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**EVALUATION OF PHOSPHATE RECOVERY AS STRUVITE TO
AVOID UNCONTROLLED PHOSPHORUS PRECIPITATION IN THE
SLUDGE LINE. THE CASE OF THE ALT MARESME NORD WWTP**



Dissertation

Author: Cambray Alvarez, Clara
Director: Cortina Pallas, José Luis
Co-Director: Romero Lestido, Adriana Lucía
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ABSTRACT

Phosphorus (P) is a non-replaceable and finite resource widely used in fertilizer production and nowadays considered as critical raw material at the European Union. High concentrations of phosphorus have been reported in wastewater treatment plants (WWTPs) streams, making them attractive as a P source. The high concentrations of P and other nutrients at some points of the sludge treatment line (e.g. anaerobic digestion stage), can lead to the uncontrolled precipitation of phosphorus minerals in the sludge line causing damage along the infrastructure. This uncontrolled precipitation phenomena suppose an increase on sludge management costs and a decrease in the overall efficiency of the process. Therefore, apart from the environmental and sustainability benefits that represents the enhance of P recycling by decreasing the dependency on the phosphatic rock deposits, phosphorus recovery in WWTPs represents an opportunity to minimize the problems related to uncontrolled precipitations of phosphorus compounds while collecting a recovered material ready to be commercialized in fertilization applications. Among the different options to recover P minerals, struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallization, appears as one of the most promising technologies to recover phosphorus from wastewater. Struvite is a valuable product for the fertilizer industry and can be sold at a profit.

This project evaluates the technical and economic feasibility of the implementation of a P-recovery system as struvite in Alt Maresme Nord (AMN) WWTP, located in Pineda (Catalunya). Uncontrolled precipitation of P has been reported in AMN WWTP since 2016 when the plant started with the management of sludges produced in five other wastewater facilities in the Maresme region. This new hub treatment facility was designed and built for the management of the external sludges received from the different wastewater works. This study is proposing a modification of the sludge treatment line and it consists on the installation of: i) an elutriation stage to enhance the P release into the liquid phase from the bio-solids and; ii) a crystallization unit to recover pure struvite from the obtained stream enriched in phosphate and ammonium.

In order to analyze the feasibility of implementing this new technology, recent studies and already implemented prototypes have been critically reviewed and analyzed. In addition, laboratory tests have been performed with the sludge received in Pineda to propose the optimum option in terms of process yield maintaining the required operating conditions to produce struvite. Among all the recovery technologies analyzed, it has been selected the *Phosphogreen* technology from *Suez Company* under evaluation in the LIFE ENRICH led by *Cetaqua*.

The results indicate that sludges arriving in AMN should be subjected to a hydration stage in an elutriation tank, followed by a thickening stage to obtain the P-enriched liquid stream which would be finally sent to the crystallization reactor to produce struvite. It has been estimated that the potential

production of struvite with the implementation of this technology would be up to 83 annual tonnes with operating conditions of pH 8,5 and a magnesium to phosphate molar ratio in the crystallization reactor of 1:1. Struvite sales would suppose an annual income up to 29.000€ for AMN WWTP.

The economic assessment demonstrates that the implementation of this kind of technology in AMN WWTP is feasible and can achieve a payback period of less than 10 years.

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1. INTRODUCTION

Phosphorus (P), is an essential and limited resource with an increasing demand in the fertilizer industry, specially, to cover the food demand with the increase in the demography and industrial activities. It has been reported that phosphate rock reserves, from which phosphorus is extracted, will be exhausted within 150 years given the current consumption rate (Spinosa, 2004). In addition, phosphate discharges into the environment have to be controlled due to problems as eutrophication of water. Streams with high concentration of phosphorus, when compared with discharge limits (e.g. 0.1 mgP/L) are found in treated wastewater in Waste Water Treatment Plants (WWTPs). Therefore, for both the need of secondary P sources and the need of reduction of P content in discharges of treated waters to natural water bodies, WWTPs have become: i) a promising secondary source of P via reuse which could be used to replace P derived from phosphate rocks (Egle et al., 2016) and; ii) becomes an opportunity to generate local supplies of P fertilizers.

Sludge, the solid, semisolid or slurry residual material produced as a by-product of wastewater treatment processes, is a potentially valuable source of nutrients and energy, hence, the aim in waste minimization should be to maximize its use as a resource. For instance, nutrients (carbon, phosphorus and nitrogen), particularly phosphorus, can be reused on land as components of compost or as organic fertilizers (Fytli and Zabaniotou, 2008; Kroiss, 2004; Spinosa, 2004).

On the other hand, the uncontrolled precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) or other minerals containing phosphorus, within the anaerobic digestion stage and post-digestion processes equipment surfaces and pipes has been widely reported in WWTPs. Precipitation problems not only lead to higher sludge management costs but also to a decrease in the overall efficiency of the process. With the allocation of a crystallization process in a WWTP, not only the phosphorous removal is achieved but also the recovery of a product with a potential use in the fertilizer sector. A crystallization step to recover struvite is in fact one of the most promising technologies to recover phosphate species. Supporting the use of struvite as a fertilizer not only involves its recovery but also the reuse of nutrients, thereby promoting sustainable WWTP management and circular economy approach.

2. OBJECTIVES

The main objective of this project is to evaluate the feasibility of implementing a phosphate recovery route as struvite to avoid uncontrolled phosphorus precipitation in the sludge line of the Alt Maresme Nord WWTP. This WWTP is used as a hub for a centralized site to manage the sludge generated in the different WWTPs of the Maresme region through an anaerobic digestion stage. The assessment of the plant operation data indicates severe scenarios of uncontrolled precipitation of struvite.

Taking advantage of the fact that by 2022 the struvite itself is expected to be commercialized in the form of fertilizer, not only the technical and economic problems caused by this uncontrolled precipitation would be overcome but also the nutrients revalorized with a certain economic potential. This option fits perfectly with the recognition of this WWTP as a biofactory and its commitment to the circularity of its processes.

In addition, the integration of the system to recover P in struvite form in the plant will be analyzed and a preliminary quantitative assessment of the amount of struvite that could be produced, performed. In this direction, an assessment of the possibility to enhance the amount of P to be recovered by the integration of elutriation processes will be carried out. From this preliminary estimation and the technological review of the main technology providers for struvite recovery from anaerobic side streams, an analysis of alternatives will be developed including a preliminary estimation of the expected investment.

3. STATE OF THE ART

3.1. Phosphorous in WWTPs: flow analysis

The water treatment industry receives large amount of phosphorous. The amount of P within wastewaters in Spain is up to 79.47 kt P/year, which is either discharged to natural water bodies or removed after transfer to sewage sludge. It is estimated that a P removal efficiency of around 61% is achieved in WWTP. Approximately 69% of the 47,75 kt P/year removed within sewage sludge is recycled in agriculture uses and 27% is directed to landfill and composting and 4% is sent to other uses (Álvarez et al., 2018). The concentration of phosphorous in the influent of a municipal WWTP is estimated to be around 9 mg/L (Brett et al., 1997).

Phosphorous can be found in several forms. In wastewater, phosphorus can be present in the form of orthophosphates (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4), polyphosphates (P_2O_7) and as organic phosphorus. Largest Contribution at the total phosphorus in the wastewater is from the orthophosphates, which together with the polyphosphates and a small portion of the organic phosphorus constitute all the soluble forms of phosphorus (Pastor, 2008).

In WWTPs with P removal chemically or biologically, approximately between 75 and 90% of the phosphorus entering the municipal WWTP is transferred into the sewage sludge (Tarayre et al., 2016; Martí et al., 2017). However, it should be mentioned that biological stages are typically difficult of being operated and chemical removal stages are characterized by their high OPEX values.

3.2. Phosphorus removal technologies

The need to reduce the levels of phosphorous entering surface water and the issue of eutrophication led in the early 1950s the development of technologies to remove phosphorous from wastewater. These technologies offer the opportunity for recycling and enhance sustainability. There are several technologies which can be used to remove and recover phosphorous. Among these technologies, chemical precipitation is the most used conventionally. More recently, biological phosphorous removal and crystallization technologies have been established.

WWTPs offer several interesting locations to implement actions to recover phosphorous. In Figure 3.1 the typical layout of a WWTP is displayed with the different streams involved. P in a soluble form can be found in the sedimentation process effluent, the biological sludge stream, the digested sludge and in the centrates stream (also called reject water stream). On the other hand, activated sludge contains organic phosphorous; part of this phosphorus is released in the form of orthophosphates during anaerobic digestion, so streams coming from anaerobic digestion processes are interesting locations for the integration of P recovery systems.

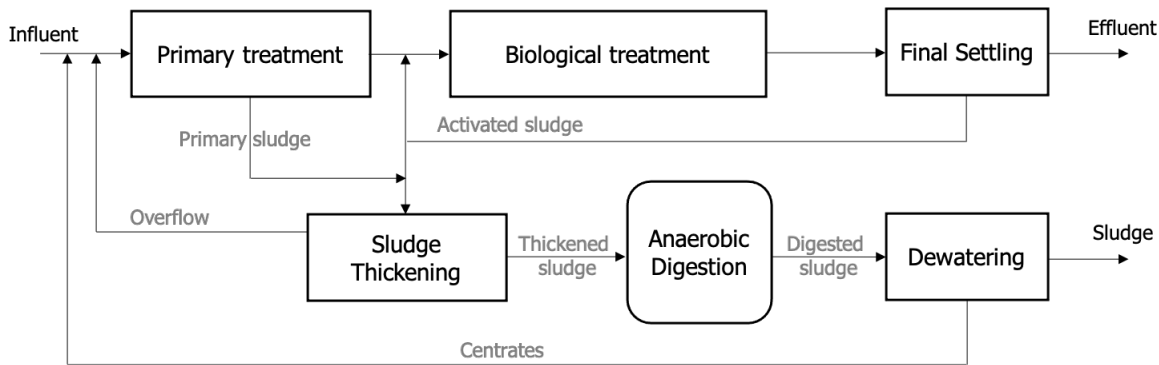
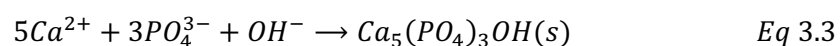
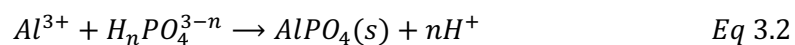
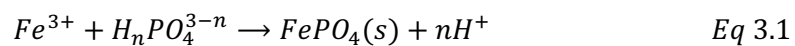


Figure 3.1 Typical flow diagram of a WWTP

The state of the art of the various technologies to remove phosphorus is provided below.

3.2.1. Chemical precipitation

The widespread use of chemical precipitation for phosphorus removal in wastewater treatment started in Switzerland during the 1950s, in response to the growing problem of eutrophication and now is established around the world (Brett et al., 1997). Chemical precipitation is based in an addition of a metal salt to wastewater to enhance the precipitation on an insoluble metal phosphate that is later settled by sedimentation, flotation or filtration. The precipitated species will finally be part of the sludges. The most suitable metals are iron (II and III) to produce iron hydroxide (eq 3.1), and aluminum (III) to precipitate aluminum phosphate (eq 3.2), usually added as chlorides or sulphates. Lime can also be added to precipitate calcium phosphate (eq 3.3) (Metcalf and Eddy, 2003).



In Figure 3.2 the solubility diagram, concentration of phosphorous as a function of the solution pH, for iron, aluminum and calcium phosphates is displayed.

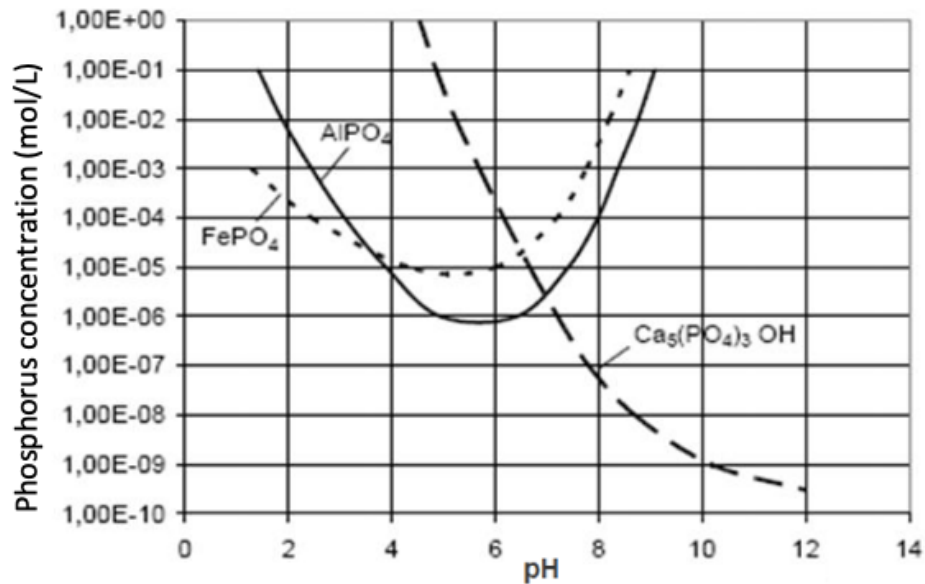


Figure 3.2 Solubility diagram for $\text{AlPO}_4(\text{s})$; $\text{FePO}_4(\text{s})$ and $\text{Ca}_5(\text{PO}_4)_3(\text{OH})(\text{s})$ as a function of pH (Adaptation from Montag, 2008)

Coagulants in base to Fe(III), Al(III) and/or Ca(II) can be applied at several stages during waste water treatment (Figure 3.3) since chemical precipitation is a very flexible approach to phosphorous removal (Brett et al., 1997). Depending on where this chemical is added, chemical precipitation can be classified as:

Primary precipitation: The precipitation agent is added before primary sedimentation and phosphorous removed in primary sludge.

Secondary or simultaneous precipitation: The chemical is dosed directly to the aeration tank of an activated sludge process and phosphate is removed in secondary sludge. Adding the salt in the aeration tank makes the mix more effective than in the primary precipitation.

Tertiary precipitation: The addition of the precipitation agent is done in the effluent of the secondary sedimentation tank. The precipitated species are eliminated by filtration of the effluent stream. Although a high-quality effluent can be produced, this approach is not generally favored because of high chemical costs and the creation of an additional, tertiary sludge.

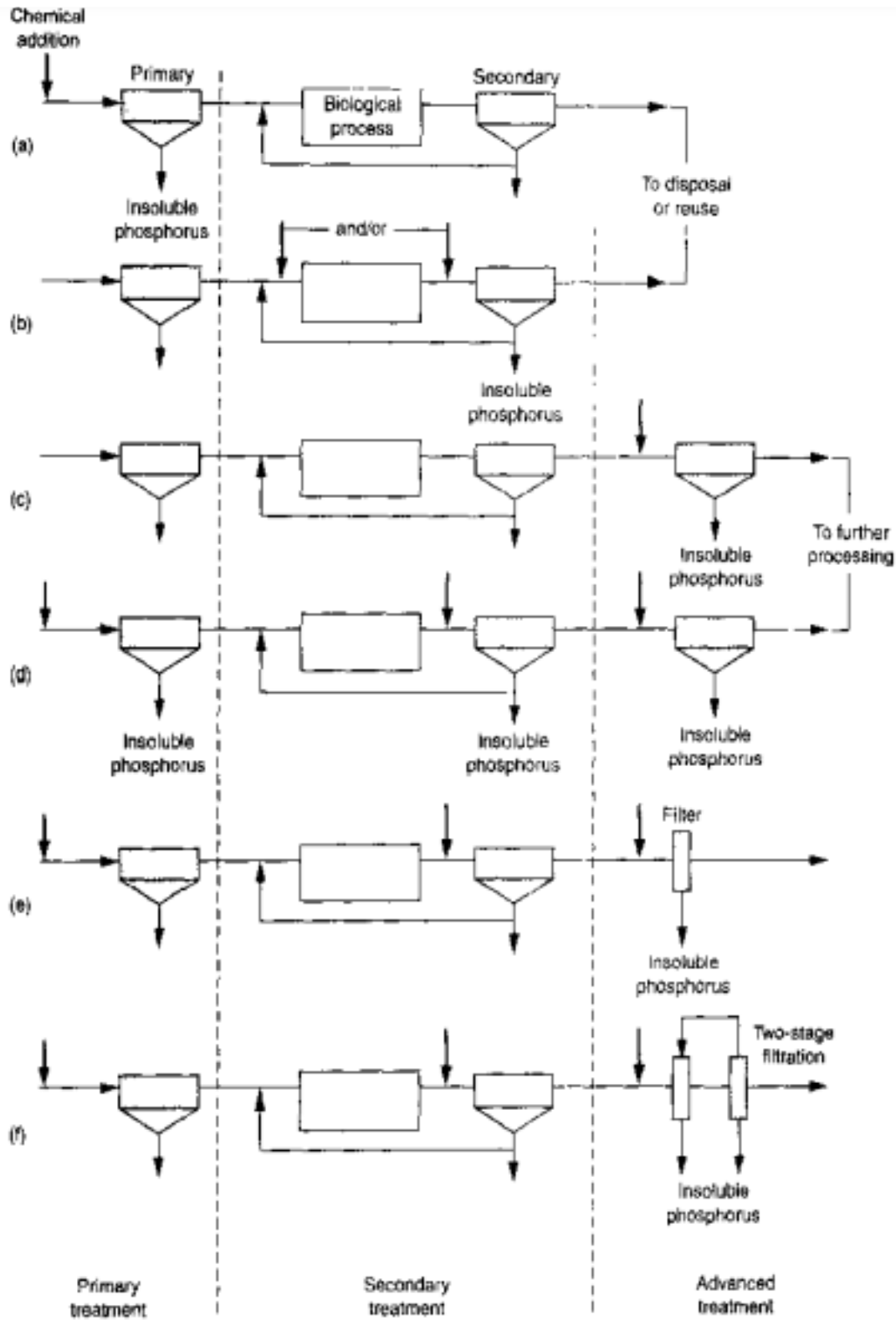


Figure 3.3 Alternative points of chemical addition for phosphorous removal a) before primary sedimentation, b) before/after biological treatment, c) following secondary treatment, d-f) split treatment: at several locations in a process (Metcalf and Eddy, 2003)

3.2.2. Natural precipitation

While wastewater treatment processes take place, phosphorous species can be removed to the sludge as a result of natural precipitation without the addition of any chemical agent to enhance this precipitation. This is explained since the achieved condition for pH, phosphate concentration and cations like Ca, Fe, Al, Mg and Zn, are the required for the precipitation of several solid forms.

3.2.2.1. Biological phosphorous removal

The development of biological phosphorous removal was based on research in the late 1950s, which found that, under certain conditions, activated sludge could take up phosphorous in considerable excess to that required for normal biomass growth (Greenberg et al., 1955).

Based on this phenomenon, several applications and processes have been developed to remove phosphorous species with the advantage of avoiding the use of chemicals and excess sludge production. While in a conventional plant of activated sludge, bacteria used the required phosphorous to satisfy their metabolic needs achieving a phosphorous removal of around 20%. However, in processes designed to remove phosphorous, the required medium is created to enhance the proliferation of bacteria that can accumulate more phosphorous than the required increasing the overall phosphorous removal rates up to 80% (Brett et al., 1997). This Bacteria are known as Polyphosphate Accumulating Organisms (PAO).

Biological phosphorous removal will be achieved in the activated sludge process by introducing an anoxic zone ahead of an aerobic zone. In the absence of oxygen and nitrated, PAO take up the acids and release phosphorous into solution. The accumulated phosphorous in biological processes, collected as polyphosphate, is removed with the sludges.

3.3. Sludge management in WWTPs

The semi-solid residue, with content of suspended solids between 1 and 30%, produced in wastewater treatment processes is known as sludge. This mixture contains a high fraction of biodegradable and recalcitrant organic compounds, pathogens, transition metals and other inorganic constituents. The main objective of sludge treatment processes is to reduce its wet and organic matter content in order to obtain a final mixture with quality enough for its reutilization or final deposition. However, its rich content in organic matter and nutrients make them potential attractive for energy and product recovery. Sludge is also a valuable source of organic carbon, nitrogen, phosphorous, as well as some inorganic compounds such as silicates, aluminates and carbonate between others, which can be

recycled or further utilized for industrial or agricultural purposes (Dentel, 2004; Fytili and Zabaniotou, 2008; Rulkens, 2004; Rulkens and Bien, 2004).

Contemporary sludge treatment approaches aim to achieve reductions in total weight and volume to facilitate transportation and provide additional treatment, stabilization of the material through destruction of pathogenic microorganisms, elimination of unpleasant odors, and reduction of the potential for putrefaction by decreasing the volatile solid content; and, more recently, addition of value by developing the economically viable recovery of energy and useful constituents (Campbell, 2000; Dentel, 2004; Fytili and Zabaniotou, 2008; Kroiss, 2004; Tchobanoglous et al., 2003).

The sludge produced after primary and secondary treatments is mainly composed by water. Reducing the water content will lead to significant reduction of sludge volume. Examples of typical water reduction processes are thickening, conditioning, dewatering, and drying. The removal organic matter from sludge is achieved via digestion, composting or incineration. In digestion processes, both aerobic (oxygenated environment), and anaerobic (no oxygen in the system), biological decomposition of organic compounds can occur with the presence of a range of microorganisms (Tchobanoglous et al., 2003). Anaerobic digestion is often preferred over aerobic digestion because the amount of biomass produced per unit of degraded substrate is much lower in anaerobic than in aerobic treatments. In addition, most of the substrates of anaerobic digestion are transformed into methane, which can be recovered and reused. Non-aeration and methane production make anaerobic digestion more energy-efficient (Pastor, 2008). In a wastewater treatment plant, The selection of the sludge treatment process will depend of a wide range of factors such as the size of the plant, the local environment regulations and economy, fuel cost, land availability, sludge characteristics, transportation distances of sludges and by-products, operational conditions, and the environmental awareness of the general public (Zhang et al., 2014).

In the next sections an overview of several commonly used techniques to deal with sludge in wastewater treatment plants is displayed according to Zhang et al. (2014) work.

3.3.1. Anaerobic digestion

Anaerobic digestion is a process that occurs in the absence of oxygen and of electron acceptors of inorganic nature like nitrate or sulphate where biodegradable organic wastes are converted into biogas; a gaseous mixture rich in methane (up to 70%) and the digested material by the action of several microorganisms. Anaerobic digestion is composed of three major stages:

Hydrolysis: It is the first stage where complex organic compounds such as fat, polysaccharides and proteins are hydrolyzed into soluble and basic structural elements like oligosaccharides and sugars,

alcohols, amino acids and fatty acids. This hydrolysis is carried out by various groups of decomposing microorganisms (Zhang et al., 2014).

Acidogenesis and acetogenesis: In this second stage, the soluble organic compounds produced in the first stage are fermented into acetic acid, hydrogen and carbon dioxide by the acidogenic microorganisms. Acetogenic microorganisms will convert more complex fermented products into organic acids (e.g. acetic and propionic acid), hydrogen and carbon dioxide ready for methanogenesis.

Methanogenesis: It is the final stage, where acetic acid, hydrogen and carbon dioxide are eventually converted to methane and CO₂ in the presence of methanogenic bacteria (Martins das Neves et al., 2009).

3.3.2. Land application

Land application generally consists of transportation, pasteurization, and land spreading (EC, 2002). This option ensures that major plant nutrients like nitrogen, phosphorus, potassium, sulfur, copper, and zinc are recycled (EC, 2008). The primary nutrients such as nitrogen and phosphorus in biosolids are in organic forms. These nutrients are stabilized in the root zone when they are gradually decomposed and mineralized and hence are easier for plants to uptake compared to commercial fertilizers (Lu et al., 2012; WEF, 2010). In European Union member states (EU27), approximately 40% of sludge generated is applied to agricultural land (EC, 2008). Stringent compliance criteria have been set by environmental agencies around the world to manage the safe practice of land application (like the European Union Council Directive 86/278/EEC and Amendments EUR-Lex, 1986). Due to increasing public concern about human health impact from the harmful effects of heavy metals and chemicals in the disposed materials, direct land application is gradually losing importance in sludge management (Campbell, 2000; Roy et al., 2011).

3.3.3. Composting

In composting, the organic waste in sludge is converted into stable, hygienic and humic-like material in a bio-oxidative process. Composting has a thermophilic stage, with its temperature ranging between 57 and 70 °C. Because of the heat, the pathogens are destroyed, and maximum stabilization is achieved (Campbell, 2000; Mousty et al., 1984; Tchobanoglous et al., 2003). Composting reduces the volume of the sludge significantly and the end product composts can be used in agriculture as fertilizers due to their high contents of carbon, nitrogen and phosphorus. To achieve a high-quality compost, factors like nutrient composition (carbon-to-nitrogen ratio 30:1), moisture content (50-60%), pH (6-8) and adequate aeration must be well managed. Although problems associated with odor emissions still needs to be addressed, composting is an economically and environmentally friendly approach for the

stabilization of sludge; not only because of its little energy input requirement but also for the final product obtained, the compost, which can be used as a soil amendment (Mousty et al., 1984).

3.3.4. Landfilling

Landfilling, disposal of waste material by burying it under layers of earth, has become a less desirable option in sludge treatment, because of the reduced lifetime of landfill sites resulted from an overloaded leachate system, issues with compacting the sludge/garbage mixture, and the associated increased NH_3 production and leaching which requires long-term monitoring of the landfill sites (Kroiss, 2004). In addition, landfilling has become less practical for places with limited space. In Europe, because of the public dissatisfaction and ban on the landfilling of organic wastes, the portion of sludge ending up in landfilling was expected to be decreased significantly, from 14% in 2010, to 7% in 2020 (EC, 2008). In the present years, only landfills which its capacity has not been reached are still in operation, but it is expected to be less than 1% in the next two years.

3.3.5. Thermo-chemical treatment processes

Thermo-chemical treatment is a major sludge disposal option, as it provides a pathway for energy recovery.

Combustion is a complex oxidation process that takes place at high temperature. With combustion bulk volume reduction is maximized and pathogenic microorganisms and toxic compounds are destroyed (Roy et al., 2011). It can destroy toxic organic contaminants present in the dewatered sludge by converting them into carbon dioxide and water. However, the combustion of sludge may also release toxic airborne contaminants such NO_x , N_2O , SO_2 , HCl, etc. Combustion is an ultimate route for sludge disposal and it is also attractive for the potential for energy recovery through the collection and reuse of the hot flue gas heat.

In addition to combustion, a wide range of thermo-chemical techniques have been reported for sludge treatment. These are processes such as pyrolysis, gasification, liquefaction or wet oxidation which are not going to be further detailed in this project.

3.4. Struvite

With more stringent standards imposed regarding nutrient removal, processes have been developed to remove compounds containing nitrogen and phosphorus. The result of removing greater concentrations of phosphorus from wastewater is that the wasted sludge has a greater concentration of phosphorus, nitrogen and magnesium. This combination of ions found in sludges produced from nutrient removal, specifically biological nutrient removal (BNR) processes, can result in the formation

of a mineral called struvite (Doyle and Parsons., 2002). Struvite is the name of the magnesium and ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, also known as MAP. Precipitation of struvite is achieved in a molar relation 1:1:1 following eq 3.4.



n can be 0, 1 or 2 depending on pH (Abbona et al., 1979).

To produce pure struvite, many factors need to be carefully controlled. Factors including component-ion ratios, potential interfering ions, and pH values (Wang et al., 2005).

Struvite will precipitate when the solubility product ($K_{S_{MAP}}$) (equation 3.5) is reached according to the concentrations of magnesium (Mg^{2+}), ammonium (NH_4^+) and phosphate (PO_4^{3-}).

$$K_{S_{MAP}} = [Mg^{2+}][NH_4^+][PO_4^{3-}] \quad Eq\ 3.5$$

Concentration of these components, as well as the solubility of struvite, will be directly dependent on the pH. As pH increases, struvite solubility decreases. Several authors have studied struvite solubility with pH variation. According to Doyle and Parsons (2002) who analyze other authors studies of struvite solubility, the solubility of struvite is minimum at pH ranges of 8.8 to 9.4. It is noticeable in Eq 3.4 that hydrogen ions are released during struvite precipitation, leading to a decrease in the pH solution. This pH reduction inhibits struvite precipitation, therefore it will be crucial to have a perfect control in the pH of the reactor to enhance struvite crystallization. Adding sodium hydroxide (NaOH), magnesium hydroxide $Mg(OH)_2(s)$ or by aeration with $CO_2(g)$ stripping are some of the ways to achieve the desired pH. Since magnesium is usually the element found in less concentration in wastewater streams, using $Mg(OH)_2(s)$ to achieve the required pH will enhance the struvite precipitation (Wang et al., 2005). However, these two parameters (pH and magnesium concentration) will not be controlled independently and so it will be usually preferred to use NaOH to increase the pH and additionally adding magnesium in salt form such as $MgCl_2$ or $MgSO_4$.

The component-ion molar ratios also have great impact on the composition of the precipitate. Mg/P, N/P, Ca/P and Ca/Mg have an important influence on the precipitation and recovery efficiencies of the crystallization process and must be considered (Peng et al., 2018). Precipitation and recovery efficiencies improve at high Mg/P and N/P ratios (Pastor et al., 2008a). Previous research revealed that a stoichiometric excess of ammonium will help drive the reaction to form relatively pure struvite (Stratful et al., 2001).

Magnesium should also be closely monitored. If the Mg/P ratio is less than 1, Mg^{2+} should be added to increase Mg concentration in the solution. Calcium is a common cation in wastewater and is also an interfering ion to struvite formation. Struvite formation is affected by the interaction of calcium and magnesium, depending on their relative concentrations struvite formation can be inhibited as calcium

phosphate precipitates (Momberg and Oellermann, 1992). By modifying the chemical composition of wastewater, increasing Mg/Ca ratios, efficient struvite formation can be achieved (Battistoni et al., 2000). Under different ratios of Mg/Ca, struvite or hydroxyapatite could be formed within the pH range of 8-10 (Battistoni et al., 2000). Struvite purity can be greatly decreased when the Ca/Mg ratio is higher than 1 (Wang et al., 2005). To maximize struvite purity, the ratio of Ca to P should be less than 0.5.

3.4.1.1. Struvite in WWTP

The uncontrolled precipitation of struvite is a common issue in the anaerobic treatments of sludges coming from biological removal of phosphorous processes. In enhanced biological phosphorous removal, phosphates and other ions (i.e. magnesium and potassium) are removed from wastewater and accumulated inside the polyphosphate accumulating bacteria (PAO) as internal granules of polyphosphate (Poly-P). Approximately between 75 and 90% of the phosphorus entering the municipal WWTP is transferred into the sewage sludge. In addition, anaerobic digestion and post-digestion processes, which show a higher pH value than the previous stages of the wastewater treatment, are more susceptible to struvite formation (Tarayre et al., 2016; Martí et al., 2017).

Struvite is mostly found in the sludge line treatment from the anaerobic digester to the end of the treatment. It occurs spontaneously not only in the digester but also in pipes, elbows, pumps and centrifuges. Struvite deposits foul pumps and cause pipe blockages, leading to a significant increase in the cost of sludge management operations. These technical problems due to the struvite formation, also precede economic losses since maintenance service is continually required and the global efficiency of the process decreases.

3.4.1.2. Struvite as a valuable product

Although unintentional struvite formation can be a problem in wastewater treatment plants, controlled formation has also been proposed as a method to recover $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ in the form of struvite, which is valuable fertilizer (Doyle and Parsons, 2002). Struvite is composed by 28,9% P_2O_5 , 5,7% of N and 16,4% of MgO (Bridger et al., 1962). These good nutritional properties make struvite interesting to be used as a fertilizer. Its low solubility suggests their use as long-lasting sources of nitrogen, phosphorous and magnesium and has good possibilities to be used as a slow release P fertilizer. In many cases, it is desired that the fertilizers have a low solubility, for example, those that are used in fields or forests where fertilizers are normally applied once every several years (Pastor, 2008). However, it is important to highlight that to achieve the requirements of NPK (nitrogen, phosphorus and potassium) of several crops, the addition of K would be required after the obtention of struvite (Doyle and Parsons, 2002).

According to Taruya et al. (2000), struvite has properties very similar to commonly used commercial fertilizers. They also confirmed that struvite precipitated from the solutions obtained after processing the sludge from three sewage treatment plants, operated to carry out the biological elimination of phosphorus, met the limits of concentrations of heavy metals that the laws require for fertilizers.

References for struvite market prices are inconsistent. Commercialization of struvite recovered has been reported. In table 3.1, several proposed prices at which struvite can be sold as a raw material in the fertilizer industry by different authors are proposed.

Table 3.1 Market prices of struvite according to different authors, country and year

Authors, country, year	Price (€/t)
Münch & Barr, Australia, 2001	188-314 €/t
Ueno & Fujii, Japan, 2001	250 €/t
Shu et al., Australia, 2006	464 €/t
Dockhorn, Germany, 2009	763 €/t

STOWA (2016) estimate the market value of struvite in Netherlands, based on present mineral fertilizer prices and its content of mineral N, soluble P and magnesium, to be about 55€ per tonne as pelletized fertilizer or raw material for the fertilizer industry. In recent studies under LIFE ENRICH umbrella, the price of struvite have been estimated to be 350€/tonne.

3.4.1.3. EU Fertilizing Products Regulation

For certain recovered wastes, such as struvite, biochar and ash-based products, within the meaning of Directive 2008/98/EC of the European Parliament and of the Council, a market demand for their use as fertilizing products has been identified. Furthermore, certain requirements are necessary for the waste used as input in the recovery operation and for the treatment processes and techniques, as well as for fertilizing products resulting from the recovery operation, in order to ensure that the use of those fertilizing products does not lead to overall adverse environmental or human health impacts

Good progress was noted on several dossiers at the EU Fertilizers Expert Group 18-19 March 2021. This meeting technically validated the finalized texts of the “STRUBIAS” (STRUvite, Biochar, or Incinerations Ashes) criteria to add struvite and phosphate salts, ash/ash derived materials and pyrolysis materials as component materials in the EU Fertilizing Products Regulation (STRUBIAS, 2018). Except some minor tidying of legal wording, the criteria remain as published for the public consultation. Hopefully, the finalized criteria will now be published in coming months, in time for the entry into implementation of

the new fertilizing Products Regulation itself in June 2022. The Commission should now engage discussions to define the conditions and legal wording for inclusion of struvite into the next update of the Organic Farming.

3.5. Phosphate recovery as struvite in WWTP

In WWTPs with Enhanced Biological Phosphorus Removal (EBPR), phosphates are removed from wastewater and accumulated inside the polyphosphate accumulating bacteria (PAO). During the anaerobic digestion of the sludge, Poly-P is released to the liquid phase. Therefore, the rejected liquors from digested sludge dewatering show high phosphorus, ammonium and magnesium concentrations which make these streams very appropriate for recovering phosphorus as struvite in a crystallization process (Pastor et al., 2010; Lahav et al., 2013).

However, at this point of the sludge line, most of the soluble P is lost due to precipitation in the anaerobic digester and post-digestion processes, which causes important maintenance problems in the WWTP (Doyle and Parsons, 2002; Barat et al., 2009; Martí et al., 2010). Thus, sludge management alternatives to reduce uncontrolled P precipitation must be evaluated to enhance P recovery in WWTPs and to reduce operating costs due to uncontrolled precipitation.

Phosphorous can be recovered at different point in wastewater treatment plants. It can be recovered either in wastewater, sewage sludge and sludge ash. Numerous technological approaches have been developed in recent years. In Figure 3.4, the different access points to recover P are displayed. The color code is used to differentiate the P recovery form aqueous phase: digester supernatant and dissolved P in anaerobically digested sludge and effluent (green), sewage sludge (blue) and sewage sludge ash (red).

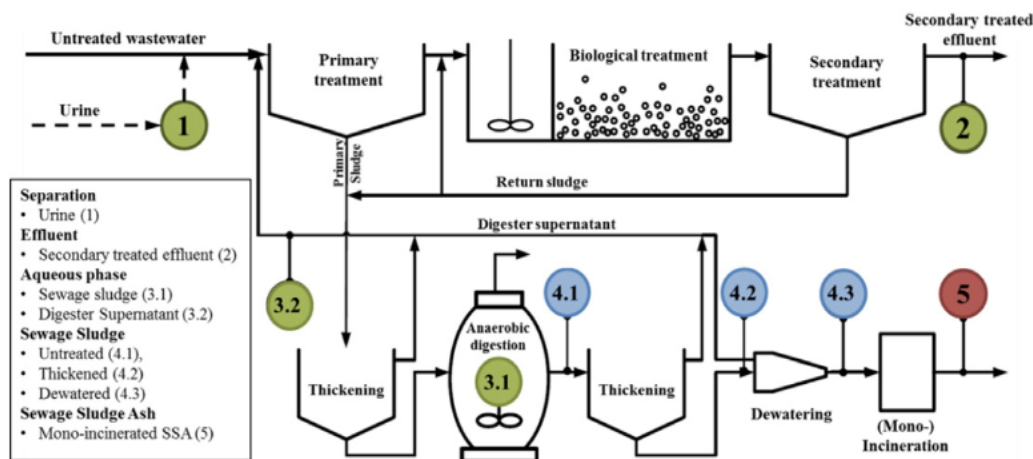


Figure 3.4 Various possible access points for P recovery approaches during wastewater and sewage sludge treatment or before/after incineration (Egle et al., 2016)

Table 3.2 summarizes the main technologies applied and reflects the main conclusions developed along the P-REX project founded by the EU along the 7th FP (Egle et al., 2016).

Table 3.2 Main technologies applied for P recovery (Adaptation from Egle et al., 2016)

AQUEOUS PHASE	SAWAGE SLUDGE	SAWAGE SLUDGE ASH
REM-NUT® [2; ion exchange, precipitation]	Gifhorn process [4.1; wet-chemical leaching]	AshDec® depollution [5; thermo-chemical, ash depollution, Cl-source]
AirPrex® [3.1; precipitation/crystallization]	Stuttgart process [4.1; wet-chemical leaching]	AshDec® Rhenania [5; thermo-chemical, Rhenaniaphosphat, Na ₂ SO ₄]
Ostara Pearl Reactor® [3.2; crystallization]	PHOXNAN [4.2; wet-oxidation]	PASCH [5; acidic wet-chemical, leaching]
DHV Crystalactor® [3.2; crystallization]	Aqua Reci® [4.2; super critical oxidation]	LEACHPHOS® [5; acidic wet-chemical, leaching]
P-RoC® [3.2; crystallization]	MEPHREC® [4.3; metallurgic melt-gassing]	EcoPhos® [5; acidic wet-chemical, leaching, P-acid production]
PRISA® [3.2; precipitation/crystallization]		RecoPhos® [5; acidic wet-chemical, extraction]
		Fertilizer Industry [5; acidic wet-chemical, extraction]
		Thermphos (P₄) [5; thermo-electrical]

The recovery of phosphate in aqueous streams by a crystallization process is winning in interest since the final product obtained offers a high purity and quality. In the next lines struvite as the phosphate recovered form is addressed.

3.5.1. Struvite crystallization reactors

Although, there are slight variations in the technologies and operational systems to recover struvite by a crystallization process, most of them are based in the same design and operational principles. Most of these technologies are based on a precipitation reactor, a fluidized bed reactor type, with pH control and magnesium addition. The main differences, beyond the criteria of shape and type and power of agitation, are usually the way in which the pH is controlled and how magnesium is supplied to control

its availability for the reaction. The Ostara Pearl Reactor solution is one of the most commonly used to obtain struvite after anaerobic digestion (www.ostara.com).

The core of Ostara's solution is the Pearl. A fully customizable and modular treatment solution, Pearl fits into the main or side-stream operations removing phosphorus from the treatment system by adding magnesium in a controlled pH setting. This allows nutrients to crystallize into highly pure fertilizer granules, which are harvested, dried and bagged ready for distribution and sale as Crystal Green®. In this reactor, the influent are the centrates or side-streams from the anaerobic digestion reactor, treating the sludge generated in the conventional aerated sludge reactor, and enter from the bottom. The struvite crystals that are formed are kept in suspension until they fall under their own weight to the bottom of the reactor, where they are collected and sent to a drying and bagging stage. The pH control is carried out by adding sodium hydroxide. The control of the availability of magnesium for the struvite formation reaction is carried out by adding magnesium chloride. The struvite precipitation reactor of Ostara is presented in Figure 3.5.

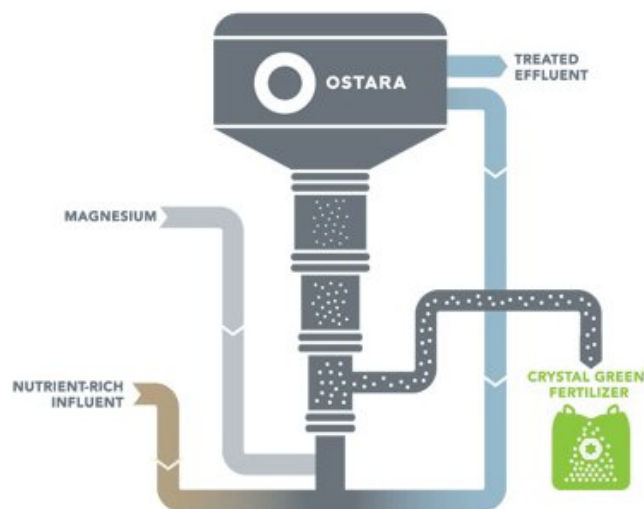


Figure 3.5 Representation of the precipitation reactor of the Ostara technology (www.ostara.com)

These technologies can be complemented with other equipment that performs nutrient release processes from the sludge received by the digester, so that these nutrients go from the solid phase to the liquid phase. These processes are usually carried out on activated sludge, the Wasstrip unit of Ostara is an example of this. Waste Activated Sludge Stripping to Remove Internal Phosphorus (WAASSTRIP) is a value-add to Pearl providing critical benefits to facilities that use anaerobic digestion. Releasing phosphorus upstream before it reaches the digester, WASSTRIP turbo-charges nutrient removal and recovery. Plus, the process protects digesters and equipment from struvite, improves dewaterability, and reduces biosolids. A typical schema for the application of The Ostara Technology with both the crystallizer reactor and the Wasstrip technology is displayed in Figure 3.6.

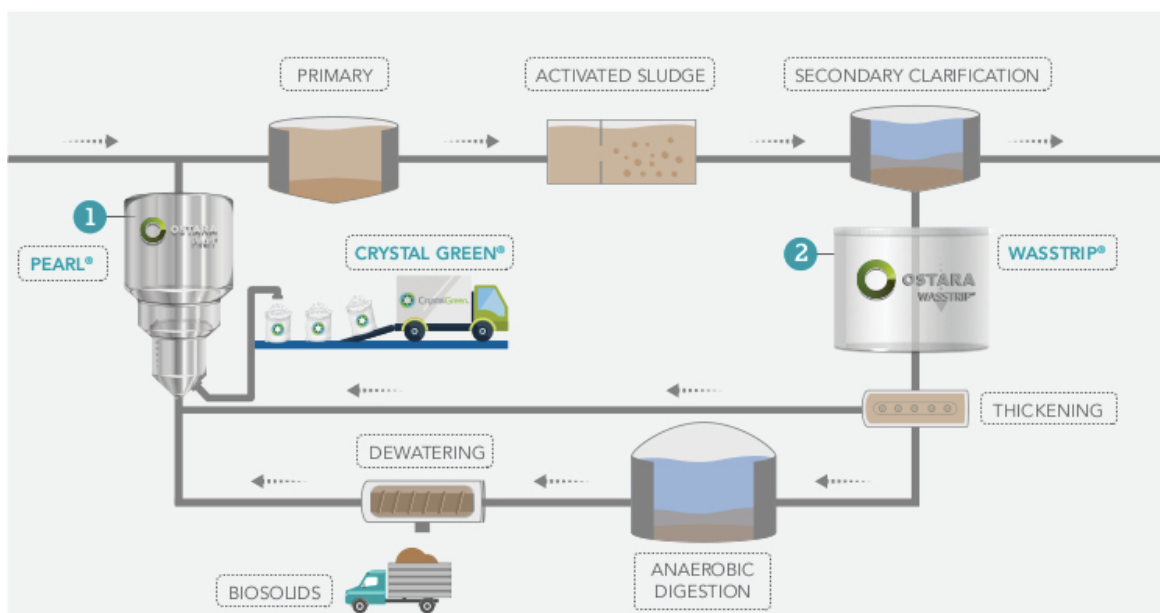


Figure 3.6 Diagram of a typical system of struvite recovery with an additional nutrient release technology (www.ostara.com)

3.6. LIFE-ENRICH Project

LIFE ENRICH (Enhance Nitrogen and phosphorus Recovery from wastewater and Integration in the value Chain) project (www.life-enrich.eu) focuses on N and P recovery from wastewater and their valorization in agriculture as fertilizers as part of The LIFE Programme, the European Union's funding instrument for the environment and climate action. The project is led by CETAQUA (www.cetaqua.com).

The fertilizer industry consumes large amounts of nutrients from natural reserves or from complex manufacturing processes while WWTP are discharging nutrients to the environment (rivers, dewatered sludge and atmosphere). The goal of the ENRICH project is therefore to establish a link between both sectors contributing to the circular economy. The aim of the project is the recovery of nutrients from wastewater treatment plants and its valorization in agriculture.

The outcomes of the LIFE ENRICH project include the recovery of 50% of P in WWTP (50% of it as struvite), 15 % of N of the whole WWTP and 10% reduction of the total OPEX (Operating Expenses) 50% of it related to the maintenance costs due to uncontrolled precipitation.

The research and development of a wide variety of P-recovery techniques from different streams after anaerobic digestion have been addressed. Several techniques to recover it from sludge streams include Airprex®, Nuresys or Elophos®. And from centrifuge centrate Naskeo®, Ostara® or Pearl®. However,

the potential of these processes is limited as they cannot avoid the uncontrolled precipitation of P-compounds (Roldán et al., 2020). Other approaches aim to overcome this limitation by recovering P before anaerobic digestion.

Pre-anaerobic digestion strategies are based on enhancing P extraction and separation by means of a novel elutriation process and a process based on the WASSTRIP®.

The elutriation process basically consists on contacting a stream of biological sludge, rich in PAO, with a stream of sludge rich in volatile fatty acids (primary sludge), in absence of oxygen. Under these conditions, PAO bacteria release the phosphorus they have stored in the form of soluble phosphorus. The term volatile fatty acids (VFA) comprises a mix of acetic acid, propionic acid, butyric acid and valeric acid, being acetic acid the dominant species in waste water and sludge from anaerobic processes. VFA play a crucial role in EBPR. The anaerobic VFA uptake by PAO and its later growth will depend on the VFA concentration in raw wastewater. Good P removal efficiencies will only be achieved if the VFA concentration in the stream is considerably high.

Enhancing the poly-P release from sludge and separating it before anaerobic digestion will lead to an increase of P recovery and a reduction of uncontrolled P compounds precipitation.

One of the cases of study and implementation target of the LIFE ENRICH project is the Murcia Este WWTP. Different configurations have been assessed in the Murcia Este WWTP by the Polytechnic University of Valencia in order to identify the best way to implement the elutriation process in the plant. The Murcia Este (ME) WWTP consists of a primary settling, an anaerobic-anoxic-oxic (A2O) biological reactor and secondary settling. The sludge line configuration consists of two primary gravity thickeners (only one is used) and two dissolved air flotation thickeners for Waste Activated Sludge (WAS). The thickened WAS is electromagnetically hydrolyzed and mixed with primary sludge in a mixing chamber and then digested and dewatered. The layout of the Murcia WWTP is shown in Figure 3.7.

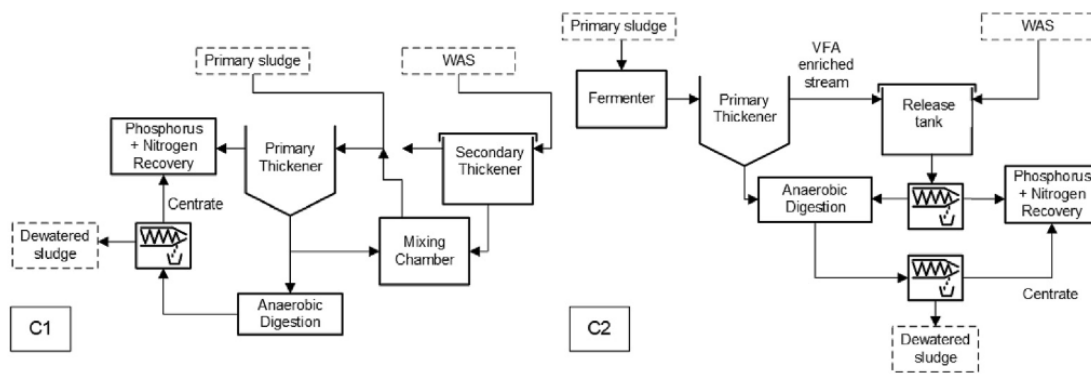


Figure 3.8 Principles for C1 (left) and C2 (right) from Roldán et al. (2020)

Among several configurations, an approach of C1 was selected as the best option to be implemented in the Murcia WWTP. Mixing thickened primary and secondary sludge in one of the floating thickeners (out of service by then) and in the mixing chamber in order to increase the hydraulic retention time of the mixing stage. Then the mixing sludge would be pumped from the mixing chamber to each of the primary sludge thickeners, where solid-liquid separation would occur, obtaining a supernatant rich in soluble phosphorous. By this approach, the retention time of the sludge into the units (floating thickener as mixing chamber plus the current mixing chamber) would be 18,6h, an adequate value to allow the maximum releasing of phosphorous in the form of soluble phosphorous. The elutriation process implementation in Murcia-Este WWTP is illustrated in Figure 3.9.

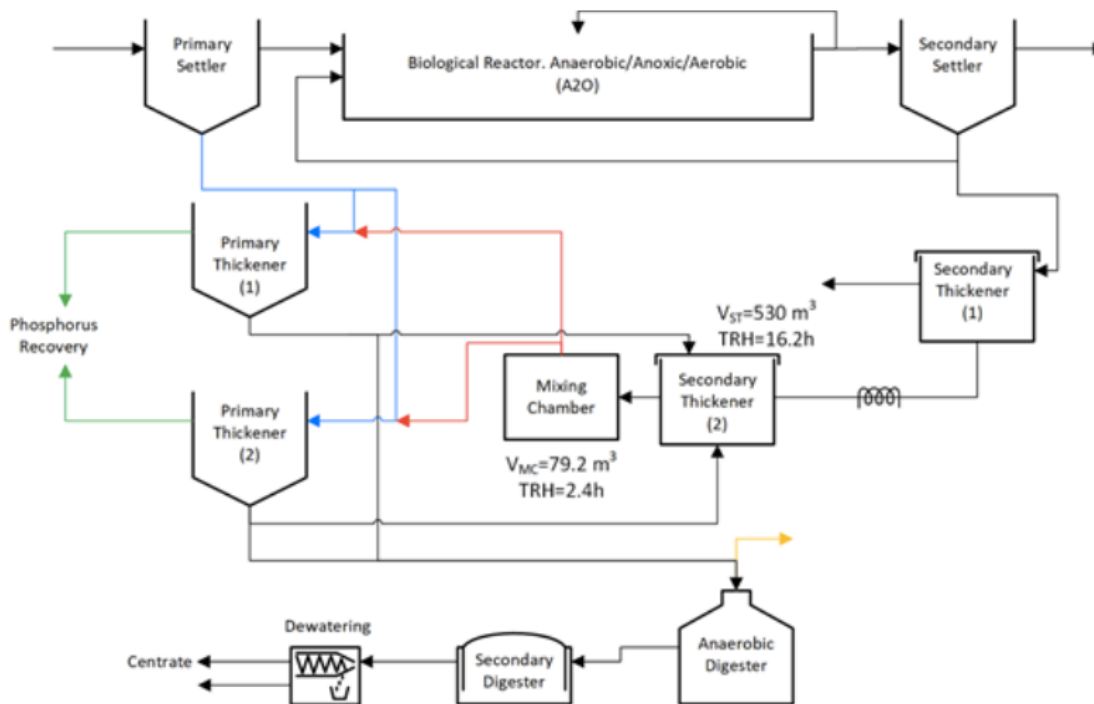


Figure 3.9 Elutriation process implementation in Murcia-Este WWTP. (LIFE16 ENV/ES/000375)

In ENRICH Project, the reactor used for the struvite production is based on the *Phosphogreen* commercial reactor from SUEZ group. It is a fluidized bed reactor with recirculation and the main characteristics of the streams involved in the technology are the following (Figure 3.10):

- Addition of $MgCl_2$ for precipitation
- Airlift system for CO_2 stripping
- Addition of NaOH if pH needs to be further adjusted
- Struvite pellets harvested from the bottom of the reactor, washed, dried and packaged to be sold

Granule size of the struvite obtained is around 2mm. Crystals smaller than 2mm are sent back to the influent of the reactor.

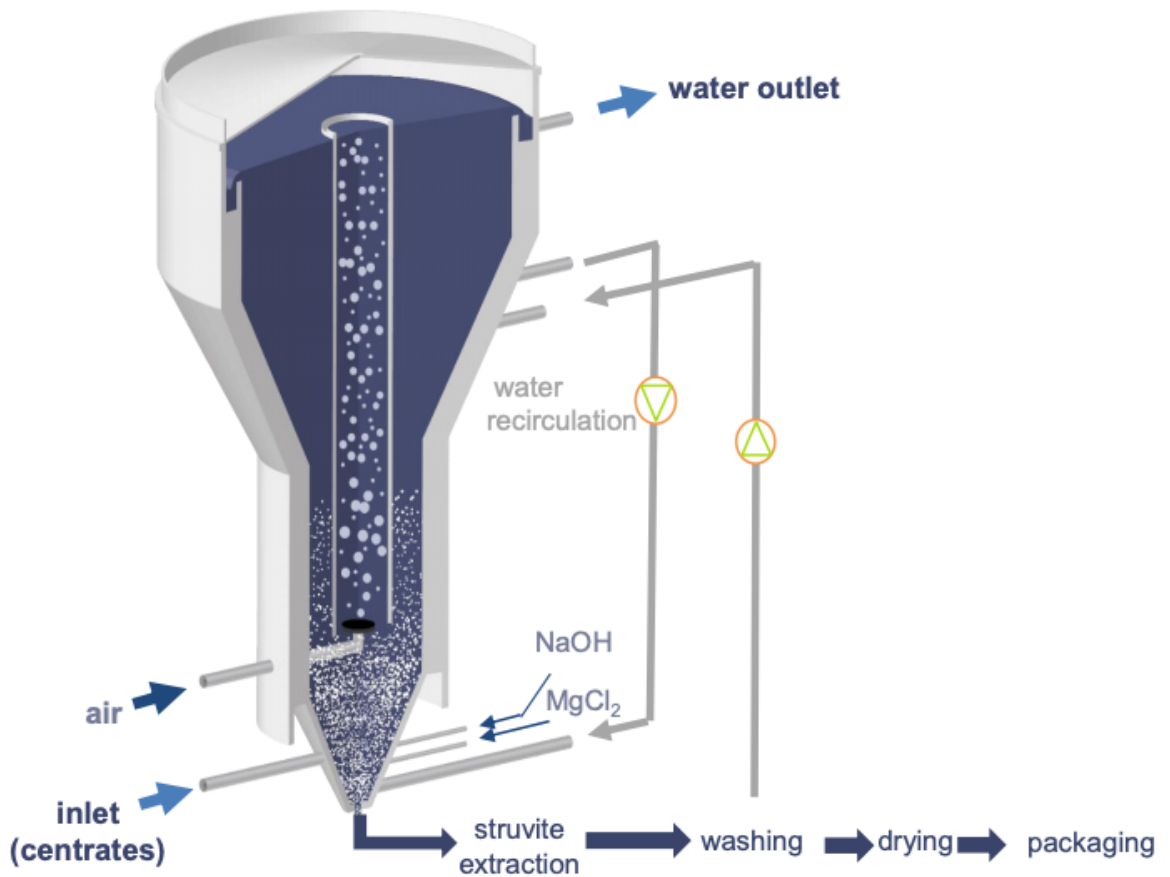


Figure 3.10 Representation of the struvite crystallization reactor Phosphogreen (SUEZ)

4. ALT MARESME NORD WWTP

Serveis Integrals de Manteniment del MAREsme (SIMMAR) is a mixed economy company, participated by Consell comarcal del Maresme (the Maresme region council) (20%) and other local brands, manages the water cycle in the region. The Maresme Regional Council presented the wastewater sanitation service in operation in the Maresme region in 1989. The Catalan agency of water delegated to El Maresme Regional Council the competences related to the administration of wastewater treatments in the region of El Maresme. Its function is to manage the operation and maintenance of El Maresme sanitation systems through indirect management with SIMMAR SL. SIMMAR operates and maintains facilities for the treatment of wastewater, from the network of upstream collectors in the region, to sewage treatment plants and submarine outfalls, being the Council of El Maresme region the administration acting of this management. In Figure 4.1 a map of all WWTPs operated by SIMMAR in the region of El Maresme is displayed.

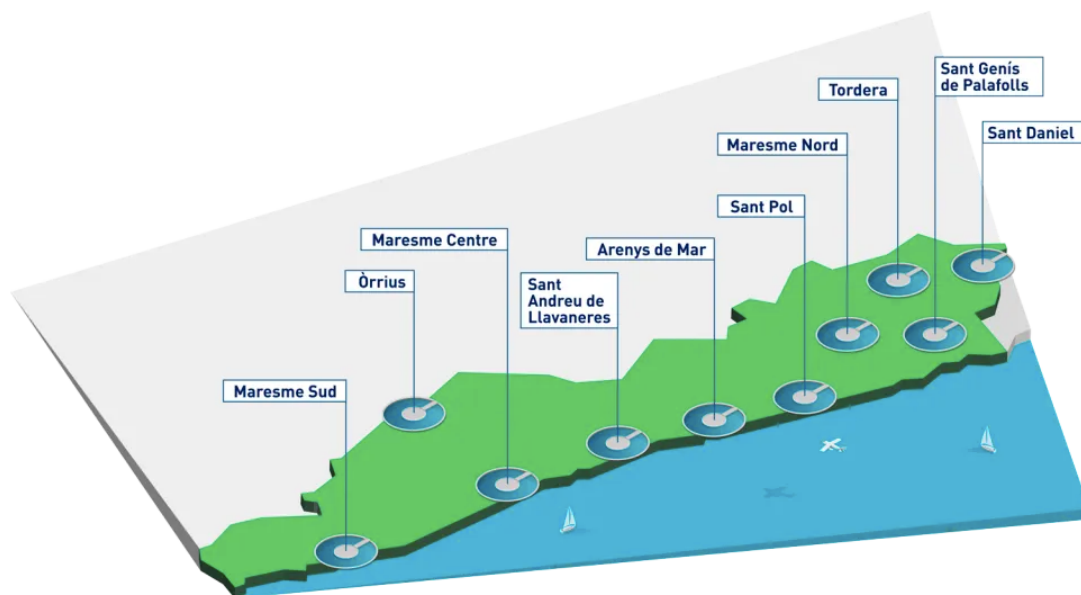


Figure 4.1 WWTPs managed by SIMMAR (web.simmar.cat)

The WWTP of Pineda-Tordera is located in the frontier of these two towns in the north of el Maresme and it is known as the Alt Maresme Nord WWTP (AMN WWTP). The plant, in service since 2012, manages the water cycle of five towns of la comarca del Maresme. Specifically, the plant collects and treat urban wastewater generated in the towns of Calella, Malgrat de Mar, Palafolls, Pineda de Mar and Santa Susanna (Figure 4.2).



Figure 4.2 Location of the WWTP of Alt Maresme Nord and the municipalities that send their urban wastewater to the plant.

4.1. Description of the plant

The plant (Figure 4.3) is designed to treat a flow, is 54.000 m³ day, equivalent to a population of 245.455 inhabitants.



Figure 4.3 Alt Maresme Nord WWTP

The water line has two physicochemical treatment lines using high density sludge sedimentation reactors, *Densadegs* (SUEZ company). Each of them with its coagulation chambers, flocculation and lamellar decanters. This high-rate system combines optimized flocculation, internal and external solids recirculation, sludge thickening and clarification in two conjoined vessels to maximize hydraulic loading and treatment efficiencies. The proprietary blend of energy input and high volume solids recirculation reduces waste volumes and results in rapid settling operation and high quality treated water

Biological treatment is performed using six flow bio-filters with ascending flux of water, which contain Biolita as natural filtration and retention media known as Biofors (SUEZ company). Once the water leaves the Biofor system, it is ready to be discharged. Biofor filters are aerobic or anoxic process biological reactors that use attached growth technology primarily for the removal of BOD, TSS and ammonia pollution. Biolite media provides surface area media for biomass growth and suspended salts filtration. The counter-current air and water up-flow enhances oxygen transfer. Biofor can replace activated sludge and secondary clarifier systems.

The sludge line has one operating line consisting of the following process units: a primary sludge purge, a thickening tank, two anaerobic digesters, a digested sludge tank and a dehydration step with two centrifuges. After the dehydration process, the sludge is stored in two sludge silos before its disposal. The biogas generated is used to heat digesters.

Since 2016, the Alt Maresme Nord WWTP do not only manage the sludges generated in their own plant but also deal with sludges produced in 5 other wastewater treatment plants in the region. Therefore, the sludge generated in wastewater treatment plants of Teià, Sant Andreu de Llavaneres, Arenys de Mar, Sant Pol and Tordera are sent to AMN WWTP to undergo the sludge management, and so go through anaerobic digestion collectively (Figure 4.4). This approach promoted by El Maresme Region Council allows the progress to a more sustainable region; a territory with a circular economy philosophy which uses resources efficiently while reducing the carbon dioxide emissions into the atmosphere. During all these years of operation, it has been possible to verify that with the integrated sludge treatment introduced at the Alt Maresme Nord WWTP, the CO₂ emissions and the generated waste have been drastically reduced.

Sludge from Teià, Llavaneres, Arenys de Mar, Sant Pol and Tordera are regularly sent to the Alt Maresme nord WWTP. When the project started, samples of the sludges were analyzed to decide how to operate in the hydration step with each sludge before being sent to the thickener, where all the sludges are mixed. Once a truck enters the Pineda WWTP, with the sludge from a specific plant, the product is weighted and hydrated in a tank which automatically adjust the amount of water required to achieve the standard moisturization just before being transferred to the mixing chamber (sludge tank).

The reception of sludges is periodically performed but sludge from the different WWTPs arrives in different amount and frequency and therefore, the composition and contribution of each plant in the mixing tank will not be always the same. Once the sludge is hydrated and sent to the mixing chamber the precedence of it is overlooked and so all the mixture is treated as a single and uniform product just before being sent to the anaerobic digestion step.

In Figure 4.4 the process flowsheet of the Alt Maresme Nord WWTP is displayed.

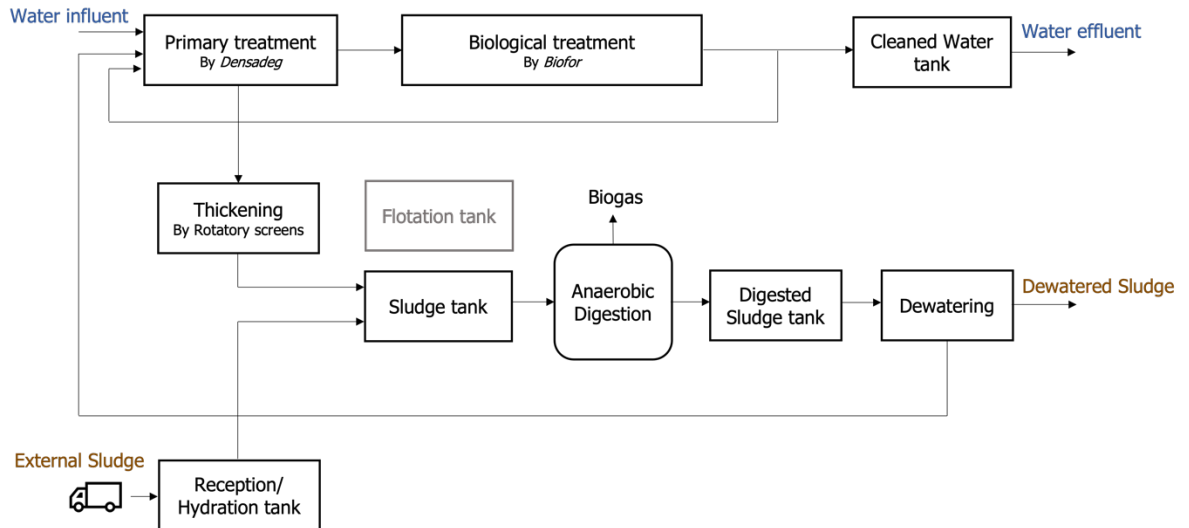


Figure 4.4 Diagram of the Alt Maresme Nord WWTP

4.2. Uncontrolled precipitation of phosphorous based mineral: the challenge to be solved

Since the sludge line in AMN WWTP started treating sludges from 5 other wastewater treatment plants apart from its own sludge, severe problems regarding deposit formation in sludge digester and downstream (pipelines, pumps, and centrifuge) have been reported. The deposit formation causes clogging, therefore, an intensive cleaning procedure on daily basis is applied. In Figure 4.5 the extent of the issue regarding the deposit formation in the equipment can be observed.

In August 2017, Kemira™, was asked to analyze a deposit sample from a pipeline in the Alt Maresme Nord WWTP. The results of analysis by Fourier transform infrared spectroscopy (FTIR) and X-Ray Diffraction (XRD) indicated the deposit was struvite. Elemental analysis by XRF (X-Ray Fluorescence) showed the deposit mainly contains phosphorous (12 wt%) and magnesium (9 wt%) and Manganese (3 wt%). Trace amounts of other elements such as iron, silica, Ca and Al were identified by XRF. The FTIR spectra was compared to Struvite. The results indicated that peaks are appearing at the same

wavelength as reference sample. The sample analyzed further with XRD indicated struvite as the main mineral phase found in the scales.



Figure 4.5 Pipelines in AMN WWTP before (left) and after a cleaning stage (right) (pictures provided by AMN WWTP)

Actions like lowering the pH, modifying the internal surface pipes, or reducing pressure drop in pipelines and pumps to remove the excess of phosphorous by coagulants and adding antiscalants are the main methods used to prevent uncontrolled struvite precipitation. However, in this project a global view of an implementation of a process modification to prevent struvite formation in digesters is addressed to determine a solution to enhance the phosphorous release outside of the digester and so enable the struvite precipitation in a crystallizer equipment, avoiding operational issues of the equipment involved during and after digestion processes while obtaining a valuable product ready to be commercialized.

5. EXPERIMENTAL METHODOLOGY

The anaerobic digester in AMN WWTP, deals with sludges coming from the secondary decanter of the activated sludge of Arenys, Sant Pol, Llavanes, Tordera and Teià as well as its own sludges generated in AMN WWTP. A spontaneous crystals precipitation has been identified in the digesters and the adjoining equipment. In order to decide, the best combination of variations and stream redirections in the sludge line, it will be important to have a perfect understanding of how the Alt Maresme Nord WWTP works. Since sludges arriving from Teià have been reported to be the most problematic in terms of phosphorous release, its characterization in terms of nutrient composition will be crucial. The deposit formation has also to be analyzed to confirm the composition of the mineral and propose the appropriate recovery route. An approach of the amount of phosphate that could be recovered in the sludge line has been estimated with previous studies data, and, after the sludges characterization, a better estimation of the amount of phosphorus that could be recovered as struvite has been performed. Finally, a proposal of the implementation of the optimal sludge line configuration at full-scale in AMN is performed.

5.1. Identification of the precipitated compounds in AMN WWTP

In order to confirm the results presented by *Kemira* in 2017, a sample of the deposit from the equipment in AMN WWTP was collected and analyzed by means of UPC on February 2021. The analysis of the sample with Field Emission Scanning Electron Microscopy (FESEM) and Energy dispersive X-ray Analysis (EDAX), confirmed a crystal of O, N, P and Mg as the main elements, with around 57% of Oxygen, 6,5% of Nitrogen, 21% of Phosphorous and 14% of Magnesium. The FESEM-EDAX analysis verify that the deposit extracted in the WWTP was a Mineral of N, Mg, P and O, for the typology of crystals and color, it was stated that it was struvite, $MgNH_4PO_4 \cdot 6H_2O$. However, Elements like Ca, S, Al, Fe and Si were found in minor quantities. Trace amounts of Calcium and Sulphur could led to think of the presence of brushite, $(CaHPO_4 \cdot 2H_2O)$ and gypsum, $(CaSO_4 \cdot 2H_2O)$ in minor amount. X -Ray Diffraction confirmed later that the deposit was in fact struvite as it can be seen in Figure 5.1. Any other mineral phase was detected indicating that neither are present as an amorphous phase or are below the limit of detection of DRX ($<0.1\%w/w$).

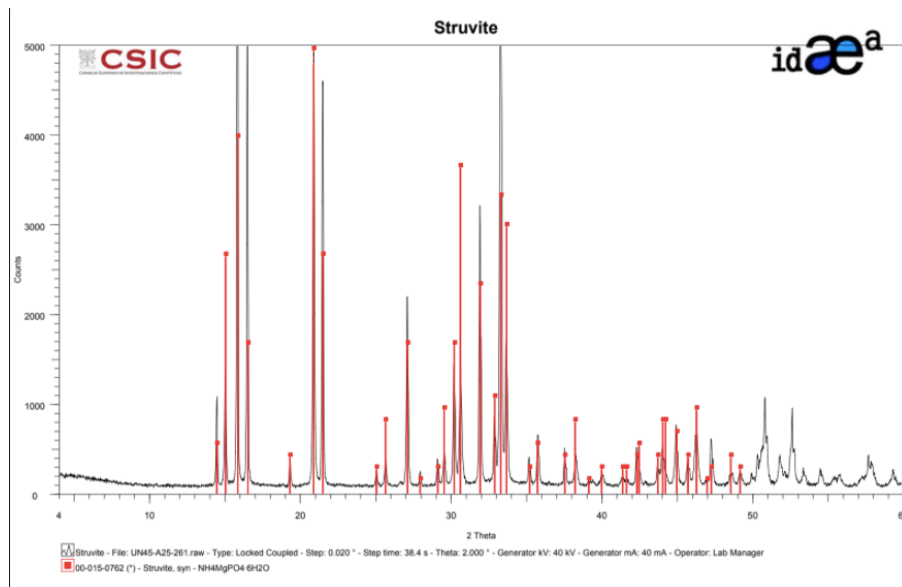


Figure 5.1 XRD results of the sample collected in AMN.

5.2. Characterization of the Phosphorous content on the sludge treated at AMN WWTP

In the Alt Maresme Nord WWTP, sludge from six different wastewater treatment plants in the zone are treated. Slight differences can be found in the way each one of the WWTP deals with its influent water. Therefore, the 5 sludges received in Pineda present different composition and properties.

Once it has been determined that the issue of uncontrolled precipitation of a crystal is due to the struvite formation, a preliminary analysis of the phosphate amount in the sludges is performed to obtain a first characterization of the sludges received as well as the sludge produced in AMN.

Among all these plants, the Teià WWTP applies the biological phosphorous removal (BPR) and so high concentrations of polyphosphates are expected to be found in Teià sludge. Predicting phosphorus precipitation is critical to be able to design sludge management alternatives that best minimizes uncontrolled phosphorus precipitation, reducing operational costs and enhancing phosphorus recovery in the WWTP.

To do so, data has been collected from the P concentrations of the influent and effluents streams of the different WWTPs. From data and recent studies provided by AMN plant, of the concentration of phosphorous in the influent and effluent of the 5 plants, in years 2016-2017, and knowing the flow treated for each of them, a first and global estimation of the amount of P contribution of each WWTP has been done. In table 5.1 the contribution in P by each plant is displayed.

The amount of phosphorous provided by each WWTP is calculated by means of the phosphorus removal efficiency of each plant, following the next equation:

$$Q_i * (P_{in} - P_{out}) \quad \text{eq 5.1}$$

Where Q_i is the wastewater flow treated by each plant, and P_{in} and P_{out} are the total concentrations of phosphorus in the inlet and in the outlet of the WWTP.

To calculate the percentage of phosphorus, the individual contribution of each plant and the total amount of P generated has been taken into account following the next equation:

$$P \text{ contribution } (\%) = \frac{Q_i \cdot (P_{in,i} - P_{out,i})}{\sum_{i=1}^6 Q_i \cdot (P_{in,i} - P_{out,i})} \cdot 100 \quad \text{eq 5.2}$$

Where subindex, i , refers to each one of the 6 WWTP supplying sludge.

Table 5.1 Contribution of each WWTP to the Sludge line in Alt Maresme Nord WWTP (SIMMAR, 2017)

	Influent (mgP /L)	Effluent (mgP/L)	Treatment Flow (m ³ /d)	P at the Sludge (kg/d)	P contribution (%)
PINEDA	5,7	4,1	20815	34,22	15,5
ARENYS	7,0	2,6	6000	26,39	11,9
LLAVANERES	6,9	3,2	4200	15,56	7,0
SANT POL	3,3	2,4	2300	2,03	0,9
TEIÀ	12,2	2,1	13000	131,25	59,3
TORDERA	5,8	1,2	2600	11,96	5,4

The total amount of P received in AMN is 221 kg/d.

Sludge from Teià has result to be the one providing the most phosphorus to the sludge line. The mean of sludges generation in tonnes per month by each of the WWTP, and therefore the amount of sludge treated in the Alt Maresme Nord is summarized in Table 5.2.

Table 5.2 Sludge generation at Pineda, Arenys, Llavaneres, Sant Pol, Teià and Tordera WWTP (SIMMAR, 2017)

	PINEDA	ARENYS	LLVANERES	SANT POL	TEIÀ	TORDERA
Sludge Generation (tonnes/month)	400	327,8	122,62	46,31	507,1	85,62

Teià sludge suppose more than 30% of the total sludge supplied in the sludge line of the Alt Maresme Nord WWTP. Therefore, having a good and deeper insight on its composition and behavior will be essential to propose a process modification to facilitate the phosphorus release in an efficient way.

5.3. Experimental study of the possible application of an elutriation stage in AMN WWTP as a potential alternative to reduce the uncontrolled precipitation of phosphorous minerals

As described, one of the objectives of this study is to evaluate the possibility of integration of an elutriation stage to control the struvite precipitation on a crystallization stage. The elutriation efficiency has been evaluated using batch experiments. The aim of the experiment is to monitor the evolution with time of the presence of phosphates and other species (NH_4^+ , Ca^{+2} , Mg^{+2} , HCO_3^- , Na^+ , K^+) in the different sludges that are mixed in the mixing chamber before getting into the digesters. The sludges produced in AMN (Pineda sludges (P) in the experiment) and Teià (T) have been analyzed.

5.3.1. Sample treatment of sludges collected for the phosphorous elutriation test

The batch elutriation test was developed using the following methodology.

1. Sludge Sample collection: Collect the 1L of hydrated sludge arrived from Teià directly from the hydration tank in the Alt Maresme Nord WWTP, in a 1L container (reactor). Sample of Pineda sludge is taken from the removal stream of *Densadeg* equipment.
2. *Reactors* will be closed and in constant agitation during all the sampling and experimentation tank imitating the behavior of a hypothetical elutriation tank, an anaerobic P-release tank.
3. Sampling from the *reactors*: At given agitation times t , of 1 hour, the agitation will be stopped and 20 mL will be extracted from both *reactors*.

In figure 5.2, the procedure followed in the laboratory to analyze the composition of the sample with Ion Chromatography (CI) and Inductive Coupled Plasma mass spectrometry (ICP) is described. With CI anions and cations were analyzed while in ICP total concentration elements (P, Ca, Mg, Na, K) were analyzed. Filtration and dilution steps are required to obtain samples with the required turbidity to go through chromatography and ICP. Before analysis, samples were filtered using 0.22 μm pore size.

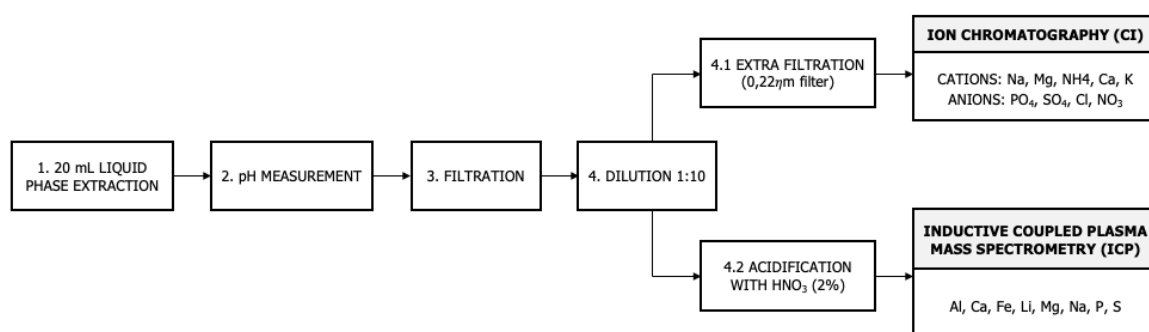
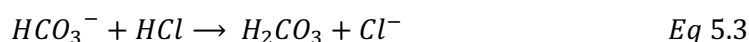


Figure 5.2 Details of sample preparation and analysis in the elutriation test for Teià and AMN sludges

While ion-chromatography allowed to study the release of the total content of orthophosphate and other ions, ICP was used to determine the total content of elements as P, were both inorganic and organic content are determined. Before the analysis by ICP, samples were acidified with a 2% of HNO₃.

The elutriation assay for both sludge samples was extend up to two days (48 hours) to simulate the elutriation time residences which has been reported to be in order of 15 to 30h (LIFE 16 ENV/ES/000375). A total of 9 samples for AMN sludge and 8 for the Teià one were prepared and analyzed by CI and ICP. Results are collected in chapter 5.3.2

In addition, bicarbonate concentration in the samples of 24h and 48h after the sludge extraction were analyzed by an acid-base titration using 0.1 M HCl solution. The reaction involved is described in equation 5.3.



From the end-point titration volumes at pH=3.7, the HCO₃⁻ concentration was calculated using eq 5.4.

$$[HCO_3^-] = \frac{V_{HCl} \cdot \frac{0,01\ mol\ HCl}{1\ L} \cdot \frac{1\ mol\ HCO_3^-}{1\ mol\ HCl} \cdot \frac{MW\ HCO_3^-}{1\ mol\ HCO_3^-}}{V_i} \quad Eq\ 5.4$$

Where V_{HCl} is the volume of HCl required to achieve the equivalence point, $MW\ HCO_3^-$ is the bicarbonate molecular weight, 62 g/mol and V_i is the volume of the sample analysed.

5.3.2. Elutriation batch test results

In Table 5.3, pH for all the samples is displayed. Pineda sludge present a higher pH than Teià one. The bicarbonates concentration in the liquid phase 1 and 2 days after the sludge collection in the WWTP (table 5.3) seems consistent with the pH value of the sludge. Pineda sludge present low concentrations of HCO₃⁻, while no detection of bicarbonates in the liquid phase of Teià sludge. At pH values below the acidity constant of the carbonic acid/bicarbonate (pKa1=6.3) the dominant species is H₂CO₃.

Table 5.3 pH values of the samples at different time extraction. And bicarbonate concentration in samples at 24h and 48h

SAMPLE NAME	pH		[HCO ₃ ⁻] mg/L	
	PINEDA	TEIÀ	PINEDA	TEIÀ
t ₀	6,45	6,29	n.a.	n.a.
t ₁ = 1h	6,98	6,17	n.a.	n.a.
t ₂ = 2h	6,87	6,09	n.a.	n.a.
t ₃ = 3h	6,58	6,27	n.a.	n.a.
t ₄ = 4h	6,82	6,27	n.a.	n.a.
t ₅ = 5h	6,59	6,19	n.a.	n.a.
t ₆ = 6h	6,65	6,23	n.a.	n.a.
t ₂₄ = 24h	6,97	5,98	68,9	<loq
t ₄₈ = 48h	6,95	5,79	16,6	<loq

Loq: limit of quantification, n.a. not analyzed

The concentrations obtained in the laboratory of the different elements and ions in all the samples of Pineda (P) and Teià (T) sludges are shown in Tables 5.4-5.7.

Table 5.4 Total concentration (Ct) of Aluminum, Calcium, Iron, Lithium, Magnesium, Sodium, Phosphorus and Sulphur in the liquid phase of Pineda sludge at different times after the extraction of sludge in the WWTP (from P0=0h to P 48h=48h).

SAMPLE NAME	Ct (mg/L)							
	Al	Ca	Fe	Li	Mg	Na	P	S
P0	1,49	139,15	25,20	0,04	73,7	777,1	46,41	60
P 1h	0,20	204,6	8,4	0,05	111,0	950,4	65,3	588,2
P 2h	0,07	143,6	8,5	0,03	74,7	626,3	55,6	41,4
P 3h	0,15	141,6	11,6	0,03	70,7	568,1	53,0	33,6
P 4h	0,03	139,1	6,8	0,03	67,8	567,2	49,9	31,9
P 5h	0,02	142,3	5,2	0,03	66,1	587,1	45,2	34,7
P 6h	0,08	142,6	7,8	0,02	65,8	523,9	46,8	33,1
P 24h	0,09	235,2	35,2	0,02	77,5	475,1	169,9	12,3
P 48h	0,06	235,7	28,0	0,02	79,5	471,8	171,2	10,7

Table 5.5 Concentration (C) of cations and anions in then liquid phase of Pineda sludge at different times after the extraction of sludge in the WWTP (from P0 to P 48h)

SAMPLE NAME	C CATIONS (mg/L)					C ANIONS (mg/L)			
	Na ⁺	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	K ⁺	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
P0	876,2	188,7	23,4	81,6	-	32,7	151,5	1274,6	2,1
P 1h	1078,9	323,5	44,1	127,0	-	120,1	176,4	1597,1	1,9
P 2h	729,6	262,7	31,6	90,2	-	131,2	111,6	1041,3	2,5
P 3h	661,4	251,4	120,0	83,1	-	120,1	96,5	1140,0	2,2
P 4h	660,4	236,3	37,1	81,1	-	132,2	91,5	951,1	2,6
P 5h	663,3	212,4	67,8	79,2	-	119,9	97,1	1023,7	2,6
P 6h	599,6	216,8	25,5	78,0	-	112,1	83,5	846,8	4,1
P 24h	532,4	236,4	23,9	87,0	2,0	385,3	13,0	704,7	2,1
P 48h	541,8	238,7	23,4	89,4	2,7	364,7	9,9	725,5	4,6

Table 5.6 Total Concentration (Ct) of Aluminum, Calcium, Iron, Lithium, Magnesium, Sodium, Phosphorus and Sulphur in the liquid phase of Teià sludge at different times after the extraction of sludge in the WWTP (from T 1h to T 48h)

SAMPLE NAME	Ct (mg/L)							
	Al	Ca	Fe	Li	Mg	Na	P	S
T 1h	4,54	242,7	5,3	0,0	110,0	887,8	304,5	1167,3
T 2h	0,79	190,0	5,5	0,0	102,0	642,4	272,3	297,2
T 3h	0,37	169,0	3,2	0,0	94,1	563,7	242,7	115,9
T 5h	1,54	272,8	8,8	0,0	114,6	625,9	339,3	1841,4
T 6h	1,35	231,3	8,2	0,0	106,8	612,1	359,5	2162,8
T 24h	0,13	217,9	34,9	0,0	117,3	394,4	443,8	40,1
T 48h	0,22	218,6	41,2	0,0	114,4	368,1	448,2	21,8

Table 5.7 Concentration (C) of cations and anions in the liquid phase of Teià sludge at different times after the extraction of sludge in the WWTP (from T 1h to T 48h)

SAMPLE NAME	C CATIONS (mg/L)					C ANIONS (mg/L)			
	Na ⁺	NH ₄ ⁺	Mg ²⁺	Ca ²⁺	K ⁺	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻
T 1h	1015,4	689,5	139,5	126	2,6	831,3	1327,9	1211,8	18,8
T 2h	690,2	497,5	117,2	111,3	2	650,7	196	1022,7	-
T 3h	652,8	424,5	80,8	103,7	1,9	567,8	199,4	947,8	4,8
T 4h	691,5	423,3	67,4	108,8	1,6	534,8	266,6	964,4	3,4
T 5h	671,2	635,9	87,9	124,4	-	798,8	1399,5	871,5	51,6
T 6h	690	734,5	89,7	123,8	-	901,9	1977,2	852,3	31,5
T 24h	435,2	863,1	81,4	131,2	-	1298	85,4	567,1	1,1
T 48h	417	611,3	74	124,6	-	1055,7	20,6	551,6	2,7

The variation of the total concentration of P by ICP, including both organic and inorganic forms, and the total concentration of P as phosphate (PO₄³⁻) determined by IC as a function of the contact time, as well as the other ions involved in the struvite formation are shown in Figures 5.3-5.5.

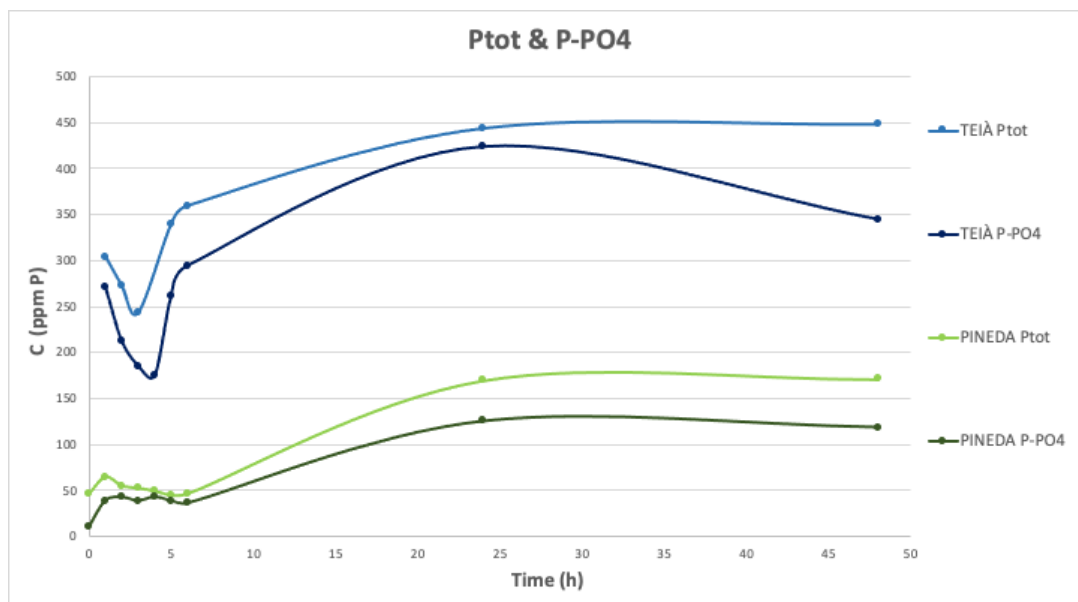


Figure 5.3 Evolution of P total (Ptot) and P as PO₄ (P-PO₄) with time in the liquid phase of Pineda (green) and Teià (blue) sludges

After 1 day, samples from Teià reached values up to 450 mg P/L, with around 95% as phosphate, while in Pineda samples, values around 170 mgP/L were measured and around 75% present in phosphate form.

A part from phosphate, the concentration of other ions are relevant to understand the uncontrolled precipitation of struvite. Magnesium and ammonium are the two other components present in struvite precipitation. In Figure 5.4 and 5.5, the concentration for the three main species involved in the precipitation of struvite are presented.

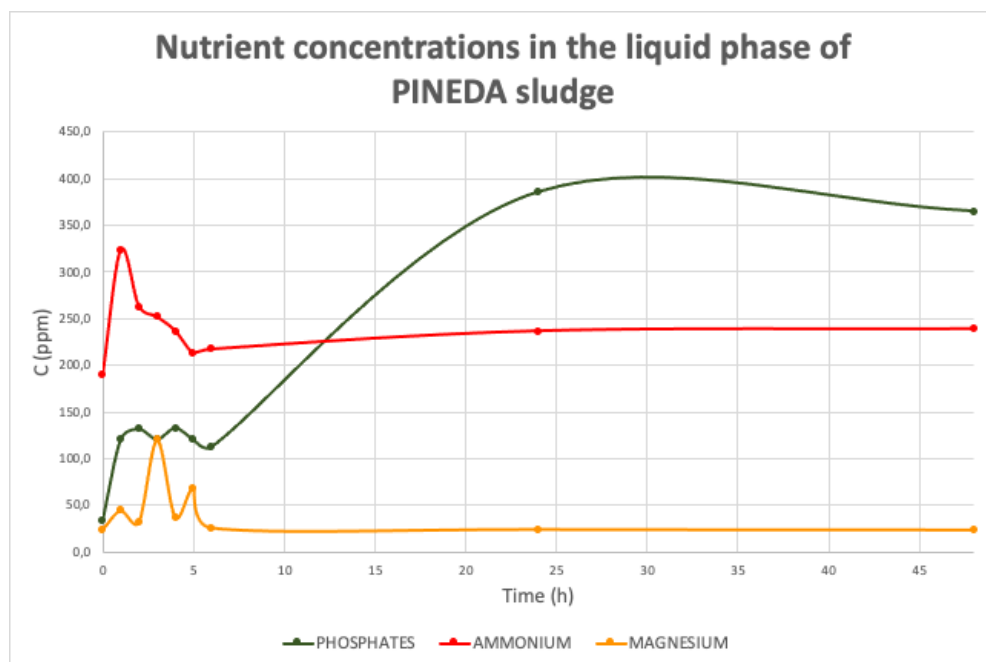


Figure 5.4 Evolution of Phosphate (green), Ammonium (red) and Magnesium (orange) with time in the liquid phase of Pineda sludge

While the release of phosphate into the liquid phase of the sludge from Pineda increases with time, stabilizing after 1 day, magnesium and ammonium show a more uniform concentration values, with oscillation in the first hours but without a specific pattern. After six hours the concentration seems to stabilize to a 25 mg/L for magnesium and 230 mg/L for ammonium.

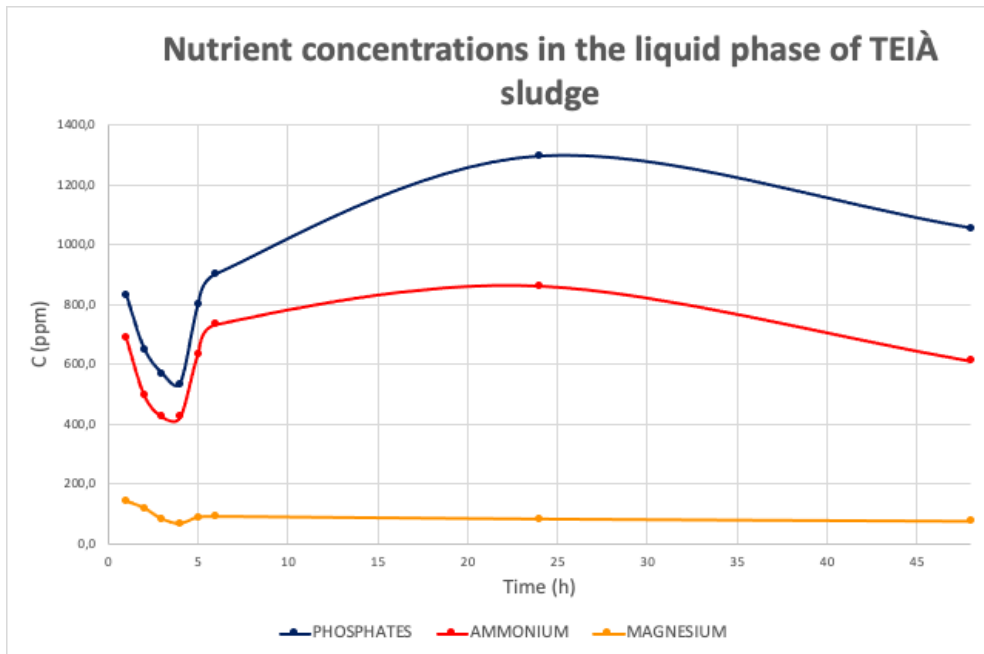


Figure 5.5 Evolution of Phosphate (green), Ammonium (red) and Magnesium (orange) with time in the liquid phase of Teià sludge

The time pattern behavior of the nutrient concentrations in the aqueous phase of Teià sludge is similar to the Pineda one. While phosphate amount increase with time, magnesium and ammonium show significant changes at the beginning (decreasing significantly the first hours) to later stabilize achieving around 85 mg/L of Magnesium and 860 mg/L in ammonium after 24 hours from the sludge collection in the Alt Maresme Nord WWTP.

Teià sludge is richer in nutrients than Pineda sludge. Concentrations of the three ions involved in the struvite precipitation are higher in all the samples of Teià sludge. However, the pattern evolution of them with time is the same for both sludges. After 24 hours, the concentrations achieved their stationary point and no significant changes were observed in the samples of 48 hours of experimentation time. This result is in agreement with published results in the Life Enrich project developed at the Murcia Este WWTP.

5.4. Definition of recommendation actions for the external sludge management at AMN WWTP

Once the analysis of the current situation in the Alt Maresme Nord WWTP have been carried out and tests to characterize the sludges with which the WWTP deal have also been done, some conclusions can be reported from the tests performed.

1. The uncontrolled precipitation in the WWTP was demonstrated to be struvite

2. When leaving the sludges of Pineda and Teià in anaerobic conditions, the release of P into the liquid phase increases with time. 24 hours is time enough to release all the phosphorous.
3. In the sludge arriving from Teià, high concentrations of phosphate and nutrients have been detected (e.g. 450 mg/L of P as PO₄).
4. The ammonium and magnesium concentration in the liquid phase remain constant.

With the results given of the high concentrations of Phosphate (Figure 5.3) and other nutrients release into the liquid phase from both samples of sludge (Figure 5.4, 5.5) a preliminary solution to minimize the uncontrolled precipitation of phosphorus compounds along the sludge line of AMN WWTP is to avoid this sludge stream rich in phosphorus get into the digestion step by enhancing the P release before the digesters and recirculating the liquid phase to a P recovery unit. Teià sludge has been confirmed to be the one having the highest content of P. However, the rest of sludges arriving in the AMN sludge treatment line from external WWTPs in the region, according to recent studies, present high concentrations of phosphorus and so are of big interest as a potential source of phosphate recovery and probably part of the problem of uncontrolled struvite precipitation in the Alt Maresme Nord sludge management line. In order to prevent this stream rich in phosphate arriving to the digester, an *Additional treatment* will be carried out with the sludges arriving from the other WWTPs in the region to obtain a P-enriched stream, separate the clarified stream and use it as the influent of a phosphorous recovery unit while no changes in the sludge management of the main treatment line will be applied. This additional treatment will be focused in the phosphate recovery as struvite. The reconfiguration proposed for the external sludge management is illustrated in Figure 5.6.

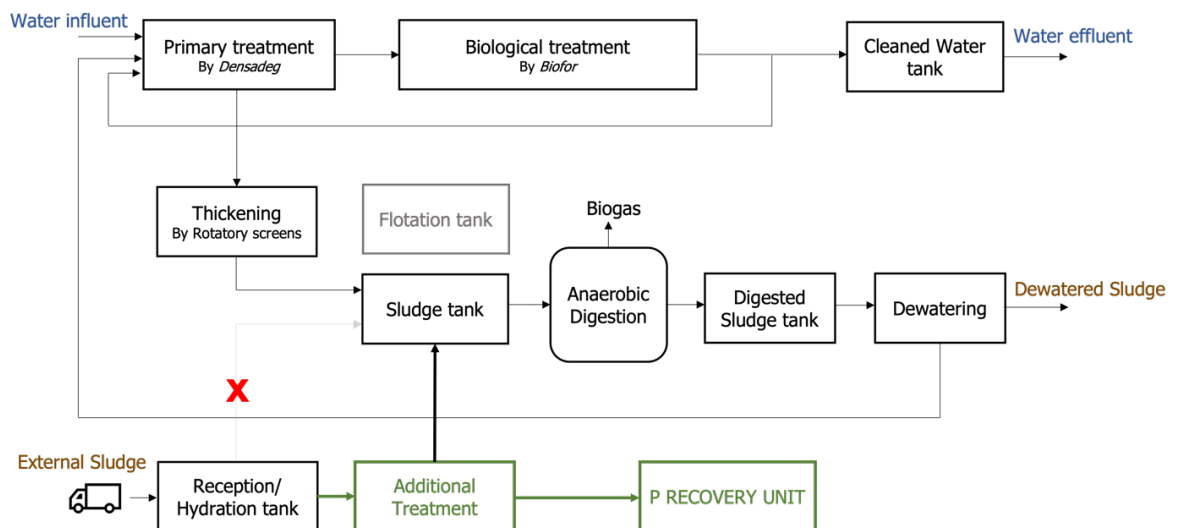


Figure 5.6 Reconfiguration proposal in the treatment of external sludges arriving in AMN WWTP

5.4.1. Struvite Recovery route

Since the laboratory analysis verified that the deposit formation found in Alt Maresme Nord WWTP was in fact struvite, the proposal of the recovery unit is a crystallizer to recover phosphate as struvite. In addition, struvite is taking importance as a potential product to be used in the fertilizing industry. An accurate design of the alternative recovery route to be implemented in Alt Maresme Nord WWTP to obtain struvite from external sludges will be crucial to obtain the maximum performance of the process.

To perform an efficient design and propose and accurate implementation of the alternative recovery route in AMN WWTP there are some parameters to keep in mind which will constrain the final layout. According to the data provided from the AMN WWTP and the previous studies carried out in the implementation of the elutriation prototype in ME WWTP, some limitations and assumptions are listed in the following lines which will be considered in the calculations and the final decision of the alternative route design.

Limitations (L):

- L1.** A hydration stage is required to enhance the separation of the P-enriched stream from the sludge and obtain a higher amount of clarified, and therefore, a higher amount of phosphorous removed from the process.
- L2.** At least 18 hours of residence time is required in the tanks to allow the sludge, release the phosphorus and nutrient into the liquid phase.
- L3.** The phosphorus concentration in the influent of the crystallizer must be at least of 70 mg/L of P as Phosphate (P-PO₄)
- L4.** The Total Solids (TS) concentration in the influent of the crystallizer cannot exceed 1 g/L (~0,1%)
- L5.** Mg/P molar ratio must be maintained at 1 in the crystallizer. N/P ratio must be at least 1 and ideally up to 4. Ca/Mg should not surpass 1. Ca/P should not surpass 0,5.
- L6.** Ions like sulphate and calcium can influence in the struvite crystallization yield by precipitating other species

Assumptions and data provided by the Alt Maresme Nord WWTP (A):

- A1.** Alt Maresme Nord WWTP receives 40 tonnes/day of external sludge.

A2. 50% of the external sludge received corresponds to Teià Sludge (TeS) and 50% to the rest of plants (ReS) (Llavaneres, Arenys de Mar, Sant Pol and Tordera).

A3. Properties and behaviour of ReS are the same as Pineda sludge.

A4. External sludges arriving in Pineda are hydrated in the reception tank from 25% of TS to a 5%. This 5% of TS sludge will be the one routed to the “additional treatment stage”.

According to these limitations, assumptions and data provided by the Alt Maresme Nord WWTP, the additional treatment proposed on the external sludges arriving in the plant will consist of a hydration stage to enhance the settling of phases and increase the amount of phosphate transported to the phosphate recovery unit. As the moisture in the sludges increase, much easier it will be to separate a liquid phase rich in nutrients from the sludge. In addition, a thickening stage will be needed in order to obtain the P-enriched stream, and the solid phase of sludges which will be thickened to its initial value of TS (5%) before being sent to the mixing chamber ready to be sent to the digestion stage. The overflow of the thickening unit will be sent to a struvite crystallizer. In Figure 5.7 the preliminary layout of the additional treatment and the crystallization unit proposed is displayed; a hydration step followed by a thickening stage and the crystallization unit.

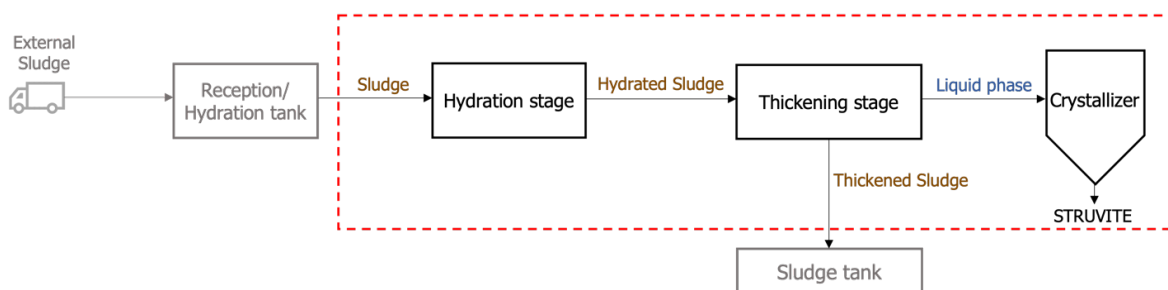


Figure 5.7 Preliminary layout of the additional treatment to be implemented in the external sludges management

With the results obtained in the laboratory and the stages of the additional treatment determined, an exhaustive analysis of each stage is performed in order to decide the more efficient way to develop the P recovery solution.

5.4.1.1. Hydration stage

The amount of total solids in external sludges once hydrated in Alt Maresme Nord WWTP is around 50% (50 g/l) according to the data provided by the Alt Maresme Nord WWTP (data of May 2021). Applying the molecular weight of the elements and the different ions, and the data from table 5.5 and 5.7, the concentration of Magnesium, Phosphorus in phosphate form (P-PO₄) and nitrogen in ammonium form (N-NH₄) in the liquid phase after 24h is estimated and displayed in table 5.8.

Table 5.8 Concentration of ions of Teià and Rest of Sludge 24 hours after the collection of the sludge

	Mg (mg/L)	P-PO4 (mg/L)	N-NH4 (mg/L)
Teià Sludge (TeS)	81,4	423,6	671,3
Rest of Sludge (ReS)	23,9	125,7	183,9

When increasing the moisture amount, the phosphorous release is spread through all the liquid phase. If the decantation takes place, more phosphorous can be removed from the sludge which will be thickened until the initial TS concentration with less presence of phosphorous and nutrients. However, underlined in L3, the concentration of phosphorus in phosphate form in the influent of the crystallizer must be at least 70 mg/L, therefore the hydration step will be limited by this constrain. On the other hand, hydrating the sludge will cause a decrease in the concentration of ions present. 3 different hydration scenarios have been studied in the design of the hydration stage, diluting by a factor of 2, 3 and 4. (Scenarios A, B and C respectively).

The concentration of phosphate, ammonium and magnesium at different hydration quantities, calculated as dilutions of the mixture of TeS and ReS 24h after its sampling is displayed in table 5.9. TS concentration in the mixture at different dilutions is also displayed in the second column.

Following A1, The concentration of phosphate and the rest of ions in the liquid stream after dilution (subindex d) can be computed by using eq 5.5:

$$[X]_D = \frac{([X]_{TeS} + [X]_{ReS}) \cdot 0,5}{D} \quad \text{eq 5.5}$$

Where $[X]$ is the concentration of the ion in mg/L, subindex i , the concentrations of TeS and ReS (Table 5.7) and D , the dilution factor applied (2, 3, or 4).

The total sludge generated once hydrated for each one of the scenarios can be computed by using eq 5.6:

$$\text{Sludge Generated (m}^3\text{/d)} = Q_{ext} * D \quad \text{eq 5.6}$$

Where Q_{ext} is the sludge flow leaving the reception tank, knowing the plant receives 40 tonnes each day and in the hydration tank a dilution factor of 5 is performed (From 25% of TS to 5%), The sludge flow (Q_{ext}) directed to the additional treatment is 200 m³/day. It is assumed that all the sludge generated in the additional hydration step will be transported to the thickening stage.

Table 5.9 Concentrations of the ions involved in struvite precipitation and sludge generated in the 3 different hydration scenarios studied

Scenario	DILUTION	TS (%)	Sludge Generated (m ³ /d)		C (mg/L)	C (mM)
initial	No	5	-	P-PO4	274,6	8,9
				N-NH4	427,6	30,5
				Mg	52,7	2,2
A	1:2	2,5	400	P-PO4	137,3	4,4
				N-NH4	213,8	15,3
				Mg	26,3	1,1
B	1:3	1,67	600	P-PO4	91,5	3
				N-NH4	142,5	10,2
				Mg	17,6	0,7
C	1:4	1,25	800	P-PO4	68,7	2,2
				N-NH4	106,9	7,6
				Mg	13,2	0,5

The maximum acceptable hydration rate would be diluting the external sludges by a factor of 3 (scenario B), obtaining a P concentration of 91,5 mg/L in the liquid phase. When diluting by a factor of 4 (Scenario C), the final concentration of P as Phosphate do not achieve the minimum required (70 mgP/L).

5.4.2. Thickening stage

Sludge thickening is important because it is the process used in wastewater treatment plants to increase the solids concentration and decrease the free water. A thickening stage in the additional process proposed will be required, not only to concentrate the external sludges before they are sent to the mixing chamber with sludges coming from AMN main line, but also to obtain and separate the clarified liquid phase rich in nutrients after the hydration step and once the time to release the phosphate and the rest of ions is achieved (at least 18h). Once this stream is separated from the concentrated sludge it will be ready to be led to the crystallization unit. In order to obtain a sludge with the usual conditions before going to the anaerobic digestion step, the process conditions of the thickening unit are the following:

1. The sludge will be thickened until its typical value of 5%
2. The thickening unit will have a yield of 97% of solid removal.

Following conditions 1 and 2 in the thickening stage, the TS content in the outlet of the thickened sludge (TS_{thick}) treated each day can be calculated by multiplying the TS amount in the influent (TS_{in}) of

the thickening unit by a factor of 0,97. TS_{in} is the total solids amount received in the plant each day computed with $A1$ and $A4$ as the product of multiplying the external sludge flow received (40 tn/day) by the total concentration of TS (25%). The TS_{clar} (total solids flow in the clarified stream) of the thickening unit can be computed by a mass balance, subtracting the TS_{thick} to the TS_{in} . The thickened sludge flow is calculated as the total volume to be extracted per day in order to obtain a stream of with a flow of TS_{thick} and a concentration of 5% (% TS_{thick}). The TS concentrations and flows of the streams involved in the thickening stage are summarized in Table 5.10. Since the sludge is assumed to be thickened up to 5% of TS working with a 97% of solid removal equipment, this operational values will be the same for the three scenarios A, B and C regardless of the hydration rate applied.

Table 5.10 Total solids (TS) flow and concentrations in the influent and effluent of the thickening stage. The last row corresponds to the thickened sludge flow.

TS_{in}	10.000 kg/d
TS_{thick}	9.700 kg/d
TS_{clar}	400 kg/d
% TS_{thick}	5%
Thickened sludge flow	194 m ³ /d

According to $L4$, $A1$, and the hydration step calculations, the flow of the clarified stream that could be redirected to the crystallizer after thickening stage (CR_{in}), The TS concentration in the clarified stream ($TS_{CR_{in}}$) and the total phosphate removed can be calculated in order to decide the best conditions in the thickening stage of this alternative struvite recovery route prototype.

CR_{in} is calculated by subtracting the thickened sludge flow (194 m³/d) to the Thickening influent which is in fact the sludge generated in the hydration step (Table 5.9). $TS_{CR_{in}}$ is computed by dividing the TS_{clar} and the CR_{in} in liters. The higher the hydration dose applied, the higher the amount of liquid that can be lead to the crystallization unit. Finally the phosphate removed in scenarios A, B and C can be obtained as a ratio of the total phosphate going to the crystallization reactor and the total phosphate released into the liquid phase could be calculated by eq 5.7.

$$\%PO_{4_{removed}} = \frac{[PO_4]_D \cdot CR_{in}}{[PO_4]_i \cdot Q_{ext}} \cdot 100 \quad \text{eq 5.7}$$

Where $[PO_4]_D$ is the phosphate concentration on each scenario and $[PO_4]_i$ is the concentration of P- PO_4 at initial conditions without dilution (Table 5.9).

The feed flow of the thickener, TH_{in} , is in fact the sludge generated in the hydration stage (Table 5.9).

Table 5.11 Design conditions of the three scenarios in the thickening stage

SCENARIO	TH _{in} (m ³ /d)	TS _{in} (%)	CR _{in} (m ³ /d)	TS CR _{in} (g/L)	PO4 removed (%)
A	400	2,5	206	1,51	52
B	600	1,67	406	0,74	68
C	800	1,25	606	0,51	76

Scenario A do not fulfill A1 since the TS content is higher than 1 g/l.

5.4.3. Crystallization process

In order to propose the most efficient recovery route, the amount of struvite (MAP) that could be recovered from sludge is estimated.

To study the precipitation process of struvite, *Visual Minteq* software has been used to predict the amount of struvite or other possible precipitations in an hypothetical phosphate recovery step. *Visual Minteq* is a chemical equilibrium program with a huge database which allow the calculation of the solubility and the equilibrium between solid and dissolved phases of minerals in aqueous solution. To do so, some designing conditions (Table 5.12) have been set to simulate the crystallization operation according to the preferred conditions to precipitate struvite (Doyle and Parsons, 2002).

Table 5.12 Operational conditions for the simulation with *Visual Minnteq*

VARIABLE	VALUE
pH	8,8
Temperature	25 °C
Mg/P molar ratio	1

Concentrations in mM of phosphate, ammonium and magnesium for the different dilutions applied, have been introduced in the *Visual Minteq* (input) as soluble (s) species in the liquid (PO₄s, NH₄s, Mgs) to study the precipitation of struvite in the P recovery unit.

The total amount of Mgs introduced in the simulation has been set as the same concentration of PO₄s to achieve the Mg/P molar ratio of 1 (L5) since the initial Mg concentration (Table 5.9) do not satisfy the constraint. The difference between the molar flow of PO₄ and Mg in the influent solution will be the required amount of magnesium to be added in the precipitation unit. The dose of magnesium to be added can be computed with equation 5.8:

$$d_{Mg} \left(\frac{kg \text{ Mg}}{d} \right) = \frac{([PO_4]_{in} - [Mg]_{in}) \cdot CR_{in} \cdot MW_{Mg}}{1000} \quad \text{eq 5.8}$$

Where $[PO_4]_{in}$ and $[Mg]_{in}$ are the concentration in mM of phosphate and magnesium coming from the clarified stream after the thickening stage (Table 5.9) and MW_{Mg} is the molar weight of magnesium, 24,3 g/mol.

The d_{Mg} for the three different scenarios of dilution studied is displayed in Table 5.13.

Table 5.13 Additional Magnesium dose in the crystallizer

SCENARIO	d_{Mg} (kg Mg/d)
A	16,7
B	22,0
C	24,6

Once Mg:P molar ratio have been studied, and the required dose to achieve the stoichiometric conditions obtained, molar ratios of N:P, Mg:P and Ca:Mg, must be also analyzed to ensure constrain L5 is satisfied. From Table 5.9 and 5.16 molar ratios can be calculated and are summarized in Table 5.14 in comparison to the required values for an efficient operation.

Table 5.14 Required molar ratios for a high-performance struvite crystallization (first column). Molar ratios in the sludges obtained with laboratory analysis (second column)

	Required values (L5)	Real values
Mg/P	>1	1
N/P	>1	3,4
Ca/P	<0,5	0,3
Ca/Mg	<1	0,3

If magnesium dose is applied in the influent of the crystallizer, molar ratios satisfy the constrains stated for an efficient struvite precipitation. However, additional strategies can be employed to increase the ammonium concentration and thus the struvite precipitation yield. Later on this section, these alternatives out of the initial scope are discussed as well as the specie to be used as magnesium source.

Visual Minteq will give a value of the dissolved and precipitated species. Since Struvite is included in the program, when running *Visual Minteq* with the input concentrations (C_{in}), it will directly give the output of struvite precipitated. In addition, the program will also return the values of soluble and particulate (p) (C_{out}) species.

Another parameter to study the performance of the crystallization process is the percentage of Phosphate that can be recovered in the process (therefore removed from the overall water treatment process) and it can be calculated by using eq 5.9:

$$\%P_{REC} = \frac{[PO_4]_p}{[PO_4]_s} * 100 \quad \text{eq 5.9}$$

Where p index is the particulate phosphate and s subindex corresponds to the soluble phosphate entering into the precipitation unit, which is assumed to be all the phosphate found after the release stage in the clarified stream (Table 5.9)

In order to know the efficiency of struvite crystallization in the precipitation process, the percentage of P recovered as struvite can also be computed by using eq 5.10:

$$\%P_{REC_STR} = \frac{[MAP]}{[PO_4]_s} * 100 \quad \text{eq 5.10}$$

Where $[MAP]$ is the concentration of struvite (*Visual Minteq* output in mM)

Two different scenarios have been considered. In the first one, only those ions involved in the struvite formation have been considered, assuming the influent of the crystallizer is only composed by PO_4 , NH_4 and Mg. In the second scenario, calcium and sulphate ions have also been considered and so their concentrations introduced in the program to allow *Visual Minteq* consider the equilibrium relations of these ions, and therefore, all the possible precipitation options involving sulphate and calcium in addition to the already introduced species that lead to Struvite precipitation (L6).

5.4.4. Simulation 1: struvite formation ions in the influent

Table 5.15 shows the input, output and results obtained for each scenario when considering only PO_4 , NH_4 and Mg. The input parameters correspond the results obtained in the laboratory tests.

Table 5.15 green: input parameters Visual Minteq, yellow: Output parameters Visual Minteq, Blue: calculated variables

			A	B	C
C_IN	PO4s	mM	4,43	2,95	2,21
	NH4s	mM	15,3	10,2	7,6
	Mgs	mM	4,43	2,95	2,21
C_OUT	PO4s	mM	0,24	0,29	0,33
	NH4s	mM	11,1	7,5	5,75
	Mgs	mM	0,24	0,29	0,33
	PO4p	mM	4,19	2,67	1,89
	NH4p	mM	4,19	2,67	1,89
	Mgp	mM	4,19	2,67	1,89
	MAP	mM	4,19	2,67	1,89
	P _{REC}	%	94,5	90,2	85,2
	P _{REC_STR}	%	94,5	90,2	85,2

Only Struvite has been found as precipitated compound in scenario 1. The Values between 85 and 95% of P recovered in the form of struvite would be obtained in the three different scenarios of dilution applied.

5.4.5. Simulation 2: introduction of ions that may interfere struvite precipitation

Other ions can be considered in the reactor which can lead to a lower efficiency in struvite crystallization. To have a general view of how the presence of ions as calcium and sulphate can badly influence the struvite crystallization process, sulphate and calcium have been taken into account for simulation 2. With the same concentrations of Phosphate, Ammonium and Magnesium the concentrations of calcium and sulphate have also been introduced in the program. The analysis of the sample (section 5.1) proved to be struvite but with the suspicion of possible trace amount of brushite and Gypsum although it was dismissed later on with the X-Ray Diffraction analysis, these compounds have been added in the program as possible solid formations. In addition to these deposits, Brucite ($\text{Mg}(\text{OH})_2(\text{s})$), has also been set in the program as possible solid deposition.

Following the procedure of the previous section, the input values used for the simulation and the results obtained are displayed in Table 5.16.

Table 5.16 green: input parameters Visual Minteq, yellow: Output parameters Visual Minteq, Blue: calculated variables

			A	B	C
C_IN	PO4s	mM	4,43	2,95	2,21
	NH4s	mM	15,3	10,2	7,6
	Mgs	mM	4,43	2,95	2,21
	Cas	mM	1,36	0,91	0,68
	SO4	mM	0,26	0,17	0,13
C_OUT	PO4s	mM	0,08	0,13	0,16
	NH4s	mM	11,73	7,91	6,14
	Mgs	mM	0,89	0,68	0,71
	Cas	nM	0	0	0
	SO4s	mM	0,26	0,17	0,13
	PO4p	mM	4,35	2,82	2,05
	NH4p	mM	3,54	2,27	1,5
	Mgp	mM	3,54	2,27	1,5
	Cap	mM	1,36	0,91	0,68
	SO4p	mM	0	0	0
	MAP	mM	3,54	2,28	1,51
	Other prec	mM PO4	0,81	0,55	0,54
	P _{REC}	%	98,2	95,5	92,7
	P _{REC_STR}	%	79,9	77,1	68,1

When introducing calcium and sulphate in the simulation, the yield for struvite decrease significantly around 12% in contrast to first scenario as other ions as sulphate and calcium can interfere into the struvite crystallization process. The simulation program suggests that according to the concentrations and the operational conditions introduced this additional precipitated that can appear in the crystallization process is Hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})(\text{s})$. Any trace of brushite nor gypsum are found.

5.4.6. Struvite production estimation

With the results obtained in the thickening stage of the flow of the clarified stream that would be sent to the crystallization process (Table 5.11) and the results obtained with the simulation of a precipitation reactor, the production of struvite (MAP Prod) can be obtained following equation 5.11.

$$\text{MAP Prod} \left(\frac{\text{kg}}{\text{d}} \right) = \frac{[\text{MAP}] \cdot \text{MW}_{\text{Str}} \cdot \text{CR}_{\text{in}}}{1000} \quad \text{eq 5.11}$$

Where MW_{Str} is the molecular weight of struvite (245,4 g/mol).

In Table 5.17, the results obtained for simulations 1 and 2 for scenarios A, B and C of the estimated struvite that can be produced are summarized.

Table 5.17 Struvite production for Scenarios 1 and 2 at different dilutions applied

			A	B	C
Simulation 1	CR _{in}	m ³ /d	206	406	606
	MAP	mM	4,19	2,67	1,89
	MAP Prod	kg/d	211,7	265,6	280,7
Simulation 2	CR _{in}	m ³ /d	206	406	606
	MAP	mM	3,54	2,28	1,51
	MAP Prod	kg/d	178,9	226,7	224,4

In simulation 2, the struvite production is lower than in simulation 1. However, results are more realistic as more inputs as possible interferences are considered in the simulation.

5.5. Final proposal for a sustainable sludge management treatment stage in AMN WWTP

Once the exhaustive analysis of the several stages of the additional treatment to be applied in the external sludge received in AMN has been carried out, the final decision of the most efficient operation conditions to implement the MAP recovery route can be taken. In this section the final proposal is explained and discuss as well as the main tips to implement the prototype in AMN WWTP in the most high-performing way. In Table 5.18 the main results in scenarios A, B and C with the limitations for an efficient operation are summarized.

Table 5.18 Comparison of the results obtained and their limitations for an efficient operation (2 first rows). Struvite production (Last row)

	A	B	C
L3. The phosphorus concentration in the influent of the crystallizer must be at least of 70 mg/L of P as Phosphate	137,3 mg/L ✓	91,5 mg/L ✓	68,7 mg/L ✗
L4. The TS concentration in the influent of the crystallizer cannot exceed 1 g/L (~0,1% of TS)	1,51 ✗	0,74 ✓	0,51 ✓
Struvite production in Simulation 2 (kg/d)	178,9	226,7	224,4

Scenario 3 is the only one meeting the requirements established so far for an efficient performance of struvite production in a crystallization reactors according to the standards, recent studies and pilot plants implemented in previous studies worldwide. The overall additional process applied into the externals sludges arriving in AMN would be the following:

1. **HYDRATION STAGE:** A 3 dilution factor will be applied in an elutriation tank where sludges will be kept during the required time to allow the total release of phosphates and nutrients into the liquid phase. 400 m³ of water will be required each day to reduce the TS from 5% to 1,67%.
2. **THICKENIG STAGE:** a thickening tank of 97% yield in solids removal will be required to treat the 600 m³ of hydrated sludge generated. Thickened Sludge at 5% of TS will be sent to the mixing chamber with the sludge generated in AMN. The liquid effluent will be sent to the crystallization unit with its adequate TS concentration of less than 1 g/L (0,74 g/L) and phosphate concentration of 91,5 mgP/L (more than the 80 required).
3. **CRYSTALLIZATION REACTOR:** A struvite crystallization reactor will be installed with the appropriate magnesium dose (22 kg/d) to achieve the preferred P/Mg ratio of 1. The simulations performed stated that more than 225 kg of struvite could be produced each day. Effluent of the crystallizer is assumed

to be the same flow as the influent and sent to the head of the plant or used as hydration source in the elutriation tank.

In figure 5.8 the flow diagram for the final proposal is displayed with the main characteristics and flow rates of the different streams and equipment performance.

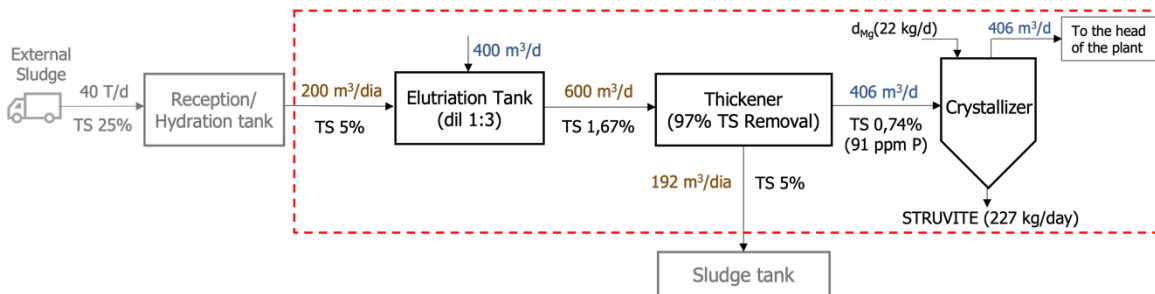


Figure 5.8 Operation conditions and streams specifications of the final proposal

The process treatment proposed is taking into account the fact that recovery of P as struvite from side streams generated in the anaerobic digestions is protected by different technology providers and the proposal developed here includes the treatment stage protected by Suez as *Phosphogreen* Technology.

5.5.1. Implementation of the struvite recovery route

To adjust the equipment to be used and its size in the struvite recovery route to be implemented in Alt Maresme Nord WWTP, the implementation of the sludge elutriation prototype in Murcia Este (ME) WWTP managed by *Emuasa* within the LIFE ENRICH project has been taken as a reference. The actions necessary to integrate the elutriation prototype to remove phosphate from the external sludges arriving in Alt Maresme Nord WWTP and recover it as struvite mineral, are summarized below:

A. Elutriation tank

It is necessary to install an additional tank to mix primary and secondary thickened sludge, respecting the hydraulic retention time. Between 18,6 and 24 hours is recommended and the results of phosphorus release test in the laboratory are consistent with it. Since a volume of 600 m³ of sludge and water will feed the elutriation tank each day (HRT around 1 day), the best option consists on installing a deposit of prefabricated plates of 700 m³ of useful volume (15% of excess volume), with a concrete base, equipped with two stirrers.

It should be mentioned that the retention time can be decreased in the elutriation tank and achieve the required time for sludges to release the nutrients later in the thickening stage.

B. Thickener

The concentration of total solids in the sludges of the current design (Table 5.10 and 5.11) of the thickening stage fit with the typical values of primary and activated sludge and thickened sludge provided in Table 5.19.

Table 5.19 Gravity thickening solids loading rates for different sludge sources (Adaptation of Droste, 1997; Corbitt, 2003; Metcalf & Eddy 2003; Andreoli et al, 2007)

	Gravity Thickener (Up to 90%)		Flotation Thickener (Up to 99%)	
	TS% Feed	TS% thickened	TS% Feed	TS% thickened
Primary sludge	2-7	5-10	5-8	
Waste Activated Sludge	1-3,5	2-5	0,5-2	3-5

Gravity thickener would be appropriate to deal with these concentrations of solids, however, it is difficult to find a gravity thickener with a solid removal efficiency of 97%. Solids removal efficiency can achieve values up to 90%. Flotation thickeners and centrifuges, can achieve a solids retention up to 99%. As described in constrain L4, The Total Solids (TS) concentration in the influent of the crystallizer cannot exceed 1 g/L (~0,1%). This parameter will be crucial in the selection of the thickening unit. With the estimations performed and the data we dispose of, only a flotation thickener or a centrifuge unit would fit to remove 97% of the TS in the thickening stage. However, a detailed study of all the sludge collected in AMN and its possible mixtures should be performed in order to determine the preferred equipment to be used in the thickening stage. At this point, an accurate selection of the thickening equipment cannot be made, however, it can be concluded that both thickening units a gravity thickener and air dissolved flotations tank show a potential to fit in the proposed route to recover struvite from external sludges arriving in AMN WWTP.

C. Phosphate recovery unit: struvite crystallizer

The estimation of the crystallization reactor scale-up has been done with data from the operating tests and implementation in ME WWTP with *Phosphogreen* technology. In ME WWTP, the full-scale design states that 5 crystallization reactors with a 2,4 m diameter and 25 m³ of volume are required to treat a flow of around 2.000-4.000 m³/day. In Alt Maresme Nord WWTP, around 400 m³ of supernatant from the thickener will feed the crystallization reactor, therefore 1 reactor of a standard size of 25 m³ would be installed.

There are several options to supply the crystallizer reactor with magnesium and control the crystallizer pH. Pure reagents such as MgSO_4 , MgCl_2 , $\text{Mg}(\text{OH})_2$, and MgO are usually used to adjust the Mg/P. They are also exploited in full-scale applications. Sodium hydroxide can be added to control the pH inside the reactor to promote struvite precipitation.

Other considerations for the final design

Several alternatives can be considered in the implementation of the elutriation prototype in AMN WWTP in order to obtain an efficient process while deploying the minimum external sources. Another interesting issue is to increase the circularity of the process by taking advantage of all the available sources in AMN WWTP. In this context, 3 different alternative are contemplated in the water supply of the hydration stage (Figure 5.9):

1. Use the centrates from the dewatering stage as the water source in the hydration stage: centrates are the streams generated after the centrifugation of the digested sludge. It is rich in nutrients like ammonium, and so it would increase the ammonium concentration in the sludge. This solution is interesting since, although ammonium concentration in the clarified stream surpasses the 1:1 standard molar ratio of N:P, an increase of the N/P molar ratio, being around 3,5, would increase the struvite precipitation process performance.
2. Use the crystallizer effluent as the water source in the hydration stage: The effluent of the crystallizer, could easily satisfy the water requirements since the flow is higher than the water required in the hydration stage. This would suppose a decrease in the total water sent to the head of the plant and so a decrease of the interference of the elutriation prototype proposed to the overall water treatment of AMN.
3. Use the effluent of AMN WWTP as the water source in the hydration stage: effluent of the AMN WWTP could also be used as water source and thus reduce the external water consumption for this additional treatment to be carried out in parallel to the water and sludge treatment already existing in AMN WWTP.

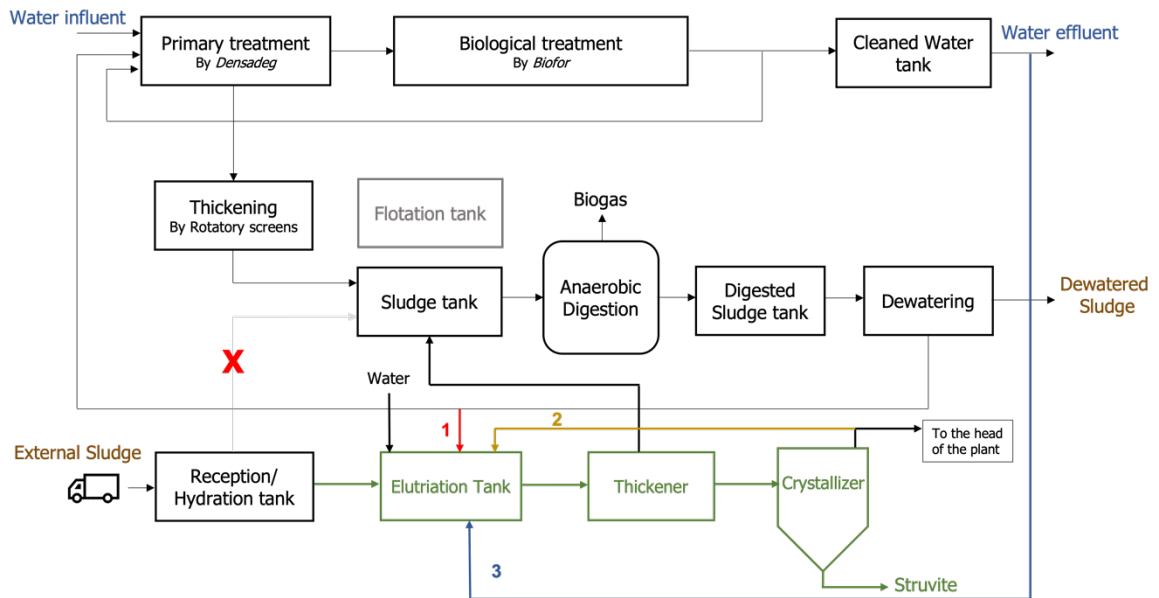


Figure 5.9 Diagram of the Alt Maresme Nord WWTP with the elutriation prototype implementation and option 1 (red), 2 (yellow), 3 (blue) of the water source supply for the hydration of sludges in the elutriation tank

5.5.2. Implementation of the struvite recovery route under CETAQUA research program on P recovery

Several considerations must be addressed in order to fit the alternative proposed for the elutriation prototype including the struvite production plant under the scope of the LIFE ENRICH project by means of CETAQUA. Some recommendations should be integrated in the process to ensure that any patent is infringed. However, a detailed study with experts in IP and patentability at the moment in which the real implementation of the process is considered, would be required.

An extra crystallization reactor (CR2 in Figure 5.10) must be installed in order to collect the centrates stream, the liquid fraction produced from dewatering of anaerobic digester. In this stage, the crystallization of inorganic phosphorus in the form of phosphorous salts is promoted in the form of Brushite to precipitate calcium contained in the centrates. Under the LIFE ENRICH program, the *Phosphogreen* reactor from SUEZ works with a N/P ratio of around 4, CR2 will not only be useful in the removal of Ca^{2+} but also in the ammonium supply. As explained so far, the centrates stream is rich in nutrients, especially in nitrogen in the form of ammonium and therefore the centrates flow will be the required to achieve the N/P ratio of 4.

The output stream resulting from the first precipitation stage (CR1) and the liquid stream coming from the thickener will be mixed in a second stage of phosphorus precipitation by crystallization of inorganic

phosphorus in the form of Struvite in the absence or lack of Ca^{2+} that competes with magnesium and ammonium for the crystallization reaction (ES 2836877 A1).

In Figure 5.10 the final process flowsheet of the final proposal for the implementation of the elutriation prototype and the struvite crystallization stage can be observed. CR2 corresponds to the crystallization reactor to collect the centrates stream and remove ion calcium and CR1 is the main crystallizer to obtain struvite with high purity. While struvite will be recovered in the bottom of the crystallization reactor, part of the other effluent will be recirculated to the thickening unit while the rest sent back to the head of the plant. This liquid stream will be used as part of the hydration agent in the thickening stage. To achieve the hydration required, external source of water will be supplied.

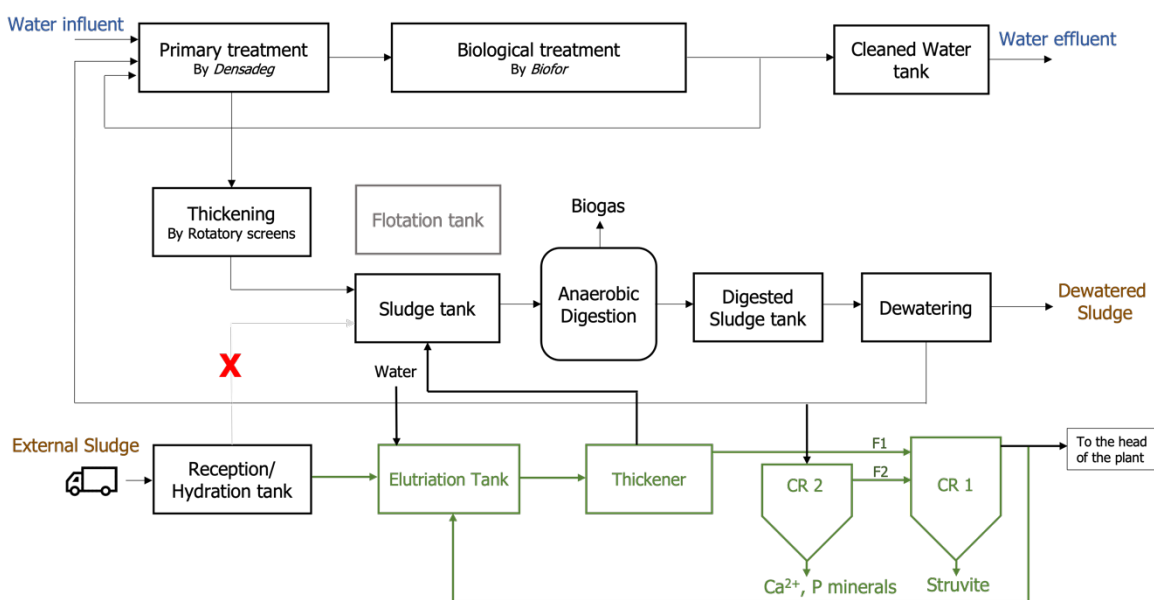


Figure 5.10 Diagram of the final proposal of the Elutriation prototype and the global recovery route of phosphorous in the form of struvite. F1 and F2 are the two streams feeding the struvite crystallizer

5.5.2.1. Sizing of crystallization reactors

In order to conclude with the design of the equipment involved in the implementation of the recovery route proposed, the size of the crystallization reactors must be addressed. The total flow supplied in CR1 will be more than the $406 \text{ m}^3/\text{d}$ detailed in Table 5.15 since an extra stream coming from CR2 will feed the struvite crystallization reactor. The flow arriving from CR2 to feed the main crystallizer (CR1) will be in fact the total amount of centrates led to CR2 from the sludge line of the main process, after the dehydration stage in AMN.

Knowing the characteristics of the liquid stream coming from the thickener unit (F1) and the centrates stream (F2), an estimation of the amount of centrates required to achieve the N/P of 4 can be

performed and so the crystallization reactor sized. By applying a mass balance of the N/P molar ratio in CR1 (Eq 5.12), the flow required from centrates can be estimated by Eq 5.13.

$$N:P_{CR1} * CR1_{inTOT} = N:P_{F1} * F1 + N:P_{F2} * F2 \left(\frac{m^3}{d} \right) \quad Eq 5.12$$

Where; $CR1_{inTOT} = F1 + F2$

$$F2 = \frac{F1 * N:P_{F1} - F1 * N:P_{F2}}{N:P_{F2} - N:P_{F1}} \left(\frac{m^3}{d} \right) \quad Eq 5.13$$

Where F1 and F2 are the flow of the two streams feeding the main crystallizer, 1 corresponding to the overflow of the thickener and 2 to the output of CR1. In table 5.20 the main characteristics of the streams involved in the design of the crystallization reactor are displayed.

Table 5.20. N:P ratios and flows (F) of the streams reaching CR1. From Table 5.15, Table 5.11 and bibliography to obtain a typical values of N/P molar ratio in centrates (LIFE ENRICH and Herrera, 2009). In blue; estimated values of flows from Eq 5.12 and 5.13.

	Stream F1	Stream F2	CR1
N/P	3.4	13	4
Flow (m3/d)	406	27	433

As described in chapter 5.5, the selection of the crystallization reactor (CR1) was set as a 25m³ reactor. Despite the addition of a crystallization reactor to collect the centrates, the difference in the feed flow of CR1 is insignificant (From 406 to 433 m³/d) and therefore the required size of it do not change. On the other hand, the sizing of the extra crystallization reactor (CR2) can be performed by scaling the already known volumes and flows of CR1 in AMN and the crystallization reactor of ME WWTP. The extra crystallization reactor (CR1) to be installed in the struvite recovery route in AMN, should be of around 1,5 m³. This little crystallization reactor can be considered affordable and not a bottleneck in the implementation of the final prototype for its little size and low design flow in comparison to the main process. In Table 5.21, crystallization reactors specifications according to the flows treated, the scaling and the main goal of its incorporation is summarized.

Table 5.21 Crystallization reactors, C1 and C2 characteristics

	Size (m³)	Main function
Crystallization reactor 1 (CR1)	25	Produce Struvite with high purity
Crystallization reactor 2 (CR2)	1,5	Remove Ca ²⁺

Data collected will be important to later perform an economic analysis of the proposed alternative.

6. Economic Assessment

An economic feasibility study of the implementation of the elutriation prototype with the struvite crystallization unit to recover phosphorus in the form of struvite while minimizing the costs of maintenance and the equipment damage due to phosphate deposits in the sludge line of AMN WWTP is performed. It is important to highlight that the values and estimations detailed in this analysis are only a first approach since they have not been obtained directly from the budget of the project.

A distinction is made between the capital costs related to the purchase of the equipment (CAPEX) and the economic costs regarding operation and maintenance of the equipment involved in the alternative line proposed to recover phosphate as struvite with external sludges of AMN WWTP (OPEX).

In addition, the generated revenue for the sale of the struvite recovered and the savings obtained due to the reduction of the maintenance costs to deal with the uncontrolled precipitation of struvite in AMN main line process are also taken into consideration ($Sales_{MAP}$ and $Savings_{SMant}$ respectively in Equations 6.1 and 6.2).

CAPEX and OPEX estimations are based in extrapolations and analysis of previous studies inside the LIFE ENRICH project, SUEZ group previous implementations, data provided by AMN WWTP and extra bibliography used to have a fair enough estimation of the price of the equipment to be purchased, the chemicals used and their operating costs. The main costs considered to obtain the OPEX are electricity costs, chemical reagents doses costs and the maintenance of the equipment involved in the struvite recovery route costs ($OPEX_{MAPrecovery}$).

The payback period of the inversion can be obtained from the annual savings in OPEX in the case of study following Equation 6.1:

$$\text{Payback period (years)} = \frac{\text{CAPEX}}{\text{Sales}_{MAP} + \text{Savings}_{mant} - \text{OPEX}_{MAPrecovery}} \quad \text{Eq 6.1}$$

Another relevant parameter to gauge the degree to which the implementation of the struvite recovery route makes money is the profit margin in year base as OPEX savings (Equation 6.2).

$$\text{Profit Margin } \left(\frac{\text{€}}{\text{year}} \right) = \text{Savings}_{mant} + \text{Sales}_{MAP} - \text{OPEX}_{MAPrecovery} \quad \text{Eq 6.2}$$

Estimation of the CAPEX

In this section the estimation of the initial investment of the equipment to be installed in AMN in the recovery route of struvite is made. In this case of study, not only the costs of the crystallizers and the struvite recovery plant are considered, but also the need of installing an elutriation tank and a thickener to enhance the phosphorous release and obtain the P-enriched stream free of suspended solids.

Struvite Crystallization plant: The price of the 2 *Phosphogreen* reactors by SUEZ can be estimated following previous analysis with same technologies where the cost of the reactor is assumed to be 354€ per m³/d of design flow. In the case study two crystallizers are needed, the main reactor (CR1) designed to produce struvite has a size of 25 m³ and flow design up to 700 m³/d. While CR2 has been design to deal with a flow of 27 m³/d of liquid stream coming from the concentrates stream.

Elutriation Tank: To have a first estimation of the cost of the elutriation tank, the Murcia Este case study where the elutriation prototype was installed under the umbrella of LIFE ENRICH project and CETAQUA, can be used as a point of reference. The size of the AMN elutriation tank has been set to 600 m³, same size as the tank installed in Murcia Este, the cost of which was 75.000€ including bombs and piping.

Thickener: An appropriate study of the sludge properties is required to size and select the preferred thickening unit. Bibliography indicates a wide range of prices, sizes and applications of gravity and dissolved air flotation thickeners depending on the characteristics of the sludge to be treated. Since it is difficult to indicate an exact price, following previous works it has been assumed an initial investment of 70.000€ for the thickening unit either if a gravity thickener is chosen or the prevailing choose is the installation of a dissolved air flotation unit.

In Table 6.1, the capitals costs of the implementation of the struvite recovery route in AMN WWTP are summarized.

Table 6.1 Summary of the initial inversion of the equipment required for the implementation of the struvite recovery route in AMN WWTP

INVERSION COSTS (€)	
Crystallization Reactor 1	244.000 €
Crystallization Reactor 2	9.558 €
Elutriation Tank	75.000 €
Thickener	70.000 €

Therefore, the sum of the capital costs is **398.558 €**.

Estimation of the OPEX

The annual costs regarding magnesium chloride, sodium hydroxide, electricity consumption and the operation and maintenance of the equipment are estimated.

Magnesium Chloride: It has been estimated a dose of 22 kg/d of magnesium to achieve the P/Mg molar ratio of 1. Magnesium chloride (both anhydrous or hydrated) is the most widely used due to its ease handling and quick dissociation, which allows shorter retention times. It is in fact, the selected magnesium source in *Phosphogreen* reactors. From the reported market prices for $MgCl_2 \cdot 6H_2O$, a price of 0,37 €/kg is estimated (Bouzas., et al. 2019).

NaOH: 50% dissolution of Sodium hydroxide is usually used at industrial scale. A flow of 0,08 kg/h is required to maintain the pH in a crystallization reactor for the production of 6 kg/d of struvite and it has been estimated the price of NaOH as 0,27 €/kg.

Electricity and O&M: Economical data available from the plant in Herning (Denmark) where the *Phosphogreen* technology has already been installed is used to estimate the costs related to the electricity consumption and the operating and maintenance costs of the plant since the crystallization reactor capacity and the struvite production rate is comparable to those in the case study of AMN WWTP.

In Table 6.2, the OPEX of the implementation of the struvite recovery route in AMN WWTP, are summarized.

Table 6.2 Summary of the operation and maintenance costs in the implementation of the struvite crystallization plant

OPEX STRUVITE CRYSTALLIZATION PLANT (€/YEAR)	
MgCl₂·6H₂O	24.820 €/year
NaOH	7.350 €/year
Electricity	6.100 €/year
O&M	12.100 €/year

The common way to have a first approach of the maintenance and operating costs of mechanic equipment is by applying a percentage of the capital costs of the equipment. It is estimated a 10% of

the equipment cost displayed in Table 6.1 as O&M costs for the elutriation tank and the thickener. Therefore, the sum of the operation and maintenance costs (total OPEX) is **64.870 €**.

Plant Income and Savings

The revenue obtained due to the implementation of this recovery route include both sales of struvite and plant economic savings due to the lack of specific maintenance for the uncontrolled precipitation of struvite in the equipment and facilities.

Struvite production: Selling price of struvite has been set at 350€/tonne. A struvite production up to 227 kg/d has been estimated when implementing this new technology in AMN WWTP. The annual income for struvite sales as fertilizer represent a value of 29.000 €.

Uncontrolled precipitates: AMN WWTP has suffered several operation damages derived from the uncontrolled precipitation of P mineral in the equipment, pipes and bombs. The costs associated to these damages have been reviewed since 2017. Not only the maintenance and cleaning costs, but also the equipment replacement forced by the damage caused. Savings related to the uncontrolled precipitation management are summarized in Table 6.3.

Table 6.3 Savings in operation and maintenance costs due to the minimization of uncontrolled precipitation in AMN facility

SAVINGS IN OPERATION AND MAINTENANCE COSTS (€/YEAR)	
Cleanups	10.025 €
Antifouling	27.336 €
O&M	34.235 €
Replacement and prevention of the equipment	4.515 €
TOTAL	76.111 €

Accordingly, and considering the sum of the previous profits, total savings represent a value of **105.111 €**.

The payback period for the implementation of the struvite recovery line can be estimated as in equation 6.1 and is **9,9 years**, while the annual savings in OPEX presented as Profit Margin in Eq 6.2 is as high as **40.240 €**.

7. Conclusions

In this project, the analysis of the precipitated compounds in the sludge line of AMN WWTP, the estimation of the potential amount of P that could be recovered in the plant and the experimentation carried out in the laboratory with the sludge generated in AMN and the external sludge received from Teià WWTP, allowed the development of the evaluation of implementing an alternative treating line with the external sludges received in the facility with the aim to obtain a P-enriched stream and produce struvite in a crystallization plant. All the results and approximations have been obtained with numerical estimations with the results of the samples analyzed in the laboratory and the knowledge of this technology in previous studies and recent implementations. The phosphate recovery route as struvite is proposed for the management of the external sludges received in AMN WWTP from Teià, Sant Andreu de Llavanes, Arenys de Mar, Sant Pol and Tordera WWTPs and the main conclusions of this preliminary assessment are:

- The selected alternative in the management of external sludges arriving in AMN to create a P-enriched liquid stream as the feed of a struvite crystallization reactor and the crystallization plant consists of:

1. An elutriation tank (700 m³) where the sludge is hydrated and P release in the liquid phase is enhanced under anaerobic conditions. When hydrating sludges by a dilution factor of 3, an average PO₄-P concentration of 91,5 mg/L is obtained in the liquid phase of sludge. A flow of water up to 400 m³/d is required in order to hydrate sludge. The effluent of the crystallization plant can be used as the water source in the elutriation tank.

2. A thickener where the overflow (around 400 m³/d) rich in P is obtained and sent to the struvite crystallization plant. The sum of retention time in the elutriation tank and the thickener must be at least 18-24h. Both options gravity and flotation thickeners are proposed as appropriate equipment.

3. A struvite crystallization plant composed by two crystallization reactors (*Phosphogreens*); 1 little reactor CR2 (1,5 m³) to remove calcium from concentrates stream and the main reactor, CR1 (25 m³) to obtain struvite from the P-enriched supernatant of the thickener and the effluent of CR2. MgCl₂·6H₂O is supplied in CR1 to achieve the required Mg/P molar ratio of 1. In addition, A NaOH solution is added as the reagent to maintain the pH in the desired value.

- The operating conditions in the crystallization plant have been defined and it has been estimated that the potential struvite production from the thickener supernatant would be around 227 kg/d, more than 80 tonnes/year, which would suppose an income for the plant up to 29.000 € in sales.

- Struvite recovery from external sludges received in AMN WWTP would be economically profitable in terms of OPEX thanks to the sales in the fertilizers industry and the economic savings regarding the uncontrolled precipitation of P minerals along the sludge treatment line. With a 40.240 € of savings in OPEX per year and a payback period of less than 10 years.

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