Weijden, R., & Buisman, C. J. N. (2019). Energy Efficient Phosphorus Recovery by Microbial Electrolysis Cell Induced Calcium Phosphate Precipitation. *ACS Sustainable Chemistry and Engineering*, *7*(9), 8860–8867. https://doi.org/10.1021/ACSSUSCHEMENG.9B00867/ASSET/IMAGES/LARGE/SC-2019-00867A_0007.JPEG

Li, S., Cooke, R. A., Wang, L., Ma, F., & Bhattarai, R. (2017). Characterization of fly ash ceramic pellet for phosphorus removal. *Journal of Environmental Management*, *189*, 67–74. https://doi.org/10.1016/j.jenvman.2016.12.042

Li, Y., Liu, C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhang, Z., Fan, J., & Jia, Z. (2006). Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *Journal of Hazardous Materials*, *137*(1), 374–383. https://doi.org/10.1016/j.jhazmat.2006.02.011

Liberti, L., Petruzzelli, D., & De Florio, L. (2001). Rem nut ion exchange plus struvite precipitation process. *Environmental Technology*, *22*(11), 1313–1324. https://doi.org/10.1080/09593330409355443

Liu, X., & Zhang, L. (2015). Removal of phosphate anions using the modified chitosan beads: Adsorption kinetic, isotherm and mechanism studies. *Powder Technology*, *277*, 112–119. https://doi.org/10.1016/j.powtec.2015.02.055

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. S. (2014). Removal and Recovery of Phosphate From Water Using Sorption. *Critical Reviews in Environmental Science and Technology*, *44*(8), 847–907. https://doi.org/10.1080/10643389.2012.741311

López-Vázquez, C. M., Hooijmans, C. M., Brdjanovic, D., Gijzen, H. J., & van Loosdrecht, M. C. M. (2008). Factors affecting the microbial populations at full-scale enhanced biological phosphorus removal (EBPR) wastewater treatment plants in The Netherlands. *Water Research*, *42*(10–11), 2349–2360. https://doi.org/10.1016/j.watres.2008.01.001

Lu, S. G., Bai, S. Q., Zhu, L., & Shan, H. D. (2009). Removal mechanism of phosphate from aqueous solution by fly ash. *Journal of Hazardous Materials*, *161*(1), 95–101. https://doi.org/10.1016/j.jhazmat.2008.02.123

Mahmudov, R., & Huang, C. P. (2011). Selective adsorption of oxyanions on activated carbon exemplified by Filtrasorb 400 (F400). *Separation and Purification Technology*, *77*(3), 294–300. https://doi.org/10.1016/j.seppur.2010.12.019

Mantovani, M., Marazzi, F., Fornaroli, R., Bellucci, M., Ficara, E., & Mezzanotte, V. (2020). Outdoor pilot-scale raceway as a microalgae-bacteria sidestream treatment in a WWTP. *Science of the Total Environment*, *710*, 135583. https://doi.org/10.1016/j.scitotenv.2019.135583

Marques, R., Ribera-Guardia, A., Santos, J., Carvalho, G., Reis, M. A. M., Pijuan, M., & Oehmen, A. (2018). Denitrifying capabilities of Tetrasphaera and their contribution towards nitrous oxide production in enhanced biological phosphorus removal processes. *Water Research*, *137*, 262–272.

https://doi.org/10.1016/j.watres.2018.03.010

Marques, R., Santos, J., Nguyen, H., Carvalho, G., Noronha, J. P., Nielsen, P. H., Reis, M. A. M., & Oehmen, A. (2017). Metabolism and ecological niche of Tetrasphaera and Ca. Accumulibacter in enhanced biological phosphorus removal. *Water Research*, *122*, 159–171. https://doi.org/10.1016/j.watres.2017.04.072

Marshall, J. A., Morton, B. J., Muhlack, R., Chittleborough, D., & Kwong, C. W. (2017). Recovery of phosphate from calcium-containing aqueous solution resulting from biochar-induced calcium phosphate precipitation. *Journal of Cleaner Production*, *165*, 27–35. https://doi.org/10.1016/j.jclepro.2017.07.042

Martins, M. C., Santos, E. B. H., & Marques, C. R. (2017). First study on oyster-shell-based phosphorous removal in saltwater — A proxy to effluent bioremediation of marine aquaculture. *Science of the Total Environment*, *574*, 605–615. https://doi.org/10.1016/j.scitotenv.2016.09.103

McKay, C. P. (1996). Elemental composition, solubility, and optical properties of Titan’s organic haze. *Planetary and Space Science*, *44*(8), 741–747. https://doi.org/10.1016/0032-0633(96)00009-8

Mehta, C. M., Khunjar, W. O., Nguyen, V., Tait, S., & Batstone, D. J. (2015). Technologies to Recover Nutrients from Waste Streams: A Critical Review. *Critical Reviews in Environmental Science and Technology*, *45*(4), 385–427. https://doi.org/10.1080/10643389.2013.866621

Metcalf&Eddy, Inc.Tchobanoglous, Stensel, G., Tsuchihashi, H. D., Burton, R., & F.L. (2014). *Wastewater Engineering: Treatment and Reuse.* (McGraw-Hill Education (ed.); 5th ed.).

Meyer, C., Preyl, V., Steinmetz, H., Maier, W., Mohn, R.-E., & Schönberger, H. (2019). The Stuttgart Process (Germany). In H. Ohtake & S. Tsuneda (Eds.), *Phosphorus Recovery and Recycling*. Springer. https://doi.org/10.1007/978-981-10-8031-9_19

Mezenner, N. Y., & Bensmaili, A. (2009). Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chemical Engineering*

*Journal*, *147*(2–3), 87–96. https://doi.org/10.1016/j.cej.2008.06.024

Micháleková-Richveisová, B., Frišták, V., Pipíška, M., Ďuriška, L., Moreno-Jimenez, E., & Soja, G. (2017). Iron-impregnated biochars as effective phosphate sorption materials. *Environmental Science and Pollution Research*, *24*, 463–475. https://doi.org/10.1007/s11356-016-7820-9

Midorikawa, I., Aoki, H., Omori, A., Shimizu, T., Kawaguchi, Y., Kassai, K., & Murakami, T. (2008). Recovery of high purity phosphorus from municipal wastewater secondary effluent by a high-speed adsorbent. *Water Science & Technology*, *58*(8), 1601–1607. https://doi.org/10.2166/wst.2008.537

Mielczarek, A. T., Nguyen, H. T. T., Nielsen, J. L., & Nielsen, P. H. (2013). Population dynamics of bacteria involved in enhanced biological phosphorus removal in Danish wastewater treatment plants. *Water Research*, *47*(4), 1529–1544. https://doi.org/10.1016/j.watres.2012.12.003

Mitrogiannis, D., Psychoyou, M., Baziotis, I., Inglezakis, V. J., Koukouzas, N., Tsoukalas, N., Palles, D., Kamitsos, E., Oikonomou, G., & Markou, G. (2017). Removal of phosphate from aqueous solutions by adsorption onto Ca(OH)2 treated natural clinoptilolite. *Chemical Engineering Journal*, *320*, 510–522. https://doi.org/10.1016/j.cej.2017.03.063

Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents-A critical review. In *Journal of Hazardous Materials* (Vol. 142, Issues 1–2, pp. 1–53). Elsevier. https://doi.org/10.1016/j.jhazmat.2007.01.006

Mohsenpour, S. F., Hennige, S., Willoughby, N., Adeloye, A., & Gutierrez, T. (2021). Integrating micro-algae into wastewater treatment: A review. *Science of The Total Environment*, *752*, 142168. https://doi.org/10.1016/j.scitotenv.2020.142168

Moody, P. W., Speirs, S. D., Scott, B. J., & Mason, S. D. (2013). Soil phosphorus tests I: What soil phosphorus pools and processes do they measure? *Crop and Pasture Science*, *64*(5), 461. https://doi.org/10.1071/CP13112

Mor, S., Chhoden, K., Negi, P., & Ravindra, K. (2017). Utilization of nano-alumina and activated charcoal for phosphate removal from wastewater. *Environmental*

*Nanotechnology, Monitoring and Management*, *7*, 15–23. https://doi.org/10.1016/j.enmm.2016.11.006

Muys, M., Phukan, R., Brader, G., Samad, A., Moretti, M., Haiden, B., Pluchon, S., Roest, K., Vlaeminck, S. E., & Spiller, M. (2021). A systematic comparison of commercially produced struvite: Quantities, qualities and soil-maize phosphorus availability. *Science of The Total Environment*, *756*, 143726. https://doi.org/10.1016/j.scitotenv.2020.143726

Netshidzivhe, T. (2020, June). *Impact of magnesium source on the yield and structure of struvite*.

Nguyen, H. T. T., Le, V. Q., Hansen, A. A., Nielsen, J. L., & Nielsen, P. H. (2011). High diversity and abundance of putative polyphosphate-accumulating Tetrasphaera-related bacteria in activated sludge systems. *FEMS Microbiology Ecology*, *76*(2), 256–267. https://doi.org/10.1111/j.1574-6941.2011.01049.x

Nicholls, H. A., & Osborn, D. W. (1979). Bacterial Stress: Prerequisite for Biological Removal of Phosphorus. *Journal (Water Pollution Control Federation)*, *51*(3), 557–569.

Nielsen, P. H., Mielczarek, A. T., Kragelund, C., Nielsen, J. L., Saunders, A. M., Kong, Y., Hansen, A. A., & Vollertsen, J. (2010). A conceptual ecosystem model of microbial communities in enhanced biological phosphorus removal plants. *Water Research*, *44*(17), 5070–5088. https://doi.org/10.1016/j.watres.2010.07.036

Nur, T., Johir, M. A. H., Loganathan, P., Nguyen, T., Vigneswaran, S., & Kandasamy, J. (2014). Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. *Journal of Industrial and Engineering Chemistry*, *20*(4), 1301–1307. https://doi.org/10.1016/j.jiec.2013.07.009

Nur, T., Johir, M. A. H., Loganathan, P., Vigneswaran, S., & Kandasamy, J. (2012). Effectiveness of purolite A500PS and A520E ion exchange resins on the removal of nitrate and phosphate from synthetic water. *Desalination and Water Treatment*, *47*(1–3), 50–58. https://doi.org/10.1080/19443994.2012.696424

Oguz, E. (2004). Removal of phosphate from aqueous solution with blast furnace slag. *Journal of Hazardous Materials*, *114*(1–3), 131–137. https://doi.org/10.1016/j.jhazmat.2004.07.010

Oguz, E. (2005). Sorption of phosphate from solid/liquid interface by fly ash. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *262*(1–3), 113–117. https://doi.org/10.1016/j.colsurfa.2005.04.016

Onnis-Hayden, A., Majed, N., Schramm, A., & Gu, A. Z. (2011). Process optimization by decoupled control of key microbial populations: Distribution of activity and abundance of polyphosphate-accumulating organisms and nitrifying populations in a full-scale IFAS-EBPR plant. *Water Research*, *45*(13), 3845–3854. https://doi.org/10.1016/j.watres.2011.04.039

Onnis-Hayden, A., Srinivasan, V., Tooker, N. B., Li, G., Wang, D., Barnard, J. L., Bott, C., Dombrowski, P., Schauer, P., Menniti, A., Shaw, A., Stinson, B., Stevens, G., Dunlap, P., Takács, I., McQuarrie, J., Phillips, H., Lambrecht, A., Analla, H., … Gu, A. Z. (2020). Survey of full-scale sidestream enhanced biological phosphorus removal (S2EBPR) systems and comparison with conventional EBPRs in North America: Process stability, kinetics, and microbial populations. *Water Environment Research*, *92*(3), 403–417. https://doi.org/10.1002/wer.1198

Ott, C., & Rechberger, H. (2012). The European phosphorus balance. *Resources, Conservation and Recycling*, *60*, 159–172. https://doi.org/10.1016/j.resconrec.2011.12.007

Pan, M., Lin, X., Xie, J., & Huang, X. (2017). Kinetic, equilibrium and thermodynamic studies for phosphate adsorption on aluminum hydroxide modified palygorskite nano-composites. *RSC Advances*, *7*(8), 4492–4500. https://doi.org/10.1039/C6RA26802A

Papadopoulos, F. H., Metaxa, E. G., Iatrou, M. N., & Papadopoulos, A. H. (2014). Evaluation of Performance of Full-Scale Duckweed and Algal Ponds Receiving Septage. *Water Environment Research*, *86*(12), 2309–2316. https://doi.org/10.2175/106143014X14062131178754

Paradelo, R., Conde-Cid, M., Cutillas-Barreiro, L., Arias-Estévez, M., Nóvoa-Muñoz, J.

C., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M. J., & Núñez-Delgado, A. (2016). Phosphorus removal from wastewater using mussel shell: Investigation on retention mechanisms. *Ecological Engineering*, *97*, 558–566. https://doi.org/10.1016/j.ecoleng.2016.10.066

Park, J. H., Wang, J. J., Kim, S. H., Cho, J. S., Kang, S. W., Delaune, R. D., & Seo, D. C. (2017). Phosphate removal in constructed wetland with rapid cooled basic oxygen furnace slag. *Chemical Engineering Journal*, *327*, 713–724. https://doi.org/10.1016/j.cej.2017.06.155

Park, T., Ampunan, V., Lee, S., & Chung, E. (2016). Chemical behavior of different species of phosphorus in coagulation. *Chemosphere*, *144*, 2264–2269. https://doi.org/10.1016/j.chemosphere.2015.10.131

Pastor, L., Mangin, D., Barat, R., & Seco, A. (2008). A pilot-scale study of struvite precipitation in a stirred tank reactor: Conditions influencing the process. *Bioresource Technology*, *99*(14), 6285–6291. https://doi.org/10.1016/j.biortech.2007.12.003

Paul Chen, J., Chua, M. L., & Zhang, B. (2002). Effects of competitive ions, humic acid, and pH on removal of ammonium and phosphorous from the synthetic industrial effluent by ion exchange resins. *Waste Management*, *22*(7), 711–719. https://doi.org/10.1016/S0956-053X(02)00051-X

Petruzzelli, D., Dell'Erba, A., Liberti, L., Notarnicola, M., & Sengupta, A. K. (2004). A phosphate-selective sorbent for the REM NUT® process: Field experience at Massafra Wastewater Treatment Plant. *Reactive and Functional Polymers*, *60*(1–3), 195–202. https://doi.org/10.1016/j.reactfunctpolym.2004.02.023

Petzet, S., & Cornel, P. (2012). Prevention of Struvite Scaling in Digesters Combined With Phosphorus Removal and Recovery—The FIX-Phos Process. *Water Environment Research*, *84*(3), 220–226. https://doi.org/10.2175/106143012X13347678384125

Pijuan, M., Guisasola, A., Baeza, J. A., Carrera, J., Casas, C., & Lafuente, J. (2006). Net P-removal deterioration in enriched PAO sludge subjected to permanent aerobic conditions. *Journal of Biotechnology*, *123*, 117–126.

https://doi.org/10.1016/j.jbiotec.2005.10.018

Pijuan, M., Oehmen, A., Baeza, J. A., Casas, C., & Yuan, Z. (2008). Characterizing the biochemical activity of full-scale enhanced biological phosphorus removal systems: A comparison with metabolic models. *Biotechnology and Bioengineering*, *99*(1), 170–179. https://doi.org/10.1002/bit.21502

Pontikes, Y., & Angelopoulos, G. N. (2013). Bauxite residue in cement and cementitious applications: Current status and a possible way forward. *Resources, Conservation and Recycling*, *73*, 53–63. https://doi.org/10.1016/j.resconrec.2013.01.005

Powell, N., Shilton, A., Chisti, Y., & Pratt, S. (2009). Towards a luxury uptake process via microalgae - Defining the polyphosphate dynamics. *Water Research*, *43*(17), 4207–4213. https://doi.org/10.1016/j.watres.2009.06.011

Pradel, M., & Aissani, L. (2019). Environmental impacts of phosphorus recovery from a “product” Life Cycle Assessment perspective: Allocating burdens of wastewater treatment in the production of sludge-based phosphate fertilizers. *Science of the Total Environment*, *656*, 55–69. https://doi.org/10.1016/j.scitotenv.2018.11.356

Pradhan, J., Das, J., Das, S., & Thakur, R. S. (1998). Adsorption of phosphate from aqueous solution using activated red mud. *Journal of Colloid and Interface Science*, *204*(1), 169–172. https://doi.org/10.1006/jcis.1998.5594

Prajapati, S. S., Najar, P. A. M., & Tangde, V. M. (2016). Removal of Phosphate Using Red Mud: An Environmentally Hazardous Waste By-Product of Alumina Industry. *Advances in Physical Chemistry*, *2016*, 1–9. https://doi.org/10.1155/2016/9075206

Pratt, C., Shilton, A., Pratt, S., Haverkamp, R. G., & Bolan, N. S. (2007). Phosphorus Removal Mechanisms in Active Slag Filters Treating Waste Stabilization Pond Effluent. *Environmental Science & Technology*, *41*(9), 3296–3301. https://doi.org/10.1021/es062496b

Pronk, M., de Kreuk, M. K., de Bruin, B., Kamminga, P., Kleerebezem, R., & van Loosdrecht, M. C. M. (2015). Full scale performance of the aerobic granular sludge process for sewage treatment. *Water Research*, *84*, 207–217. https://doi.org/10.1016/j.watres.2015.07.011

Qiu, G., Zuniga-Montanez, R., Law, Y., Thi, S. S., Nguyen, T. Q. N., Eganathan, K., Liu, X., Nielsen, P. H., Williams, R. B. H., & Wuertz, S. (2019). Polyphosphate-accumulating organisms in full-scale tropical wastewater treatment plants use diverse carbon sources. *Water Research*, *149*, 496–510. https://doi.org/10.1016/j.watres.2018.11.011

Rashid, S. S., Liu, Y. Q., & Zhang, C. (2020). Upgrading a large and centralised municipal wastewater treatment plant with sequencing batch reactor technology for integrated nutrient removal and phosphorus recovery: Environmental and economic life cycle performance. *Science of the Total Environment*, *749*, 141465. https://doi.org/10.1016/j.scitotenv.2020.141465

Regulation EU. (2019). Regulation of the european parliament and of the council laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. *Official Journal of the European Union*, *2019*(2003), 114. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32019R1009&from=EN

Rickson, R. J., Deeks, L. K., Graves, A., Harris, J. A. H., Kibblewhite, M. G., & Sakrabani, R. (2015). Input constraints to food production: the impact of soil degradation. *Food Security*, *7*(2), 351–364. https://doi.org/10.1007/s12571-015-0437-x

Ridder, M. De, Jong, S. De, Polchar, J., & Lingemann, S. (2012). Risks and Opportunities in the Global Phosphate Rock Market: Robust Strategies in Times of Uncertainty. In *… pdf (accessed on 18 October 2013 …*.

Rittmann, B. E., & McCarty, P. L. (2012). *Environmental biotechnology: principles and applications*. McGraw Hill Education.

Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F. S., Lambin, E. F., Lenton, T. M., Scheffer, M., Folke, C., Schellnhuber, H. J., Nykvist, B., de Wit, C. A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P. K., Costanza, R., Svedin, U., … Foley, J. A. (2009). A safe operating space for humanity. *Nature*, *461*(7263), 472–475. https://doi.org/10.1038/461472a

Sansalone, J. J., & Ma, J. (2009). Parametric Evaluation of Batch Equilibria for Storm-Water Phosphorus Adsorption on Aluminum Oxide Media. *Journal of Environmental Engineering*, *135*(9), 737–746. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000041

Schmidt, H.-P. (2015). *European Biochar Certificate (EBC) - guidelines version 6.1*. https://doi.org/10.13140/RG.2.1.4658.7043

Shaddel, S., Ucar, S., Andreassen, J.-P., & Østerhus, S. W. (2019). Enhancing efficiency and economics of phosphorus recovery process by customizing the product based on sidestream characteristics – an alternative phosphorus recovery strategy. *Water Science and Technology*, *79*(9), 1777–1789. https://doi.org/10.2166/wst.2019.178

Siciliano, A., Limonti, C., Curcio, G. M., & Molinari, R. (2020). Advances in Struvite Precipitation Technologies for Nutrients Removal and Recovery from Aqueous Waste and Wastewater. *Sustainability*, *12*(18), 7538. https://doi.org/10.3390/su12187538

Song, Y., Hahn, H. H., & Hoffmann, E. (2002). Effects of solution conditions on the precipitation of phosphate for recovery: A thermodynamic evaluation. *Chemosphere*, *48*(10), 1029–1034. https://doi.org/10.1016/S0045-6535(02)00183-2

Sowmya, A., & Meenakshi, S. (2013a). Removal of nitrate and phosphate anions from aqueous solutions using strong base anion exchange resin. *Desalination and Water Treatment*, *51*(37–39), 7145–7156. https://doi.org/10.1080/19443994.2013.771286

Sowmya, A., & Meenakshi, S. (2013b). An efficient and regenerable quaternary amine modified chitosan beads for the removal of nitrate and phosphate anions. *Journal of Environmental Chemical Engineering*, *1*(4), 906–915. https://doi.org/10.1016/j.jece.2013.07.031

Spears, B. M., Meis, S., Anderson, A., & Kellou, M. (2013). Comparison of phosphorus (P) removal properties of materials proposed for the control of sediment p release in UK lakes. *Science of the Total Environment*, *442*, 103–110. https://doi.org/10.1016/j.scitotenv.2012.09.066

Stendahl, K., & Jäfverström, S. (2004). Recycling of sludge with the Aqua Reci process. *Water Science & Technology*, *49*(10), 233–240. https://doi.org/10.2166/wst.2004.0652

Stewart, W. M., Dibb, D. W., Johnston, A. E., & Smyth, T. J. (2005). The Contribution of Commercial Fertilizer Nutrients to Food Production. *Agronomy Journal*, *97*(1), 1–6. https://doi.org/10.2134/agronj2005.0001

Stokholm-Bjerregaard, M., Mcilroy, S. J., Nierychlo, M., Karst, S. M., Albertsen, M., & Nielsen, P. H. (2017). A critical assessment of the microorganisms proposed to be important to enhanced biological phosphorus removal in full-scale wastewater treatment systems. *Frontiers in Microbiology*, *8*, 718. https://doi.org/10.3389/fmicb.2017.00718

Stratful, I., Scrimshaw, M. D., & Lester, J. N. (2004). Removal of Struvite to Prevent Problems Associated with its Accumulation in Wastewater Treatment Works. *Water Environment Research*, *76*(5), 437–443. https://doi.org/10.2175/106143004X151491

Sturm, B. S. M., & Lamer, S. L. (2011). An energy evaluation of coupling nutrient removal from wastewater with algal biomass production. *Applied Energy*, *88*(10), 3499–3506. https://doi.org/10.1016/j.apenergy.2010.12.056

Suleiman, A. K. A., Lourenço, K. S., Clark, C., Luz, R. L., da Silva, G. H. R., Vet, L. E. M., Cantarella, H., Fernandes, T. V., & Kuramae, E. E. (2020). From toilet to agriculture: Fertilization with microalgal biomass from wastewater impacts the soil and rhizosphere active microbiomes, greenhouse gas emissions and plant growth. *Resources, Conservation and Recycling*, *161*, 104924. https://doi.org/10.1016/j.resconrec.2020.104924

Sutherland, D. L., Howard-Williams, C., Turnbull, M. H., Broady, P. A., & Craggs, R. J. (2014). Seasonal variation in light utilisation, biomass production and nutrient removal by wastewater microalgae in a full-scale high-rate algal pond. *Journal of*

*Applied Phycology*, *26*(3), 1317–1329. https://doi.org/10.1007/s10811-013-0142-0

Sutherland, D. L., Turnbull, M. H., & Craggs, R. J. (2017). Environmental drivers that influence microalgal species in fullscale wastewater treatment high rate algal ponds. *Water Research*, *124*, 504–512. https://doi.org/10.1016/j.watres.2017.08.012

Świątczak, P., & Cydzik-Kwiatkowska, A. (2018). Performance and microbial characteristics of biomass in a full-scale aerobic granular sludge wastewater treatment plant. *Environmental Science and Pollution Research*, *25*(2), 1655–1669. https://doi.org/10.1007/s11356-017-0615-9

Takhim, M., Sonveaux, M., & Ruiter, R. de. (2019). The Ecophos Process: Highest Quality Market Products Out of Low-Grade Phosphate Rock and Sewage Sludge Ash. In H. Ohtake & S. Tsuneda (Eds.), *Phosphorus Recovery and Recycling* (pp. 209–219). Springer. https://doi.org/10.1007/978-981-10-8031-9_14

Tangde, V. M., Prajapati, S. S., Mandal, B. B., & Kulkarni, N. P. (2017). Study of Kinetics and Thermodynamics of Removal of Phosphate from Aqueous Solution using Activated Red Mud. *International Journal of Environmental Research*, *11*, 39–47. https://doi.org/10.1007/s41742-017-0004-8

Tian, J., Ge, F., Zhang, D., Deng, S., & Liu, X. (2021). Roles of Phosphate Solubilizing Microorganisms from Managing Soil Phosphorus Deficiency to Mediating Biogeochemical P Cycle. *Biology*, *10*(2), 158. https://doi.org/10.3390/biology10020158

Timofeeva, A., Galyamova, M., & Sedykh, S. (2022). Prospects for Using Phosphate-Solubilizing Microorganisms as Natural Fertilizers in Agriculture. *Plants*, *11*(16), 2119. https://doi.org/10.3390/plants11162119

Toja Ortega, S., Pronk, M., & de Kreuk, M. K. (2021). Effect of an Increased Particulate COD Load on the Aerobic Granular Sludge Process: A Full Scale Study. *Processes*, *9*(8), 1472. https://doi.org/10.3390/pr9081472

Tong, J., & Chen, Y. (2007). Enhanced Biological Phosphorus Removal Driven by Short-Chain Fatty Acids Produced from Waste Activated Sludge Alkaline

Fermentation. *Environmental Science & Technology*, *41*(20), 7126–7130. https://doi.org/10.1021/es071002n

Tsuji, K., Midorikawa, I., Aoki, H., Omori, A., Shimizu, T., & Hashimoto, T. (2011). Pilot Testing of a High Efficiency Adsorbent System for Phosphorus Removal and Recovery From Municipal Wastewater Secondary Effluent. *Proceedings of the Water Environment Federation*, 978–986. https://doi.org/10.2175/193864711802867252

Tua, C., Ficara, E., Mezzanotte, V., & Rigamonti, L. (2021). Integration of a side-stream microalgae process into a municipal wastewater treatment plant: A life cycle analysis. *Journal of Environmental Management*, *279*, 111605. https://doi.org/10.1016/j.jenvman.2020.111605

Ugurlu, A., & Salman, B. (1998). Phosphorus removal by fly ash. *Environment International*, *24*(8), 911–918. https://doi.org/10.1016/S0160-4120(98)00079-8

US EPA. (2007). *Advanced Wastewater Treatment to Achieve Low Concentration of Phosphorus Advanced Treatment to Achieve Low Concentration of Phosphorus*.

Vaccari, D. A., & Strigul, N. (2011). Extrapolating phosphorus production to estimate resource reserves. *Chemosphere*, *84*(6), 792–797. https://doi.org/10.1016/j.chemosphere.2011.01.052

van de Wiel, C. C. M., van der Linden, C. G., & Scholten, O. E. (2016). Improving phosphorus use efficiency in agriculture: opportunities for breeding. *Euphytica*, *207*(1), 1–22. https://doi.org/10.1007/s10681-015-1572-3

van Dijk, K. C., Lesschen, J. P., & Oenema, O. (2016). Phosphorus flows and balances of the European Union Member States. *Science of the Total Environment*, *542*, 1078–1093. https://doi.org/10.1016/j.scitotenv.2015.08.048

Van Kauwenbergh, S. J. (2010). *World Phosphate Rock Reserves and Resources. International Fertilizer Development Center (IFDC), Muscle Shoals, Al.*

VDI, V. D. I. (2012). guideline 4600: Cumulative energy demand (KEA)–Terms, definitions, methods of calculation. *Verein Deutscher Ingenieure, Düsseldorf*.

Wang, D., Tooker, N. B., Srinivasan, V., Li, G., Fernandez, L. A., Schauer, P., Menniti, A., Maher, C., Bott, C. B., Dombrowski, P., Barnard, J. L., Onnis-Hayden, A., & Gu, A. Z. (2019). Side-stream enhanced biological phosphorus removal (S2EBPR) process improves system performance - A full-scale comparative study. *Water Research*, *167*, 115109. https://doi.org/10.1016/j.watres.2019.115109

Wang, J., Li, Q., Qi, R., Tandoi, V., & Yang, M. (2014). Sludge bulking impact on relevant bacterial populations in a full-scale municipal wastewater treatment plant. *Process Biochemistry*, *49*(12), 2258–2265. https://doi.org/10.1016/j.procbio.2014.08.005

Wang, M., Yang, H., Ergas, S. J., & van der Steen, P. (2015). A novel shortcut nitrogen removal process using an algal-bacterial consortium in a photo-sequencing batch reactor (PSBR). *Water Research*, *87*, 38–48. https://doi.org/10.1016/j.watres.2015.09.016

Wang, X., Hu, Y., Tang, Y., Yang, P., Feng, X., Xu, W., & Zhu, M. (2017). Phosphate and phytate adsorption and precipitation on ferrihydrite surfaces. *Environmental Science: Nano*, *4*(11), 2193–2204. https://doi.org/10.1039/C7EN00705A

Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., Wang, L., Xiao, H., & Deng, S. (2015). Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH4+), nitrate (NO3−), and phosphate (PO43−). *Chemosphere*, *119*, 646–653. https://doi.org/10.1016/j.chemosphere.2014.07.084

Weigand, H., Bertau, M., Hübner, W., Bohndick, F., & Bruckert, A. (2013). RecoPhos: Full-scale fertilizer production from sewage sludge ash. *Waste Management*, *33*(3), 540–544. https://doi.org/10.1016/j.wasman.2012.07.009

Westholm, L. J. (2006). Substrates for phosphorus removal - Potential benefits for on-site wastewater treatment? *Water Research*, *40*(1), 23–36. https://doi.org/10.1016/j.watres.2005.11.006

Withers, P. J. A., Elser, J. J., Hilton, J., Ohtake, H., Schipper, W. J., & van Dijk, K. C. (2015). Greening the global phosphorus cycle: how green chemistry can help achieve planetary P sustainability. *Green Chemistry*, *17*(4), 2087–2099.

https://doi.org/10.1039/C4GC02445A

Withers, P. J. A., van Dijk, K. C., Neset, T.-S. S., Nesme, T., Oenema, O., Rubæk, G. H., Schoumans, O. F., Smit, B., & Pellerin, S. (2015). Stewardship to tackle global phosphorus inefficiency: The case of Europe. *AMBIO*, *44*(S2), 193–206. https://doi.org/10.1007/s13280-014-0614-8

Wu, B., Wan, J., Zhang, Y., Pan, B., & Lo, I. M. C. (2020). Selective Phosphate Removal from Water and Wastewater using Sorption: Process Fundamentals and Removal Mechanisms. *Environmental Science & Technology*, *54*(1), 50–66. https://doi.org/10.1021/acs.est.9b05569

Wu, H., Ikeda-Ohno, A., Wang, Y., & Waite, T. D. (2015). Iron and phosphorus speciation in Fe-conditioned membrane bioreactor activated sludge. *Water Research*, *76*, 213–226. https://doi.org/10.1016/j.watres.2015.02.020

Wu, T., & Sansalone, J. (2013). Phosphorus Equilibrium. II: Comparing Filter Media, Models, and Leaching. *Journal of Environmental Engineering*, *139*(11), 1325–1335. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000756

Xia, L., Li, Y., Huang, R., & Song, S. (2017). Effective harvesting of microalgae by coagulation–flotation. *Royal Society Open Science*, *4*(11). https://doi.org/10.1098/rsos.170867

Xiao, K., Zhou, L., He, B., Qian, L., Wan, S., & Qu, L. (2016). Nitrogen and phosphorus removal using fluidized-carriers in a full-scale A 2 O biofilm system. *Biochemical Engineering Journal*, *115*, 47–55. https://doi.org/10.1016/j.bej.2016.08.004

Xiong, J., He, Z., Mahmood, Q., Liu, D., Yang, X., & Islam, E. (2008). Phosphate removal from solution using steel slag through magnetic separation. *Journal of Hazardous Materials*, *152*(1), 211–215. https://doi.org/10.1016/j.jhazmat.2007.06.103

Xiong, W., Tong, J., Yang, Z., Zeng, G., Zhou, Y., Wang, D., Song, P., Xu, R., Zhang, C., & Cheng, M. (2017). Adsorption of phosphate from aqueous solution using iron-zirconium modified activated carbon nanofiber: Performance and mechanism. *Journal of Colloid and Interface Science*, *493*, 17–23.

https://doi.org/10.1016/j.jcis.2017.01.024

Xu, X., Gao, B., Wang, W., Yue, Q., Wang, Y., & Ni, S. (2009). Adsorption of phosphate from aqueous solutions onto modified wheat residue: Characteristics, kinetic and column studies. *Colloids and Surfaces B: Biointerfaces*, *70*(1), 46–52. https://doi.org/10.1016/j.colsurfb.2008.12.006

Xu, X., Gao, B. Y., Yue, Q. Y., & Zhong, Q. Q. (2010). Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal. *Bioresource Technology*, *101*(22), 8558–8564. https://doi.org/10.1016/j.biortech.2010.06.060

Xue, Y., Hou, H., & Zhu, S. (2009). Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag. *Journal of Hazardous Materials*, *162*(2–3), 973–980. https://doi.org/10.1016/j.jhazmat.2008.05.131

Yao, S., Wang, M., Liu, J., Tang, S., Chen, H., Guo, T., Yang, G., & Chen, Y. (2018). Removal of phosphate from aqueous solution by sewage sludge-based activated carbon loaded with pyrolusite. *Journal of Water Reuse and Desalination*, *8*(2), 192–201. https://doi.org/10.2166/wrd.2017.054

Ye, J., Cong, X., Zhang, P., Zeng, G., Hoffmann, E., Wu, Y., Zhang, H., & Fang, W. (2016). Operational parameter impact and back propagation artificial neural network modeling for phosphate adsorption onto acid-activated neutralized red mud. *Journal of Molecular Liquids*, *216*, 35–41. https://doi.org/10.1016/j.molliq.2016.01.020

Ye, Y., Ngo, H. H., Guo, W., Liu, Y., Li, J., Liu, Y., Zhang, X., & Jia, H. (2017). Insight into chemical phosphate recovery from municipal wastewater. In *Science of the Total Environment* (Vol. 576, pp. 159–171). Elsevier B.V. https://doi.org/10.1016/j.scitotenv.2016.10.078

Yin, J., Zhang, P., Li, F., Li, G., & Hai, B. (2015). Simultaneous biological nitrogen and phosphorus removal with a sequencing batch reactor-biofilm system. *International Biodeterioration & Biodegradation*, 1–6. https://doi.org/10.1016/j.ibiod.2015.02.019

Yu, J., Liang, W., Wang, L., Li, F., Zou, Y., & Wang, H. (2015). Phosphate removal from domestic wastewater using thermally modified steel slag. In *Journal of Environmental Sciences (China)* (Vol. 31, pp. 81–88). Chinese Academy of Sciences. https://doi.org/10.1016/j.jes.2014.12.007

Yue, Q., Wang, W., Gao, B., Xu, X., Zhang, J., & Li, Q. (2010). Phosphate Removal from Aqueous Solution by Adsorption on Modified Giant Reed. *Water Environment Research*, *82*(4), 374–381. https://doi.org/10.2175/106143009X12529484815719

Zhang, B., Chen, N., Feng, C., & Zhang, Z. (2018). Adsorption for phosphate by crosslinked/non-crosslinked-chitosan-Fe(III) complex sorbents: Characteristic and mechanism. *Chemical Engineering Journal*, *353*, 361–372. https://doi.org/10.1016/j.cej.2018.07.092

Zhang, M., & Gao, B. (2013). Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite. *Chemical Engineering Journal*, *226*, 286–292. https://doi.org/10.1016/j.cej.2013.04.077

Zhong, Z., Yu, G., Mo, W., Zhang, C., Huang, H., Li, S., Gao, M., Lu, X., Zhang, B., & Zhu, H. (2019). Enhanced phosphate sequestration by Fe( <scp>iii</scp> ) modified biochar derived from coconut shell. *RSC Advances*, *9*(18), 10425–10436. https://doi.org/10.1039/C8RA10400J

Zilles, J. L., Hung, C.-H., & Noguera, D. R. (2002). Presence of Rhodocyclus in a full-scale wastewater treatment plant and their participation in enhanced biological phosphorus removal. *Water Science and Technology*, *46*(1–2), 123–128. https://doi.org/10.2166/wst.2002.0467

Zilles, J. L., Peccia, J., & Noguera, D. R. (2002). Microbiology of Enhanced Biological Phosphorus Removal in Aerated-Anoxic Orbal Processes. *Water Environment Research*, *74*(5), 428–436. https://doi.org/10.2175/106143002X140224

Zou, Y., Grace, M. R., Roberts, K. L., & Yu, X. (2017). Thin ferrihydrite sediment capping sequestrates phosphorus experiencing redox conditions in a shallow temperate lacustrine wetland. *Chemosphere*, *185*, 673–680. https://doi.org/10.1016/j.chemosphere.2017.07.052

# ANNEXES

The following Figures show pictures of some sections of municipal WWTP of Andria.

Figure S1. Screening.

Figure S2. Conveyor belt and container for municipal solid waste

Figure S3. Equalization tank.

Figure S4. Weir outlet section of a sedimentation tank.

Figure S5. Activated sludge treatment.

Figure S6. Aeration system of activated sludge treatment.

Figure S7. Wastewater after secondary sedimentation.

Figure S8. Disinfection tank.

Figure S9. Static thickener and anaerobic digestors.

Figure S10. Gasometer.

Figure S11. Centrifuge.

Figure S12. Stabilized sludge.

# ***CURRICULUM VITAE***

## Generalities

| | |
|---|---|
| Name | Simona de Sario |
| Place and date of birth | Foggia (IT), 10/10/1990 |
| Structure | Polytechnical University of Bari - Department of Civil, Environmental, Land, Building Engineering and Chemistry |
| Address | Via E. Orabona 4, 70125, Bari (Italy) |
| Phone | +39 3392406977 |
| E-mail address | simona.desario@poliba.it |
| Web-page | Research gate:<br>https://www.researchgate.net/profile/Simona-De-Sario<br>LinkedIn:<br>https://www.linkedin.com/in/simona-de-sario-332564169/ |

## Education

- November, 2015, 17: bachelor's degree in Civil Engineering at Polytechnic University of Bari, discussing a thesis on "*Greenhouse gas emission reduction methodologies: collection, transport and geological storage of* $CO_2$". Supervisor: prof. C. Fidelibus
- December, 2018, 14: Master's degree in Civil Engineering with full marks Polytechnic University of Bari, discussing a thesis on "*Analysis of trends and anomalies of climate indicators*". Supervisors: prof. V. Iacobellis and prof. A. Gioia. Cosupervisors: prof. V. Totaro and eng. T. Bisantino.
- August 2022, 2: enabling as Safety Coordinator during the design and execution of work at AIFES
- August 2022, 4: enabling as Head of Prevention and Protection Service at AIFES
- Novembre 26, 2019 – current: Ph. D. student in the XXXV cycle of the PhD course in Risk and environmental, territorial and building development at Polytechnic University of Bari. Supervisor: prof. U. Fratino

## Professional experience

| | |
|---|---|
| [ 12/2022-current ] | Research Fellow at Polytechnic University of Bari for the project "*Evaluation of the flow rates having predetermined return period in control sections via probability models*". Scientific responsible: prof. V. Iacobellis. |
| [ 05/2021 – 05/2021 ] | Activities as co-supervisor of the Bachelor's thesis in Civil-environmental engineering (environmental curriculum) entitled "Recovery of phosphorus from the sludge of the Andria sewage plant" |
| [ 04/2019 – 11/2019 ] | Research collaborator for an activity that involved the hydraulic charac- |

## Professional experience

| | |
|---|---|
| | terization of dam structures, retaining barriers and hydroelectric plants, through experimentation on physical model present in the Laboratory of Hydraulics and Hydraulic Constructions of the DICATECh department of the Polytechnic of Bari |
| [ 02/2018 – 04/2018 ] | Trainee at the decentralized functional center (CFD) of Civil Protection of Bari. During the period indicated, a large database of thermo-pluviometric data was created and then carried out an analysis of changes in the historical period analyzed. |

## Skills

| | |
|---|---|
| Spoken languages | Italian (Mother), English |
| Digital | Microsoft Office, Microsoft Word, Microsoft Excel, Social Media, Microsoft Powerpoint, Matlab and C++ knowledge through the corresponding courses, Basics knowledge of working in AutoCAD, Mendeley software |
| Soft skills | Leadership, team working, organizational, communicative and relational skills, rapid learning, problem solving, curiosity. |

## Scientific production

- Ferraro, A., **de Sario, S.,** Attanasio, A., Capua, F. Di, Gorgoglione, A., Fratino, U., Mascolo, M. C., Pirozzi, F., Trancone, G., & Spasiano, D. (2022). Phosphorus recovery as struvite and hydroxyapatite from the liquid fraction of municipal sewage sludge with limited magnesium addition. Journal of Environmental Quality. https://doi.org/10.1002/jeq2.20446
- Di Capua, F., **de Sario, S.,** Ferraro, A., Petrella, A., Race, M., Pirozzi, F., Fratino, U., & Spasiano, D. (2022). Phosphorous removal and recovery from urban wastewater: Current practices and new directions. Science of The Total Environment, 823, 153750. https://doi.org/10.1016/j.scitotenv.2022.153750
- Malcangio D., **de Sario S.,** Fratino U., Pagano A., Renna F. (2020). Hydraulic characterization of flow under high head gates: laboratory setup. 6th IAHR Europe Congress Warsaw, Poland (Virtual Event)
- **de Sario S.,** Fratino U., Malcangio D., Pagano A., Renna F. (2020). Caratterizzazione idraulica di organi di ritenuta a presidio di scarichi di fondo. XXXVIII National Conference of Hydraulics and Hydraulic Constructions (IDRA), Italy (Virtual Event)

## Awards

Recognition **2nd place** for training activities within the third edition of the Mediterranean PhD School organized by the Department Civil Engineering, Construction and Environmental University of Naples Federico II, entitled "From Sustainable to Regenerative Design".
https://openbadges.bestr.it/public/assertions/T9jEe9z0SVKEjNhI_n9Hjg

## Volunteer activities

[ 04/2022 – 08/2022 ] Volunteer for education for Save the Children, to combat educational poverty and early school leaving by offering support to students and elementary school students, middle and upper ages who had difficulty managing remote learning.