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# Treball Final de Grau

**Phosphorus recovery from digestates by crystallization to produce fertilizers**
**Recuperació de fòsfor de digestats mitjançant cristal·lització per produir adobs**

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*La ciència és bella i és per aquesta bellesa que hem de treballar en ella, i pot ser, qualsevol dia, un descobriment científic, com el radi, por arribar a beneficiar a tota la humanitat.*

Marie Curie

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# SUMMARY

Phosphorus is an essential and limited resource that is extracted from mining operations. It is expected that the current level of exploitation will not be maintained on a long term. Phosphorus is also found in wastewater, especially in the sludge from anaerobic digestion, and it is necessary to extract it before its disposal as it is one of the causes of eutrophication.

Hence, this project aims to study the process of phosphorus recovery from an anaerobic digestion stage followed by an osmosis stage to a crystallization stage as struvite. At the crystallization stage, the parameters Mg:P ratio, pH and presence of Ca are studied.

First, an exhaustive research of wastewater composition was performed. Once the composition of the water to be studied was chosen, in order to simulate a stage of osmosis, the concentration of the ions that made up the water is multiplied by two and four..

For these three situations (without osmosis stage, osmosis stage concentrated by 2 and osmosis stage concentrated by four), the same experiments were carried out in order to compare them.

On the one hand, the optimum value of the Mg: P ratio and the pH for the recovery of phosphorus in the form of struvite were studied by simulations with Visual Minteq and OLI software.

Then, at laboratory scale, the waters corresponding to the three situations studied were synthesized with the Optimum Ratio determined in the simulations. Different samples were prepared from each experiment and were analyzed by means of Inductively coupled plasma - Optimal emission spectrometry and X-ray diffraction.

With the results obtained it was possible to confirm that the phosphorus recovery process with the osmosis stage improves the results obtained, that an increase in the pH increases the amount of phosphorus recovered and that almost 100% of the phosphorus can be recovered as struvite.

**Keywords**: Phosphorus, struvite, crystallization.

# RESUM

El fòsfor és un recurs essencial i limitat que s'extreu de les explotacions mineres. S'espera que el nivell actual d'explotació no es pugui mantenir a llarg termini. El fòsfor també es troba a les aigües residuals, especialment als fangs procedents de la digestió anaeròbia, i es necessari extraure'l d'elles abans de que es deposite ja que es un dels causants de l'eutrofització.

Per tant, en aquest projecte es pretén estudiar el procés de recuperació de fòsfor des de la digestió anaeròbia seguida d'una etapa d'osmosi fins a la cristal·lització en forma d'estruvita. En la cristal·lització s'estudien els paràmetres ratio Mg:P, presència de Ca i pH.

En primer lloc, es va realitzar una exhaustiva investigació sobre la composició d'aigües residuals. Una vegada es va triar la composició de l'aigua a estudiar, amb l'objectiu de simular una etapa d'osmosi, es va multiplicar la concentració dels ions que formàven l'aigua per dos i per quatre.

Per a aquestes tres situacions (sense osmosi, fase d'osmosi aigua residual concentrada per 2 i fase osmosi aigua residual concentrada per quatre), es van realitzar els mateixos experiments ja que d'aquesta forma es podrien comparar els resultats.

D'una banda, es va estudiar el valor òptim del ratio Mg:P i el pH per a la recuperació del fòsfor en forma d'estruvita mitjançant simulacions amb els programes Visual Minteq i OLI.

Per altra banda, a escala de laboratori, les aigües corresponents a les tres situacions estudiades es van sintetitzar amb el ratio Mg:P òptim determinat en les simulacions i es van preparar diferents mostres de cadascuna que es van analitzar mitjançant plasma acoblat inductivament. Espectrometria òptima d'emissió i difracció els raigs X.

Amb els resultats obtinguts, es va poder confirmar que el procés de recuperació de fòsfor amb l'etapa d'osmosi millora els resultats obtinguts, que un augment del pH augmenta la quantitat de fòsfor recuperat i que quasi el 100% del fòsfor es pot recuperar com estruvita.

**Paraules clau**: Fòsfor, estruvita, cristal·lització.

# 1. INTRODUCTION

The Phosphorus (P) is an essential chemical element in the earth, fundamental for the development of living beings, important especially in agriculture field.

Phosphorus is present in wastewater (WW). The presence of P and N in WW is the cause of eutrophication problems. Therefore, the elimination of these two elements of WW is a necessary treatment in Waste Water Treatment Plants (WWTP), especially when the discharge of this water is to be carried out in areas classified as sensitive [1].

Among the most common process to carry out the elimination of P and N from the WW are the biological elimination processes. Furthermore, anaerobic digestion is the most advantageous process in WWTP of medium and large size [1].

The streams resulting from the treatment of biological elimination and anaerobic sludge digestion, have become potential sources from which nutrient P can be recovered, not only eliminated.. This is an important issue as P is a scarce and non-renewable resource. In addition, the recovery of this element from WW has great importance, not only because it is a non-renewable resource, but because of the interest that a possible sale of the product arouses [1].

The biological elimination of P together with a crystallization process as struvite ($MgNH_4PO_4 \cdot 6H_2O$) is a way to achieve these objectives: elimination and recovery [1].

Often, recovery and elimination is not profitable as a large volume of water needs to be treated to get a small amount of struvite. That is why in this project, in addition to studying the struvite crystallization parameters of the waters coming from a real WWTP, the introduction of an osmosis stage in the process would eliminate large amounts of water to be treated without reducing P content [1].

This section describes in detail what the eutrophication is and the problems it causes, as well as the current state of the natural P reserves. It also explains the process of P recovery as struvite from anaerobic digestion to the process of struvite crystallization including the osmosis stage. As well as, it was explained that is struvite, its function as fertilizer and problems that cause its unwanted precipitation in WWTP.

## 1.1. EUTROPHICATION

P and nitrogen, mainly as phosphate and nitrate respectively, are considered responsible of eutrophication degradation [2]. Eutrophication in an enrichment of water by nutrient salts that causes structural changes to the ecosystem such as: increased production of algae and aquatic plants, depletion of fish species, general deterioration of water quality and other effects that reduce and preclude use [3].

Natural eutrophication is a slow and irreversible process. By contrast, it is the anthropogenic causes that accelerate this process, although in this case it can be reversible if the contribution of nutrients is stopped [1]. The natural origin of P compounds is due by the dissolution of soils compounds, the decomposition of organic matter and the cellular decomposition of microorganism. Its anthropogenic source is related to domestic and industrial wastes, detergents, animal excrement and fertilizers [2].

## 1.2. NATURAL SOURCES OF P

The global population increase has resulted in a growing demand for food production and consequently an increasing need for P to support agricultural activity The main source of P is phosphate ($PO_4^{3-}$) rock, a nonrenewable resource rapidly being depleted as a result of increasing exploitation of $PO_4^{3-}$ and sedimentation through the natural P cycle [4]. The maximum production of reserved rock P will continue up to 2030 and then will be started to decrease, which might increases its price [5]. For all this reasons, there is an urgent need for alternative renewable sources of P [4].

## 1.3. STRUVITE

Struvite ($MgNH_4PO_4 \cdot 6\ H_2O$) is a white crystalline substance, consisting of equimolar amounts of magnesium, ammonium and phosphate, as well as six waters of hydration [6].

Figure 1. SEM microphotographs of struvite 400x

Struvite forms according to the general reaction showns below:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6 \cdot H_2O \longleftrightarrow MgNH_4PO_4 \cdot 6H_2O$$

Struvite consists of $PO_4^{3-}$ (tetrahedral) $Mg(6 \cdot H2O)^{2+}$ (octahedral), and $NH_4^{+}$ (tetrahedral) groups which are held together by hydrogen bonds.

The $PO_4^{3-}$ tetrahedron is regular with mean P-O bond length of 1.543 A° . The $Mg \cdot 6 \cdot H_2O$ octahedron is distorted with mean bond $Mg\text{-}H_2O$ length of 2.0810 A°, and $H_2O\text{-}O$ length of 0.792 A°. The water O-H bond length is significantly smaller than the intermolecular separation which may be due to H atom taking part in bond formation [6].

Chemical characteristics of struvite crystals are detailed in Table 1.

Table 1. Chemicals characteristics of struvite crystals [6]

| Property | Value |
|---|---|
| Molecular weight | 247.42 g/mol |
| Hydrogen bond donor count | 10 |
| Hydrogen bond acceptor count | 11 |
| Exact mass | 247.05 g/mol |
| Topological polar Surface area | 84.8 Å |
| Heavy atom count | 13 (not counting H) |
| Complexity | 49.8 |
| Covalently bonded unit count | 9 |

### 1.3.1. Struvite as fertilizer

Fertilizers are substances that increase the fertility of the land. Plants need to take from the soil the elements that, in the right proportions, are essential to achieve their normal development. The lack of these elements can be corrected by simple addition to the floor compounds that contain elements as N, P, K, S, Ca or Mg, which together with carbon and hydrogen, are elements that are in greatest proportion in vegetables. The seconds are elements such as Fe, Zn, Mn, Cu, B or Mo which, being essential for vegetables, are in small proportions in them and are called microelements or trace elements.

Fertilizers containing macronutrients are used in large quantities, the most used being those containing N, P, K or mixtures of them. The most commonly used P fertilizers are orthophosphates and above all calcium and ammonium fertilizers. Ammonium phosphates are very soluble (30-70 g / 100 ml). However, orthophosphates are very poorly soluble.

Specifically, struvite is an effective fertilizer because it has a low leaching rate and can slowly release nutrients during the growing season of the plant. In addition, the excessive application of struvite does not burn the roots, a common inconvenience in traditional ammonium phosphate fertilizers.

Furthermore, its Mg content makes it also valid as a lawn fertilizer because it is the vital element of chlorophyll [5].

### 1.3.2. Problems at WWTP

The uncontrolled precipitation of struvite is a common phenomenon in anaerobic treatments of WW from biological P removal processes because these residues contain concentrations above the normal values of orthophosphate, ammonium and Mg, ions that form struvite mineral [1].

This uncontrolled precipitation occurs spontaneously in pipes, pumps, band filters, especially in all those places where pressure changes take place. The consequence of this precipitation is blockages in the pipes, leading to problems such as the decrease in the efficiency of the processes [1].

For these reasons, it is important to know in more detail under what conditions struvite precipitates in order to avoid this precipitation.

## 1.4. ANAEROBIC DIGESTION

Anaerobic digestion is a biochemical process that harnesses the complex metabolic reactions of a specific community of synergistic microorganisms. These microorganisms, in the absence of oxygen, are able to progressively transform organic materials into biogas (methane 60-70%, carbon dioxide 30-40%) and an innocuous solid and liquid residue [7].

This process is developed in four stages , in each stage participate several groups of microorganisms:

The first stage is the hydrolysis, whereby particulate and colloidal matter of the biomass is disintegrated and solubilized by a group of microorganisms known as hydrolytic bacteria.

The second is the acidogenesis, microorganisms break down the products of hydrolysis phase to produce hydrogen, carbon dioxide, alcohols and volatile fatty acids like propionate or butyrate [7] [8].

The third is the acetogenesis, is performed by acetogenic bacteria, which form the link between acidogenesis and methanogenesis. During this phase the fermentation products of the acidogenesis, like volatile fatty acids or long chain fatty acids, are oxidized into acetic acid, carbon dioxide, hydrogen and water [7] [8].

Finally, the fourth stage is the methanogenesis, a community of microorganisms known as methanogenic transform the acetic acid, hydrogen and carbon dioxide into methane ($CH_4$), carbon dioxide ($CO_2$) and water ($H_2O$) [7] [8].

## 1.5. OSMOSIS

Osmosis is a physical phenomenon that has been exploited by human beings since the early days of mankind [9] (ex. Use salt to preserve meat). There are three types of applications in the industry of this physical phenomenon.

However, forward osmosis (FO) has been developing rapidly in recent years and demonstrated its advantages in various applications [10].

### 1.5.1. Reverse osmosis

Reverse osmosis is the reverse process of osmosis. The driving force of the reverse osmosis process is the hydraulic pressure that is used to oppose and overcome the osmotic pressure of an aqueous feed solution.

### 1.5.2. Pressure-retarded osmosis

Pressure-retarded osmosis can be viewed as an intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to reverse osmosis). However, the net water flux is still in the direction of the concentrated draw solution (similar to FO) [9].

### 1.5.3. Forward Osmosis (FO)

Forward osmosis is the run-up to the crystallization of struvite in this project. FO has been developing rapidly in the last decade and demonstrated its advantages in various applications [10].

FO is the transport of water from a solution of greater chemical potential of water to a solution of lower chemical potential of water separated by a selectively permeable membrane that allows the passage of water and rejects most molecules or ions of solute driven by a difference in osmotic pressure. The driving force in this case is the difference in osmotic pressure.

## 1.6. CRYSTALLIZATION

Crystallization, from a physical point of view, is a change of state that leads, from a liquid or gaseous phase, to a solid organized structure, called crystal. It corresponds to a displacement towards the state of equilibrium in given conditions of temperature, pressure and concentration. It needs a driving force that in this case is called supersaturation [1]. Supersaturation occurs when the concentration of the solute is greater than its solubility.

In the processes of precipitation or crystallization by reaction, supersaturation is not achieved by an action on the physical properties (ex. Temperature). It is obtained by a chemical reaction between two soluble components, giving rise to a less soluble product which crystallizes. The formed solids are called precipitates and may not be crystalline [1].

### 1.6.1. Phases of crystallization

Crystallization occurs in two stages: nucleation and crystal growth.

#### *1.6.1.1. Nucleation*

The nucleation corresponds to the apparition of new particles. Several mechanism are possible for struvite crystallization depending on the supersaturation level in the crystallizer [5].

Homogeneous primary nucleation corresponds to the nuclei apparition directly in the supersaturated solution. Heterogeneous primary nucleation takes place on foreign surfaces, which can be dustin suspension or parts of the crystallize itself [5].

Secondary nucleation, needs to have already suspension particles of the same specie as the solid which is crystallized. Indeed, surface secondary nucleation corresponds to the nuclei formation on the surface of this particles [5].

### *1.6.1.2. Crystal growth*

The crystal growth consists of two stages: diffusion of the mass and integration of the elements of growth in the crystalline lattice.

When the mass transfer rate of the solute is significantly lower than the surface integration rate, that is, the first stage is the limiting stage, the crystal growth is controlled by diffusion. When the solute transfer rate is high, then the crystal growth is controlled by surface integration of the solute into the crystal [1] [6].

## **1.6.2. Parameters of struvite precipitation**

This subsection explains the parameters that affect struvite precipitation.

So that struvite precipitates, the solution must be supersaturated.

The solubility of struvite is dependent on temperature, stirring, pH, Mg:P ratio, presence of Ca, N:P ratio but this subsection only explains the dependence of pH, Mg:P ratio and presence of Ca because this parameters are the studied in this project.

As struvite contains three specific ions ($Mg^{2+}$, $NH_4$ and $PO_4^{3-}$), and its solute concentration can be defined by the ion activity product (IAP). When the IAP is greater than the solubility product ($K_{sp}$)the system is supersaturated and struvite may nucleate and grow, returning the system to equilibrium. The struvite IAP value is $7.08 \cdot 10^{14}$ [5].

$$IAP = [Mg^{2+}][NH_4][PO_4^{3-}]$$

### *1.6.2.1. pH*

The solution pH is one of the most influential parameters for struvite crystallization because it is associated with the solubility of products and the supersaturation of the solution.

Struvite crystallization is a reversible reaction, with complex equilibria that are significantly influenced by the pH value of the solution [4]. Struvite has low solubility in water and readily soluble in acidic environments. Struvite can be precipitated at a wide range of pH (7.0–11.5), but the suitable pH ranges between 7.5 to 9.0 [5].

The solution pH also affects the characteristics of the crystal. An increase in solution pH from 8 to 10 decreased the average size of struvite by 5 times in synthetic solutions. And an increase in solution pH from 9 to 11 decreased the crystal size by more than 2 times in a continuous flow struvite crystallizer. This is because an increase in pH produces higher nuclei population densities. In addition, higher pH is not only responsible for smaller particles, but also higher size diversity [4] [5].

On the other hand, raising pH may cause co-precipitation of heavy metals hydroxides with struvite and thus reduce the value of the precipitate as a potential soil fertilizer [11].

#### *1.6.2.2. Mg:P ratio*

The molar ratio of participating ions in solution has an important role during P crystallization because of the effects of these ions on the supersaturation level of the solution [4].

For the precipitation of struvite is necessary a molar ratio ($Mg:NH_4:PO_4^{3-}$) equal to (1:1:1) due to the stoichiometry. However, the constituents species in WW vary according to the origin of the WW. The Mg:P molar ratio in the supernatants is usually lower than 1, this means a deficit in Mg for struvite precipitation. This parameter is usually adjusted by the addition of $MgCl_2 \cdot 6H_2O$ to achieve the desired value [12].

Although stoichiometric ratio for struvite precipitation is 1:1:1, it has been shown that an increase in the Mg:P ratio increases the amount of P recovered as well as increasing the size of the crystals[4] [5].

#### *1.6.2.3. Calcium*

The presence of calcium (Ca) reduces the percentage of P precipitated as struvite, due to the presence of Ca might preferentially react with $PO_4^{3-}$ to produce hydroxyapatite, dicalcium phosphate and octacalcium phosphate [5] [12.]

After analyzing the problems caused by the presence of P in the WW, the current state of P resources and the different stages of the P recovery process as struvite, the project's objectives are detailed below.

# 2. OBJECTIVES

The main aim of this Project is the P recovery as struvite from a real WW subsequent of anaerobic digestion by crystallization. To achieve this, there are different specific objectives:

- Study the process of P recovery as struvite: anaerobic digestion, pretreatment, forward osmosis and crystallization.
- Find the composition of a real WW from an anaerobic digestion treatment.
- Study the effect of the parameters that influence the precipitation of struvite: presence of Ca, pH and Mg:P ratio.
- Study the increase in effectiveness of the process by adding a FO stage.

# 3. METHODS AND MATERIAL

This section explains the materials and the procedure used in the P recovery study.

## 3.1. CHEMICALS AND REAGENTS

The following reagents were used.(Table 2)

Table 2. Chemical properties of all reactive required in this work

| Entry | Name | Formula | Company | Purity [%] |
|---|---|---|---|---|
| **1** | di-Sodium Hydrogen Phosphate 12-hydrate | $Na_2HPO_4 \cdot 12\ H_2O$ | 131678.1211Panreac | 99 |
| **2** | Magnesium Chloride 6-hydrate | $MgCl_2 \cdot 2\ H_2O$ | (201396.0416) Panreac | 99 |
| **3** | Calcium sulphate 2-hydrate | $CaSO_4 \cdot 2\ H_2O$ | 131235.1211 panreac | 98 |
| **4** | Sodium bisulfate anhydrous | $Na_2SO_4$ | 71656 Fluka | 99 |
| **5** | Potassium sulfate | $K_2SO_4$ | Probus | - |
| **6** | Potassium chloride | KCl | (141494.1211) Panreac | 99 |
| **7** | Ammonium chloride | $NH_4Cl$ | (131121.0914) Panreac | 99.5 |
| **8** | Ammonium carbonate | NH4CO3 ch5no3 | 1.59504.0250 Merck | >30 |

Table 2. Chemical properties of all reactive required in this work (Continuation)

| Entry | Name | Formula | Company | Purity [%] |
|---|---|---|---|---|
| **9** | Sodium Hydroxide | $NaOH$ | (131687.1211)<br>Panreac | >97 |
| **10** | Hydrochloric acid | $HCl$ | (186985.1211)<br>Panreac | 96 |
| **11** | Nitric acid | $HNO_3$ | 231-714-2 Quimics dalmau | 61 |

Reagents 1 to 7 were used to synthesize WW, reagents 8 and 9 to change the pH and reagent 10 to prepare the samples that were sent to analysis.

## 3.2. SOFTWARE

The software used to simulate the experiments are shown below.

### 3.2.1. Visual Minteq ver. 3.1

Visual Minteq ver. 3.3 (VM) is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, sorption, etc for naturals waters. It combines state-of-the-art descriptions of sorption and complexation reactions with easy-to-use menus and options for importing and exporting data from/to Excel[13]. This software was used for the computational simulation of these two process stages: pretreatment (elimination of $Ca_5(PO4)_3(OH)$ and crystallization.

### 3.2.2. OLI Studio (Stream analyser) v.9.5

OLI Studio (Stream analyzer) v.9.5 (OLI) features single point equilibrium calculations, multiple point survey calculations for trend analysis for temperatures, pressure, pH and composition effects, and simple mix and separate capability. This software was used to balance equivalent charges of the WW[14].

The combination of both programs was necessary because OLI, despite being a highly developed program with a high capacity, does not contain the struvite mineral, unlike the VM program that has less capacity but does contain struvite mineral.

## 3.3. EXPERIMENTAL DEVICES

The equipment used is detailed below.

- Magnetic stirrer. Model IKA ® bib squid (white) (0-2500) rpm
- SartoriusTE 214S Balance , capacity 210 g and accurancy to 0.0001 mg.
- pH meter – sensION™+pH3 LANGE HACH. Measuring error 0.002
- Filtration equipment: Vacuum pump, filter plate, Type Hamp (0.45 μm membrane) Milliipore.
- Volumetric instruments.
- Dessicator with silica gel.

## 3.4. ANALYTICAL METHODS

The following methods and measurements were used. On the one hand, pH measurement used to synthesize the mixtures at the desired pH value and control the undesired precipitation of struvite during the experiments is explained. On the other hand, the methods used to analysis of liquid and solid samples after the precipitation experiments are explained.

### 3.4.1. pH measurement

The determination of pH was done with pH meter sensION™+pH3 LANGE HACH . Consists in the measurement of the potential which is developed through a thin glass membrane that separate three solutions with different proton concentration, so it is necessary to know the sensitivity and the selectivity of the glass membrane in front of pH. For this reason, calibration was required every day 4.0, 7.0 and 10.0 buffers to ensure the accurance [15].

### 3.4.2. Inductively coupled plasma – Optimal emission spectrometry (IPC-OES)

IPC-OES is a technique in which the composition of elements in samples can be determinate using plasma and a spectrometer.

The solution to analyze is conducted by a peristaltic pump through a nebulizer into a spray chamber. The produced aerosol is lead into a argon plasma. Plasma is the forth state of matter, next to the solid, liquid and gaseous state. In the IPC-OES the plasma is generated at the end of a quarts torch by a cooled induction coil through which a high frequency alternate current flows. As a consequence, an alternate magnetic fields is induced which accelerated electrons into a circular trajectory. Due to collision between the argon atom and the electrons ionization occurs, giving rise to a stable plasma. The plasma is extremely hot, 6000-7000 K. In the induction zone it can even reach 10000 K. In the torch desolvation, atomization and ionizations of the sample takes place. Due to the thermic energy taken up by the electrons, they reach a higher “excited” state. When the electrons drop back to ground level energy is liberated as light (protons). Each element has an own characteristic emission spectrum that is measured with a spectrometer. The light intensity on the wavelength is measured and with the calibration calculated into a concentration [16].

### 3.4.3. XRD or X-ray

XRD is a technique which determines the X-ray diffraction pattern of a crystal, and thanks to it, its molecular and atomic structure can be describe. For example, in this particular case, this technique would identify crystalline struvite in the precipitated obtained if it were present. X-rays are applied to sample with a known angle while it rotates. The electrons in the atoms of the crystal scatter those rays in different directions, in what is known as elastic scattering, therefore a regular array of electrons from a multitude of waves. Destructive interferences make some waves cancel each other, while constructive interferences, which take place only when Bragg’s Law is accomplished, cause a diffraction pattern [17].

## 3.5. EXPERIMENTAL PROCEDURE

The main objective of the project is to study the optimal conditions for P recovery from a real WW by crystallization. To achieve this, the following line of investigation was carried out.

First of all, an exhaustive bibliographical research was made of WW that would adapt to the project, that is, a WW from anaerobic digestion stage, of which the necessary data were available to synthetize it and correspond to municipal WW.

Secondly, different Mg:P Ratio and pH values were studied for determinate which value is the optimal to P recovery as struvite. These experiments were carried out with OLI and VM.

Lastly, once known the optimum value of Mg:P Ratio for the P recovery, experiments with different pH at laboratory scale were performed to study these parameters influence on P recovery.

Figure 2. Research line.

### 3.5.1. Identification of WW composition

An exhaustive bibliographic research of different types of WW from anaerobic digestion was carried out. This was one of the most important parts of the project as more than 100 articles had to be read from different databases. Not all the articles detailed all the necessary information, such as the concentration of the components of the WW, its origin, existence of a previous stage of anaerobic digestion or details of any other additional treatment.

Then, it was determined which of these WW was the most representative for the study. The criteria used for the WW selection were the following: a representative real WW, of which the most important components were known, coming from anaerobic digestion and that there were different samples.

In the bibliography, not all the data of the water composition chosen was found although there were data from enough samples from which the mean value was calculated. Therefore, the total concentration of the water studied was determined taking into account the salts available at the laboratory(Entry 1 to 7 **Error! No s'ha trobat l'origen de la referència.**) without varying the known data. This composition was calculated by mass balance. This composition was used for computational simulation and for experiments in the laboratory with the aim of comparing both results.

### 3.5.2. Computational simulation

The steps followed are shown in Figure 3.

#### *3.5.2.1. Balance equivalent charges*

In order to obtain an equivalent concentration of water equal to zero, the concentration of the less important ions for struvite formation was varied. In this case, only the modification of the chlorine concentration was necessary. The software used was OLI and the input stream data was provided in ppm.

#### *3.5.2.2. Pretreatment*

The concentration studied was simulated in the VM software and it was observed that hydroxyapatite was precipitating. .

These results were not expected as the WW chosen was from the supernatant of a centrifugation operation, subsequent to anaerobic digestion. This results was related to the lack of data about the composition of the WW chosen, such as information about complexing agents of real water.

On the other hand, studying the composition calculated taking onto account the salts of the laboratory, it was concluded that, as had been studied in section *1.6.2*, the presence of Ca caused the precipitation of hydroxyapatite.

For these reasons, it was concluded that to study struvite precipitation it would be necessary to introduce a pre-treatment step into the process. The type of pre-treatment is not within the scope of this project, however, the amount of hydroxyapatite precipitated was calculated and substracted from the composition studied, simulating a pre-treatment.

These calculations were performed using the VM software.

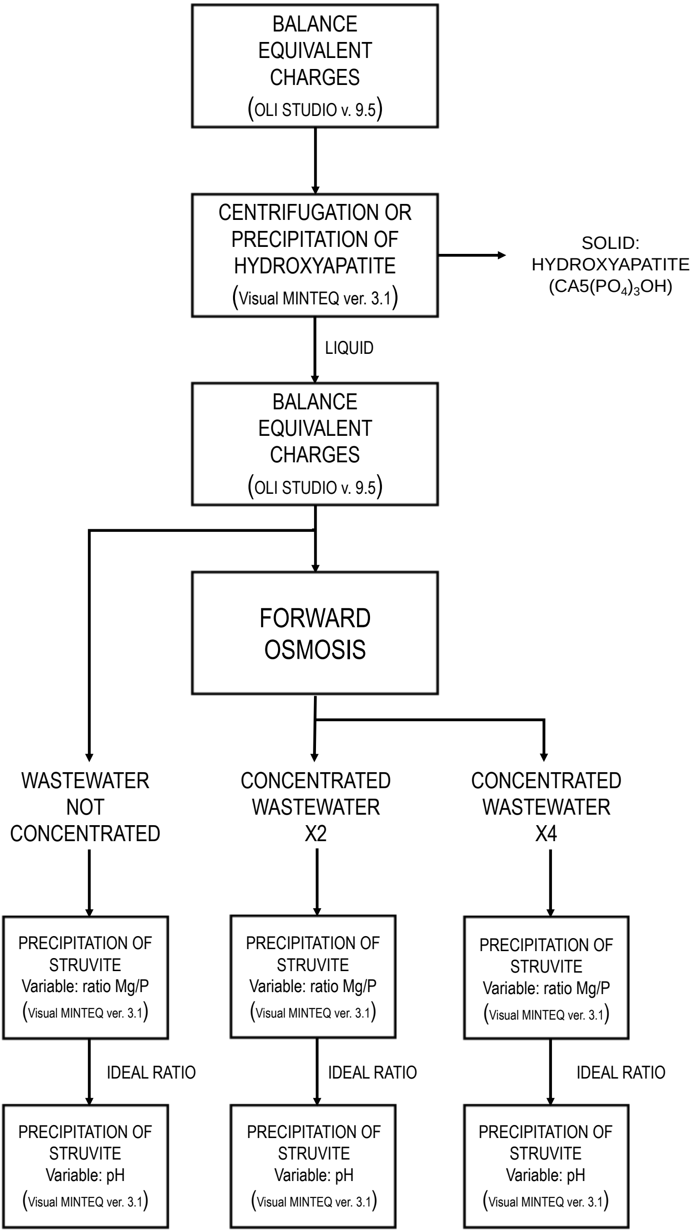


Figure 3. Block diagram of computational simulation

### *3.5.2.3. Balance equivalent charges*

Once the concentration of the liquid phase after pre-treatment stage was known, the concentration of the less important ions for struvite formation was varied again so that the sum of cations was equal to the sum of anions. The modified concentration this time was also that of chlorine.

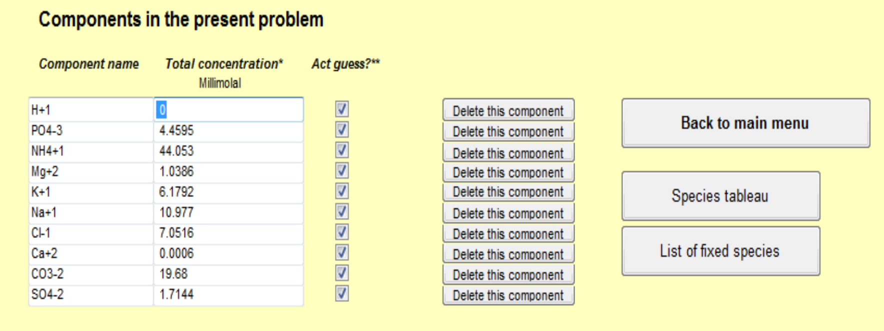
In the same way as in Subsection 3.5.2.1, OLI software was used for this purpose.

### *3.5.2.4. Forward Osmosis*

This stage aims to reduce the volume of water to be treated in the precipitation stage. In order to study if this stage increases efficiency of the process, the concentration of the compounds dissolved on the water studied was multiplied by two and four simulating the FO stage. In this way, it was possible to study these two situations in comparison to the results obtained without this stage. That is, three situations were studied: Situation 1 (process without FO stage), Situation 2 (process with FO that concentrates WW by 2) and Situation 3 (process with FO that concentrates WW by 4).

### *3.5.2.5. Struvite precipitation*

Once the concentration was calculated for each of the three situations studied, these data were entered into the VM software (Figure 4) and the following steps were followed.



**Components in the present problem**

| *Component name* | *Total concentration** Millimolal | *Act guess?*** |
|---|---|---|
| H+1 | 0 | ☑ |
| PO4-3 | 4.4595 | ☑ |
| NH4+1 | 44.053 | ☑ |
| Mg+2 | 1.0386 | ☑ |
| K+1 | 6.1792 | ☑ |
| Na+1 | 10.977 | ☑ |
| Cl-1 | 7.0516 | ☑ |
| Ca+2 | 0.0006 | ☑ |
| CO3-2 | 19.68 | ☑ |
| SO4-2 | 1.7144 | ☑ |

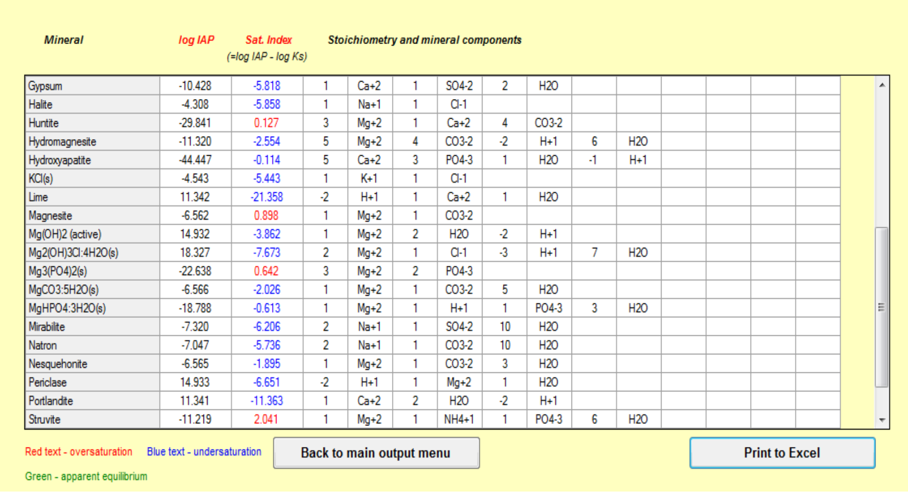
Figure 4. Data entry interface VM

The steps that are explained below were carried out for the three situations. First, these steps were performed by varying the Mg:P ratio. Once the optimal ratio was determined, basing the choice on the relation (amount of P recovered/ amount of Mg added), the same steps were followed varying the pH. For this, sodium hydroxide or hydrogen chloride was added to the WW composition.

First of all, it was analyzed which compound was more prone to precipitate. On the one hand, if the mineral with more tendency to precipitate was struvite, its precipitation was simulated and the amount of each ion remaining in the liquid phase and the amount of each ion that had precipitated was calculated. These calculations were carried out knowing as explained in Subsection 1.6.2 that, if the IAP is greater than its solubility product, this mineral is supersaturated and precipitated. Therefore, knowing that the saturation index is:

$$\text{Sat. index} = \log(\text{IAP})-\log(K_{ps})$$

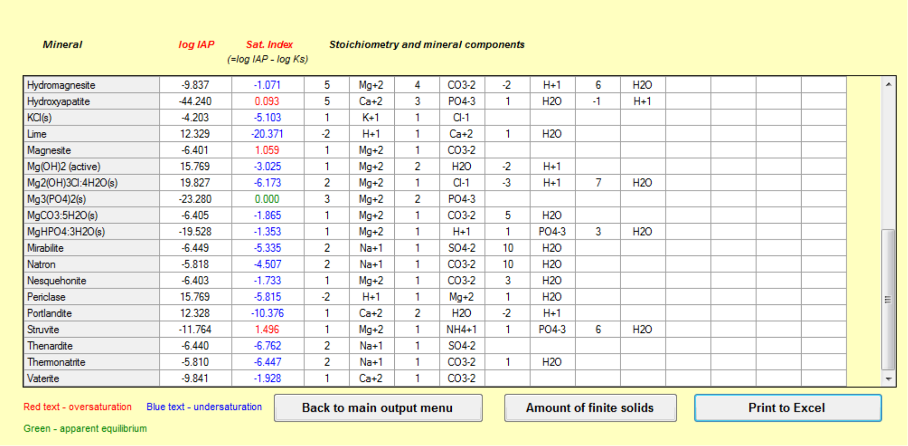
If the saturation index is positive it means that the mineral has a tendency to precipitate (Figure 5).



| *Mineral* | *log IAP* | *Sat. Index* (=log IAP - log Ks) | *Stoichiometry and mineral components* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Gypsum | -10.428 | -5.818 | 1 | Ca+2 | 1 | SO4-2 | 2 | H2O | | |
| Halite | -4.308 | -5.858 | 1 | Na+1 | 1 | Cl-1 | | | | |
| Huntite | -29.841 | 0.127 | 3 | Mg+2 | 1 | Ca+2 | 4 | CO3-2 | | |
| Hydromagnesite | -11.320 | -2.554 | 5 | Mg+2 | 4 | CO3-2 | -2 | H+1 | 6 | H2O |
| Hydroxyapatite | -44.447 | -0.114 | 5 | Ca+2 | 3 | PO4-3 | 1 | H2O | -1 | H+1 |
| KCl(s) | -4.543 | -5.443 | 1 | K+1 | 1 | Cl-1 | | | | |
| Lime | 11.342 | -21.358 | -2 | H+1 | 1 | Ca+2 | 1 | H2O | | |
| Magnesite | -6.562 | 0.898 | 1 | Mg+2 | 1 | CO3-2 | | | | |
| Mg(OH)2 (active) | 14.932 | -3.862 | 1 | Mg+2 | 2 | H2O | -2 | H+1 | | |
| Mg2(OH)3Cl:4H2O(s) | 18.327 | -7.673 | 2 | Mg+2 | 1 | Cl-1 | -3 | H+1 | 7 | H2O |
| Mg3(PO4)2(s) | -22.638 | 0.642 | 3 | Mg+2 | 2 | PO4-3 | | | | |
| MgCO3:5H2O(s) | -6.566 | -2.026 | 1 | Mg+2 | 1 | CO3-2 | 5 | H2O | | |
| MgHPO4:3H2O(s) | -18.788 | -0.613 | 1 | Mg+2 | 1 | H+1 | 1 | PO4-3 | 3 | H2O |
| Mirabilite | -7.320 | -6.206 | 2 | Na+1 | 1 | SO4-2 | 10 | H2O | | |
| Natron | -7.047 | -5.736 | 2 | Na+1 | 1 | CO3-2 | 10 | H2O | | |
| Nesquehonite | -6.565 | -1.895 | 1 | Mg+2 | 1 | CO3-2 | 3 | H2O | | |
| Periclase | 14.933 | -6.651 | -2 | H+1 | 1 | Mg+2 | 1 | H2O | | |
| Portlandite | 11.341 | -11.363 | 1 | Ca+2 | 2 | H2O | -2 | H+1 | | |
| Struvite | -11.219 | 2.041 | 1 | Mg+2 | 1 | NH4+1 | 1 | PO4-3 | 6 | H2O |

Figure 5. Saturation index interface

On the other hand, if the mineral with more tendency to precipitate was not struvite, the precipitation of this mineral was simulated first (Figure 6) .



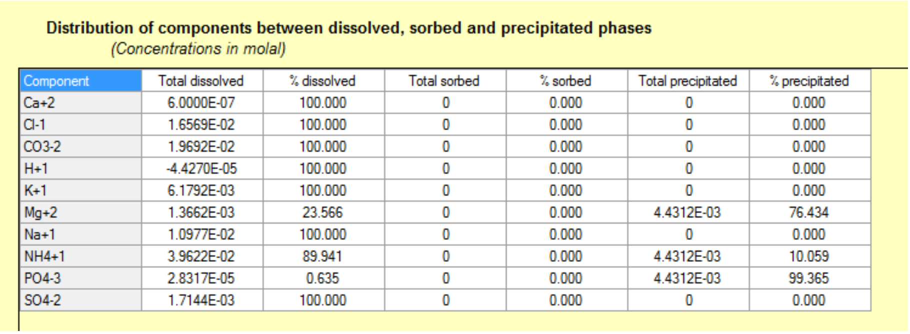
| Mineral | log IAP | Sat. Index (=log IAP - log Ks) | Stoichiometry and mineral components | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Hydromagnesite | -9.837 | -1.071 | 5 | Mg+2 | 4 | CO3-2 | -2 | H+1 | 6 | H2O |
| Hydroxyapatite | -44.240 | 0.093 | 5 | Ca+2 | 3 | PO4-3 | 1 | H2O | -1 | H+1 |
| KCl(s) | -4.203 | -5.103 | 1 | K+1 | 1 | Cl-1 | | | | |
| Lime | 12.329 | -20.371 | -2 | H+1 | 1 | Ca+2 | 1 | H2O | | |
| Magnesite | -6.401 | 1.059 | 1 | Mg+2 | 1 | CO3-2 | | | | |
| Mg(OH)2 (active) | 15.769 | -3.025 | 1 | Mg+2 | 2 | H2O | -2 | H+1 | | |
| Mg2(OH)3Cl:4H2O(s) | 19.827 | -6.173 | 2 | Mg+2 | 1 | Cl-1 | -3 | H+1 | 7 | H2O |
| Mg3(PO4)2(s) | -23.280 | 0.000 | 3 | Mg+2 | 2 | PO4-3 | | | | |
| MgCO3:5H2O(s) | -6.405 | -1.865 | 1 | Mg+2 | 1 | CO3-2 | 5 | H2O | | |
| MgHPO4:3H2O(s) | -19.528 | -1.353 | 1 | Mg+2 | 1 | H+1 | 1 | PO4-3 | 3 | H2O |
| Mirabilite | -6.449 | -5.335 | 2 | Na+1 | 1 | SO4-2 | 10 | H2O | | |
| Natron | -5.818 | -4.507 | 2 | Na+1 | 1 | CO3-2 | 10 | H2O | | |
| Nesquehonite | -6.403 | -1.733 | 1 | Mg+2 | 1 | CO3-2 | 3 | H2O | | |
| Periclase | 15.769 | -5.815 | -2 | H+1 | 1 | Mg+2 | 1 | H2O | | |
| Portlandite | 12.328 | -10.376 | 1 | Ca+2 | 2 | H2O | -2 | H+1 | | |
| Struvite | -11.764 | 1.496 | 1 | Mg+2 | 1 | NH4+1 | 1 | PO4-3 | 6 | H2O |
| Thenardite | -6.440 | -6.762 | 2 | Na+1 | 1 | SO4-2 | | | | |
| Thermonatrite | -5.810 | -6.447 | 2 | Na+1 | 1 | CO3-2 | 1 | H2O | | |
| Vaterite | -9.841 | -1.928 | 1 | Ca+2 | 1 | CO3-2 | | | | |

Red text - oversaturation Blue text - undersaturation

Green - apparent equilibrium

Figure 6. Saturation index interface $(Mg_3PO_4)_2$ precipitated

Then, it was verified that the next compound to be precipitated was struvite. In this case, the amount of each ion that remained in the liquid phase after the precipitation and the amount of each precipitated ion was calculated.



**Distribution of components between dissolved, sorbed and precipitated phases**

*(Concentrations in molal)*

| Component | Total dissolved | % dissolved | Total sorbed | % sorbed | Total precipitated | % precipitated |
|---|---|---|---|---|---|---|
| Ca+2 | 6.0000E-07 | 100.000 | 0 | 0.000 | 0 | 0.000 |
| Cl-1 | 1.6569E-02 | 100.000 | 0 | 0.000 | 0 | 0.000 |
| CO3-2 | 1.9692E-02 | 100.000 | 0 | 0.000 | 0 | 0.000 |
| H+1 | -4.4270E-05 | 100.000 | 0 | 0.000 | 0 | 0.000 |
| K+1 | 6.1792E-03 | 100.000 | 0 | 0.000 | 0 | 0.000 |
| Mg+2 | 1.3662E-03 | 23.566 | 0 | 0.000 | 4.4312E-03 | 76.434 |
| Na+1 | 1.0977E-02 | 100.000 | 0 | 0.000 | 0 | 0.000 |
| NH4+1 | 3.9622E-02 | 89.941 | 0 | 0.000 | 4.4312E-03 | 10.059 |
| PO4-3 | 2.8317E-05 | 0.635 | 0 | 0.000 | 4.4312E-03 | 99.365 |
| SO4-2 | 1.7144E-03 | 100.000 | 0 | 0.000 | 0 | 0.000 |

Figure 7. Composition(liquid and solid phase) after precipitation of struvite interface

Although the concentration of all the ions was calculated, the study focused on phosphate and magnesium (Mg) only because the others were not part of struvite and the ammonium of the water studied was in excess.

### 3.5.3. Laboratory experiments

The steps followed are shown in Figure 8.

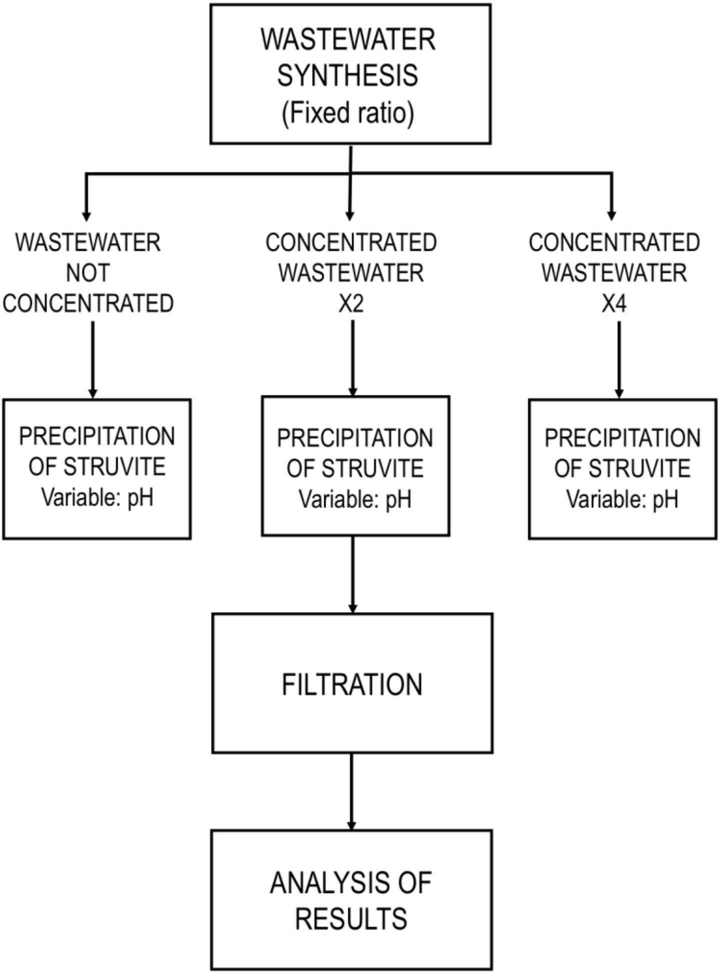


Figure 8. Block diagram of laboratory experiments

#### *3.5.3.1. WW synthesis*

The first step to carry out the experiments was the synthesis of the wastewater. Two liters (L) of water were synthesized for each of the situations studied. The composition of these samples corresponded to the optimal Mg:P ratio studied for each of them in the computational simulation.

First of all, the necessary amount of each of the salts was calculated for the synthesis of the water. Each of the salts was weighed and crushed. Then, these salts were placed in 25-mL beaker separately, understirring at 200 rpm.

The salts were added in the same beaker in the following order. First, the salts that least affected the pH were added ($Na_2PO_4$, KCl, $Na_2SO_4$, $K_2SO_4$). Then, $NH_4CO_3$ was added carefully, because this salt greatly increases the pH. Last, $MgCl_2$ was added. At the same time as the salts were added, the pH was measured and HCl was added to control that the pH value did not achieve the pH value of struvite precipitation that had been studied in the computational simulation. This solution was leveled in a 2-L volumetric flask.

### *3.5.3.2. Precipitation of struvite*

Firstly, 25-mL of synthesized water was placed in a stirred tank-reactor. Then, at the same time as the pH was measured, NaOH was added until achieve the desired pH value.

These samples were stirred for 30 min and at rest for 48 hours (h).

This procedure was performed for four different pH values of each situation studied.

### *3.5.3.3. Filtration*

The obtained solution was filtered under vacuum. On the one hand, a drop of $HNO_3$ was added to the liquid phase so that nothing precipitated before the samples was analyzed. On the other hand, the solid phase was dried for a day to be analyzed correctly. Finally, both phases were sent for analysis.

# 4. RESULTS AND DISCUSSION

The main objective of the project is to determinate the optimum conditions of struvite precipitation for the recovery of phosphorus from a real WW coming from anaerobic digestion treatment. The results and discussion are shown below.

## 4.1. LOOKUP OF WW COMPOSITION

The table below shows the composition and pH of the WW found after an exhaustive bibliographic research. The composition observed in Table 4 corresponds to the composition of the WW after the anaerobic digestion treatment.

Table 4. Composition and pH of WW from anaerobic digestion.

| **Entry** | **WW** | | **$P_t$** [mg/L] | **$PO_4$-P** [mg/L] | **$NH_4$-N** [mg/L] | **$Ca^{2+}$** [mg/L] | **$K^+$** [mg/L] | **$Mg^{2+}$** [mg/L] | **pH** |
|---|---|---|---|---|---|---|---|---|---|
| **1** | Animal manure | Swine[18] | - | - | - | 120 | 97.5 | 24.5 | - |
| **2** | | Swine [19](centrigugalized) | 20.20 | - | - | - | - | - | - |
| **3** | | Bovine[20] | 384 | - | 2700 | - | - | - | - |
| **4** | | Pig manure[21] | 53.30 | - | 1361 | - | - | 84.62 | 7.5 |
| **5** | | Poultry (pre-treated) | 370 | - | 1318 | - | - | - | 7.95 |
| **6** | | Dairy manure[22] | 100 | - | 255 | - | - | - | 7.45 |
| **7** | | | 450 | - | 519 | - | - | - | 7.93 |

Table 4. Composition and pH of WW from anaerobic digestion (Continuation)

| **Entry** | **WW** | | **$P_t$** [mg/L] | **$PO_4$-P** [mg/L] | **$NH_4$-N** [mg/L] | **$Ca^{2+}$** [mg/L] | **$K^+$** [mg/L] | **$Mg^{2+}$** [mg/L] | **pH** |
|---|---|---|---|---|---|---|---|---|---|
| **8** | | Swine[23] | - | - | 798 | - | - | - | 7.8-8.1 |
| **9** | Municipal/ Urban | Bejine China | 211 | - | 368 | 37 | 103 | 28 | 7.76 |
| **10** | | Urban wáter[24] | - | - | 185 | 51.7 | 15 | 48.5 | - |
| **11** | | | - | - | 232 | 79 | 20 | 47 | - |
| **12** | | New Jersey[25] | - | - | 1142 | 51 | - | 72 | - |
| **13** | | Anaerobic digestion supernatant [2]1(EDAR Carraixet) | 176 | 169 | - | 76 | 241 | 34 | 8.7 |
| **14** | | | 153 | 147 | - | 106 | 266 | 40 | 8.7 |
| **15** | | | 76 | 70 | - | 164 | 236 | 64 | 8.7 |
| **16** | | | 167 | 160 | - | 77 | 204 | 48 | 8.7 |
| **17** | | | 169 | 159 | - | 92 | 228 | 44 | 8.5 |
| **18** | | | 189 | 173 | - | 38 | 286 | 10 | 8.7 |
| **19** | | EDAR Carraixet 2[2] | 179 | 165 | - | 77 | 215 | 35 | 8.7 |
| **20** | | | 93 | 79 | - | 48 | 260 | 37 | 8.7 |
| **21** | | | 79 | 65 | - | 66 | 164 | 51 | 8.7 |
| **22** | | | 70 | 58 | - | 73 | 193 | 36 | 8.7 |
| **23** | | | 102 | 95 | - | 72 | 158 | 51 | 8.7 |
| **24** | | | 114 | 101 | - | 83 | 159 | 43 | 8.7 |
| **25** | | | 75 | 69 | - | 78 | 171 | 52 | 8.7 |
| **26** | | | 79 | 70 | - | 74 | 174 | 50 | 8.7 |
| **27** | | | 66 | 54 | - | 98 | 108 | 76 | 8.7 |

Table 4. Composition and pH of WW from anaerobic digestion (Continuation)

| **Entry** | **WW** | | **$P_t$** [mg/L] | **$PO_4$-P** [mg/L] | **$NH_4$-N** [mg/L] | **$Ca^{2+}$** [mg/L] | **$K^+$** [mg/L] | **$Mg^{2+}$** [mg/L] | **pH** |
|---|---|---|---|---|---|---|---|---|---|
| **28** | | | 65 | 54 | - | 77 | 132 | 55 | 8.7 |
| **29** | | | 47 | 44 | - | 132 | 36 | 51 | 8.7 |
| **30** | | | 56 | 45 | - | 117 | 68 | 60 | 8.7 |
| **31** | Industrial | Starch processing[26] | 22.7 | - | 217.6 | 72.8 | 102.3 | 97.6 | 7.3 |
| **32** | | | 40.2 | - | 334.7 | 102.3 | 176.4 | 166.9 | 7.5 |

The waters chosen for the P recovery study were the waters coming from the supernatant of a centrifugation subsequent to anaerobic digestion of the Carraixet WWTP (entry 13 to 18). These waters was chosen because there was several samples. These waters represent urban WW that are the most common.

For the study of P recovery, the average composition of the water chosen was calculated, without taking into account entry 15 because this composition was different from the rest.

The results obtained are indicated in Table 5.

Table 5. WW composition studied.

| **WW** | **$P_t$** [mg/L] | **$PO_4$-P** [mg/L] | **$NH_4$-N** [mg/L] | **$Ca^{2+}$** [mg/L] | **$K^+$** [mg/L] | **$Mg^{2+}$** [mg/L] | **pH** |
|---|---|---|---|---|---|---|---|
| EDAR Carraixet (supernatant) | 169.98 | - | 617.17 | 68.71 | 241.62 | 25.25 | 8.7 |

As shown in Table 5 , taking into account the stoichiometry of struvite, N is in excess and Mg is insufficient.

The concentration of the ions calculated for knowing the total composition of the WW taking into account the available salts in the laboratory are indicated in Table 5.

Table 6. Ion concentration

| Ions | Concentration [mg/L] |
|---|---|
| $PO_4^{3-}$ | 521.18 |
| $NH_4^+$ | 794.66 |
| $Mg^{2+}$ | 25.25 |
| $K^+$ | 241.62 |
| $Na^+$ | 252.35 |
| $Cl^-$ | 1157.52 |
| $Ca^{2+}$ | 68.71 |
| $CO_3^{2-}$ | 1181.68 |
| $SO_4^{2-}$ | 164.69 |

## 4.2. COMPUTATIONAL SIMULATION

This section shows the results obtained in the simulations carried out with OLI and VM software about phosphorus recovery process.

### 4.2.1. Balance equivalent charges

As explained in Section 3, it was necessary to equalize de equivalent concentration to obtain the electro-neutrality of the water studied. Table 7 shows the composition of the water after equaling the equivalent concentration with the OLI program.

Table 7. Equalization of equivalent concentration OLI

| Ion | Unequal equivalent concentration [mg/L] | Equal equivalent concentration [mg/L] |
|---|---|---|
| $PO_4^{3-}$ | 521.18 | 521.18 |
| $NH_4^+$ | 794.66 | 794.66 |
| $Mg^{2+}$ | 25.25 | 25.25 |
| $K^+$ | 241.62 | 241.62 |
| $Na^+$ | 252.35 | 252.35 |
| $Cl^-$ | 1157.52 | 265.00 |
| $Ca^{2+}$ | 68.71 | 68.71 |
| $CO_3^{2-}$ | 1181.68 | 1181.68 |
| $SO_4^{2-}$ | 164.69 | 164.69 |

It was only necessary to modify the chlorine concentration. With this composition the sum of equivalent charges was very small ($3.35 \cdot 10^{-5}$ eq/L). Therefore, it could be considered that it is a neutral composition.

### 4.2.2. Pretreatment

Table 8 illustrated the composition of the liquid phase and solid phase of the water studied after the elimination of the amount of hydroxyapatite that was formed.

Table 8. Composition precipitated as hydroxyapatite in centrifugation stage VM

| **Ion** | **Total dissolved** [mg/L] | **Total precipitated** [mg/L] |
|---|---|---|
| $PO_4^{3-}$ | 423.52 | 97.65 |
| $NH_4^+$ | 794.45 | 0 |
| $Mg^{2+}$ | 25.25 | 0 |
| $K^+$ | 241.62 | 0 |
| $Na^+$ | 252.35 | 0 |
| $Cl^-$ | 265.00 | 0 |
| $Ca^{2+}$ | 0.025 | 68.68 |
| $CO_3^{2-}$ | 1181.68 | 0 |
| $SO_4^{2-}$ | 164.69 | 0 |

As can be seen in Table 8, a considerable amount of phosphorus has been lost in this stage of the process. This loss is necessary for the elimination of Ca that prevents the precipitation of struvite.

### 4.2.3. Balance equivalent charge

Again, it was necessary to equal the charges of the solution (Table 9).

Table 9. Equalization of equivalent concentration OLI

| **Ion** | **Unequal equivalent concentration** [mg/L] | **Equal equivalent concentration** [mg/L] |
|---|---|---|
| $PO_4^{3-}$ | 423.52 | 423.52 |
| $NH_4^+$ | 794.45 | 794.45 |
| $Mg^{2+}$ | 25.25 | 25.25 |

Table 9. Equalization of equivalent concentration OLI (Continuation)

| Ion | Unequal equivalent concentration [mg/L] | Equal equivalent concentration [mg/L] |
|---|---|---|
| $K^+$ | 241.62 | 241.62 |
| $Na^+$ | 252.35 | 252.35 |
| $Cl^-$ | 265.00 | 250.00 |
| $Ca^{2+}$ | 0.025 | 0.025 |
| $CO_3^{2-}$ | 1181.68 | 1181.68 |
| $SO_4^{2-}$ | 164.69 | 164.69 |

With this composition the sum of equivalent charges are $4.61 \cdot 10^{-5}$ eq/L. Therefore, it could be considered that it is a neutral composition.

### 4.2.4. FO

Table 10 shows an approximation of the waters in three different situations studied.

Table 10. Composition of WW ( without FO stage "Situation 1", FO stage concetrated x 2 "Situation2" and FO x 4 "Situation 3")

| Ion | Situation 1 | Situation 2 (concentrated x 2) | Situation 3 (concentrated x4) |
|---|---|---|---|
| $PO_4^{3-}$ | 423.52 | 847.04 | 1694.07 |
| $NH_4^+$ | 794.45 | 1588.90 | 3177.81 |
| $Mg^{2+}$ | 25.25 | 50.48 | 100.95 |
| $K^+$ | 241.62 | 483.19 | 966.38 |
| $Na^+$ | 252.35 | 504.70 | 1009.40 |

Table 10. Composition of WW ( without FO stage “Situation 1”, FO stage concetrated x 2 “Situation2” and FO x 4 “Situation 3”) (Continuation)

| Ion | Situation 1 | Situation 2 (concentrated x 2) | Situation 3 (concentrated x4) |
|---|---|---|---|
| $Cl^-$ | 250.00 | 500 | 1000.00 |
| $Ca^{2+}$ | 0.025 | 0.05 | 0.10 |
| $CO_3^{2-}$ | 1181.68 | 2363.32 | 4726.63 |
| $SO_4^{2-}$ | 164.69 | 329.37 | 658.75 |

### 4.2.5. Precipitation of struvite

This subsection shows the results obtained by varying the Mg/P ratio and pH in the simulations with VM.

#### *4.2.5.1. Mg:P Ratio*

For each situation studied, different values of Mg:P Ratio were simulated.

When entering the composition data VM calculate the saturation index of all possible minerals. In this table, therefore, it is possible to observe which is the most prone mineral to precipitate.

Table 11. Saturation index of all minerals in the solution VM

| Mineral | Sat. index |
|---|---|
| Anhydrite | -6,07 |
| Aragonite | -1,82 |
| Artinite | -1,23 |
| Brucite | -2,17 |
| Ca3(PO4)2 (am1) | -7,91 |
| Ca3(PO4)2 (am2) | -5,16 |
| Ca3(PO4)2 (beta) | -4,49 |
| Ca4H(PO4)3:3H2O(s) | -7,84 |
| CaCO3xH2O(s) | -3,01 |

Table 11. Saturation index of all minerals in the solution VM (Continuation)

| Mineral | Sat. index |
|---|---|
| CaHPO4(s) | -3,10 |
| CaHPO4:2H2O(s) | -3,38 |
| Calcite | -1,67 |
| Dolomite (disordered) | -0,18 |
| Dolomite (ordered) | 0,37 |
| Epsomite | -4,71 |
| Gypsum | -5,82 |
| Halite | -5,86 |
| Huntite | 0,13 |
| Hydromagnesite | -2,55 |
| Hydroxyapatite | -0,11 |
| KCl(s) | -5,44 |
| Lime | -21,36 |
| Magnesite | 0,90 |
| Mg(OH)2 (active) | -3,86 |
| Mg2(OH)3Cl:4H2O(s) | -7,67 |
| Mg3(PO4)2(s) | 0,64 |
| MgCO3:5H2O(s) | -2,03 |
| MgHPO4:3H2O(s) | -0,61 |
| Mirabilite | -6,21 |
| Natron | -5,74 |
| Nesquehonite | -1,90 |
| Periclase | -6,65 |
| Portlandite | -11,36 |
| Struvite | 2,04 |
| Thenardite | -7,63 |
| Thermonatrite | -7,68 |
| Vaterite | -2,24 |

In this case the mineral with more tendency to precipitate is struvite (Table 11).

Also with VM the precipitation of the mineral is simulated and it observes that quantity of each component has precipitated and that amount is dissolved.

Table 12. Example of the results obtained after precipitation simulation VM

| Component | Total disolved(mg soluto / Kg solvente) | % dissolved | Total sorbed | % sorbed | Total precipitated | % precipitated |
|---|---|---|---|---|---|---|
| Ca+2 | 6,00E-07 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |
| Cl-1 | 7,05E-03 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |
| CO3-2 | 1,97E-02 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |
| H+1 | -6,85E-05 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |
| K+1 | 6,18E-03 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |
| Mg+2 | 1,12E-05 | 1,08 | 0 | 0 | 1,03E-03 | 98,92 |
| Na+1 | 1,10E-02 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |
| NH4+1 | 4,30E-02 | 97,67 | 0 | 0 | 1,03E-03 | 2,33 |
| PO4-3 | 3,43E-03 | 76,96 | 0 | 0 | 1,03E-03 | 23,04 |
| SO4-2 | 1,71E-03 | 100,00 | 0 | 0 | 0,00E+00 | 0,00 |

The data shown in Table 11 and Table 12 corresponds to the Mg:P initial ratio. These data only have been shown to facilitate the understanding of the simulations carried out.

The data shown below are summary the results obtained of each Mg:P Ratio or pH studied about the amount of $PO_4^{3-}$ precipitated and dissolved and the mineral precipitated in order to obtain ease of interpretation and be able to compare the results.

### Situation 1: WW not concentrated

Table 13. Results precipitation “Situation 1” (Variable: Mg:P Ratio) VM

| Mg:P Ratio | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| Initial | 76.96 | 23.04 | Struvite |
| 1:1 | 4.17 | 95.83 | Struvite |
| 1.2:1 | 0.89 | 99.11 | Struvite |
| 1.3:1 | 0.63 | 99.36 | Struvite |
| 1.5:1 | 23.70 | 76.29 | $Mg_3(PO4)_2$ |

It can be observed in Table 13 that the optimal recovery values of P recovery are those corresponding to Mg:P Ratio 1.2:1 and 1.3:1. Taking into account the small difference of recovered P obtained between both and the costs that would suppose the addition of Mg to the amounts of water that are treated in the WWTP, it has been determinated that optimum value of precipitation in this situation is 1.2:1.

### Situation 2: WW concentrated x 2

Table 14. Results precipitation “Situation 2” (Variable: Mg:P Ratio) VM

| Mg:P Ratio | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| Initial | 76.77 | 23.23 | Struvite |
| 1:1 | 2.02 | 97.98 | Struvite and huntite |
| 1.2:1 | 0.22 | 99.78 | Struvite and huntite |

As may be seen, the precipitate of both Mg:P Ratio is formed by huntite and struvite, therefore, it was conclude that the optimum ratio was the one with the highest percentage of P recovered, that is, Mg:P Ratio 1.2:1 (Table 14).

Situation 3: WW concentrated x 3

Table 15. Results precipitation "Situation 3" (Variable Mg:P Ratio) VM

| Mg:P Ratio | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **Initial** | 76.73 | 23.27 | Struvite |
| **1:1** | 1.01 | 98.99 | Struvite, huntite and $Mg_3(PO4)_2$ |
| **1.2:1** | 0.08 | 99.92 | Struvite, huntite and hydromagnesite |

The precipitate obtained for Mg:P Ratio 1.2:1 is formed by huntite, hydromagnesite and struvite. Huntite and hydromagnesite precipitated before than struvite, none of them is formed by P and both contain Mg. That is, Mg is being precipitated at the same time it is added. Therefore, although a precipitate exclusively formed by struvite is not obtained, it was considered that the optimum Mg:P Ratio was 1:1(Table 15).

### *4.2.5.2. pH*

As it has been done with the Mg:P Ratio, the results obtained in the simulations where the pH effect was studied are shown. These simulations were carried out on the composition of the water corresponding to the optimum pH.

Situation1: WW not concentrated Mg:P Ratio 1.2

Table 16. Results precipitation "Situation 1" (Variable: pH) VM

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **6.03** | - | - | - |
| **6.42** | - | - | - |
| **6.61** | - | - | - |
| **6,66** | 97.74 | 2,26 | Struvite |
| **6,67** | 96.53 | 3,47 | Struvite |
| **6,70** | 94.13 | 5,87 | Struvite |

Table 16. Results precipitation "Situation 1" (Variable: pH) VM (Continuation)

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **7,00** | 70.60 | 29,40 | Struvite |
| **7,12** | 63.01 | 36,99 | Struvite |
| **7,54** | 44.56 | 55,44 | Struvite |
| **8,34** | 12.04 | 87,96 | Struvite |
| **8,70** | 2.92 | 97,08 | Struvite |
| **8,93** | 1.58 | 98,42 | Struvite |
| **9,54** | 0.80 | 99,20 | Struvite and $Mg_3(PO4)_2$ |
| **9,87** | 0.84 | 99,16 | Struvite and $Mg_3(PO4)_2$ |

According to the results of Table 16, struvite precipitates from a pH value of 6.66. In addition, when the pH increases, the amount of precipitated struvite increases and therefore, the P recovered. However, from a pH value of approximately 9.54 the precipitated is made up of $Mg_3PO_4$ and struvite.

Situation 2: WW concentrated x2 Mg:P Ratio 1.2

Table 17. Results precipitation "Situation 2" (Variable: pH) VM

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **5.98** | 100,00 | 0,00 | Struvite |
| **6.28** | 83.55 | 16,45 | Struvite |
| **6.50** | 51.16 | 48,84 | Struvite |
| **6.83** | 24.48 | 75,52 | Struvite |
| **7.10** | 13.31 | 86,69 | Struvite |
| **7.59** | 4.55 | 95,45 | Struvite |
| **8.13** | 1.38 | 98,62 | Struvite |
| **8.44** | 0.73 | 99,27 | Struvite |
| **8.79** | 0.38 | 99,62 | Struvite |

Table 17. Results precipitation “Situation 2” (Variable: pH) VM (Continuation)

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **9.03** | 0.27 | 99,73 | Srruvite and huntite |
| **9.21** | 0.22 | 99,78 | Srruvite and huntite |
| **9.38** | 0.38 | 99,62 | Srruvite and huntite |
| **9.68** | 0.28 | 99,72 | Srruvite, huntite and hydromagnesite |
| **9.84** | 0.36 | 99,64 | Srruvite, huntite and hydromagnesite |
| **10.25** | 0.60 | 99,40 | Srruvite, huntite and hydromagnesite |
| **11.24** | 2.22 | 97,78 | Srruvite, huntite and hydromagnesite |

In this situation, it is possible to recover up to 99.62% of P by precipitating only struvite for a pH value equal to 8.79. In addition, this situation considerably reduces the flow of water to be treated (Table 17).

### Situation 3: WW concentrated x 4 Mg:P Ratio 1

Table 18. Results precipitation “Situation 3” (Variable: pH) VM

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **7.04** | 24.49 | 75.51 | Struvite |
| **8.01** | 2.4 | 97.6 | Huntite and struvite |
| **8.83** | 1.46 | 98.54 | Huntite, struvite and Mg3(PO4)2 |
| **9.03** | 1.18 | 98.82 | Huntite, struvite and Mg3(PO4)2 |
| **9.16** | 1.07 | 98.93 | Huntite, struvite and Mg3(PO4)2 |

Table 18. Results precipitation “Situation 3” (Variable: pH) VM (Continuation)

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|
| **9.23** | 1.91 | 98.99 | Huntite, struvite and Mg3(PO4)2 |
| **10** | 1.04 | 98.96 | Hydromagnesite and struvite |

Although the results obtained are positive, such high P recovery were not achieved as in situations 1 and 2. In addition, the precipitate corresponds to a mixture of huntite, struvite and $Mg_3(PO_4)_2$ (Table 18).

The amount of huntite in the composition of the precipitate was considered negligible ashuntite is formed by Ca, which almost everything has been eliminated in the pretreatment to avoid the formation of hydroxyapatite.

Therefore, it was considered that the optimum value of pH for the struvite precipitation would be worth approximately 8.

After analyzing the results obtained in the three situations studied, taking into account that the goal is the P recovery as struvite as pure as possible, it was concluded that the optimal parameters for it would be the following:

Table 19. Optimum value of the parameters of P recovery as struvite

| Situation | Mg:P Ratio | pH | % $PO_4^{3}$ precipitated | Precipitated mineral |
|---|---|---|---|---|
| **Situation 1** | 1.2:1 | 8.5-9 | 97-98.5 | Struvite |
| **Situation 2** | 1.2:1 | 8.4-8.8 | 99-99.6 | Struvite |
| **Situation 3** | 1.1:1 | 8 | 97.6 | Huntite and struvite |

In Table 19 it is observed that the results obtained at the computational simulations relatively agree with what was predicted theoretically for both parameters: Mg:P Ratio and pH.

In respect of Mg:P Ratio in the bibliography it was observed that an increase in the Mg:P ratio increases the amount of P recovered as struvite like the results obtained at the computational simulations.

On the other hand, in respect of pH, in the bibliography it was observed that the suitable pH ranges for the struvite precipitation, that is, P recovery, ranges between 7.5 to 9 but in the results obtained in the project it was observed that the best results correspond to 8-9 range.

In addition, it can be observed that the highest percentage of recovery as struvite only corresponds to Situation 2. This situation corresponding to a process with an FO stage that would double the concentration of the studied waters.

## 4.3. LABORATORY EXPERIMENTS

This section shows the results obtained for the same situations of the Subsection 4.2.5.2 pH at laboratory scale.

### 4.3.1. WW synthesis

The composition of the synthesized waters are illustrated in the Table 19.

Table 20. Composition of WW with fixed Mg:P Ratio studied at simulations ( without FO stage “Situation 1”, FO stage concetrated x 2 “Situation2” and FO x 4 “Situation 3”)

| Ion | Situation 1 | Situation 2 (concentrated x2) | Situation 3 (concentrated x 4) |
|---|---|---|---|
| $PO_4^{3-}$ | 423.52 | 847.04 | 1694.07 |
| $NH_4^+$ | 794.45 | 1588.90 | 3177.81 |
| $Mg^{2+}$ | 130.04 | 260.08 | 433.463 |
| $K^+$ | 241.62 | 483.19 | 966.38 |
| $Na^+$ | 252.35 | 504.70 | 1009.40 |
| $Cl^-$ | 555.80 | 1111,06 | 1970.249 |
| $Ca^{2+}$ | 0.025 | 0.05 | 0.10 |

Table 20. composition of WW with fixed Mg:P Ratio studied at simulations ( without FO stage “Situation 1”, FO stage concetrated x 2 “Situation2” and FO x 4 “Situation 3”) (Continuation)

| Ion | Situation 1 | Situation 2 (concentrated x2) | Situation 3 (concentrated x 4) |
|---|---|---|---|
| $CO_3^{2-}$ | 1181.68 | 2363.32 | 4726.63 |
| $SO_4^{2-}$ | 164.69 | 329.37 | 658.75 |

The quantities of the salts necessary for the synthesis of the waters, calculated by mass balances are the following.

Table 21. Among of salt necessary to synthetize WW studied ( without FO stage “Situation 1”, FO stage concetrated x 2 “Situation2” and FO x 4 “Situation 3”)

| Salt | Situation 1 [g] | Situation 2 (concentrated x 2) [g] | Situation 3 (concentrated x 4) [g] |
|---|---|---|---|
| $Na_2HPO_4 \cdot 12\ H_2O$ | 3.19 | 6.39 | 12.78 |
| $MgCl_2 \cdot 2\ H_2O$ | 2.18 | 4.35 | 7.25 |
| $NH_4CO_3$ | 3.11 | 6.23 | 12.44 |
| $CaSO_4 \cdot 2\ H_2O$ | $1.27 \cdot 10^{-4}$ | $2.54 \cdot 10^{-4}$ | $5.09 \cdot 10^{-4}$ |
| $Na_2SO_4$ | 0.29 | 0.58 | 1.17 |
| $K_2SO_4$ | 0.24 | 0.48 | 0.95 |
| KCl | 0.72 | 1.43 | 2.97 |
| $NH_4Cl$ | $9.11 \cdot 10^{-4}$ | $1.82 \cdot 10^{-3}$ | $3.64 \cdot 10^{-3}$ |

Finally, the salts $CaSO_4 \cdot 2\ H_2O$ and $NH_4Cl$ are not added because the balance available did not allow it. Hence, huntite precipitation is not possible because there is no Ca in the solution.

## 4.3.2. Precipitation of struvite

In this section the results obtained after analysing the liquid samples and the solid samples are shown.

### *4.3.2.1. Liquid phase*

The results shown below correspond to the liquid phase of the solution after having been at rest for 48 hours and having been filtered.

#### Situation1: WW not concentrated Mg:P Ratio 1.2:1

Table 22. Results precipitation "Situation 1" (Variable: pH)

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated |
|---|---|---|
| **3.02** | 91.82 | 8.18 |
| **7.17** | 48.03 | 51.97 |
| **8.55** | 21.87 | 78.13 |
| **9.20** | 15.43 | 84.57 |
| **10.80** | 12.48 | 87.52 |

#### Situation2: WW concentrated x 2 Mg:P Ratio 1.2:1

Table 23. Results precipitation "Situation 2" (Variable: pH)

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated |
|---|---|---|
| **2.25** | 93.16 | 6.84 |
| **6.77** | 44.91 | 55.09 |
| **8.44** | 12.72 | 87.28 |
| **9.39** | 10.91 | 89.09 |
| **11.69** | 3.26 | 96.74 |

Situation 3: WW concentrated x 4 Mg:P Ratio 1:1

Table 24. Results precipitation “Situation 3” (Variable: pH)

| pH | % $PO_4^{3-}$ dissolved | % $PO_4^{3}$ precipitated |
|---|---|---|
| **2.25** | 78.49 | 21.51 |
| **7.09** | 7.72 | 92.28 |
| **8.09** | 1.85 | 98.15 |
| **9.18** | 0.53 | 99.47 |
| **10.05** | 0.26 | 99.74 |

As can be seen at the tables: Table 22, Table 23 and Table 24 when the pH increases, the percentage of P recovered increases. In addition, the best results are obtained as the concentration increases.

On the other hand, it is observed that in Situation 3, that is, the most concentration solution is the one that obtains the highest percentage of P recovery.

Is important to note that, with this analysis technique, only the percentage of recovered P is known, but it cannot be known which mineral has precipitated.

### *4.3.2.2. Solid phase*

In this section the results obtained through X Ray diffraction of the precipitate obtained are detailed.

To verify that the precipitate is struvite, the theoretical diffractogram of the struvite is compared with the diffractogram of the sample.

In all the samples it was observed that the diffractogram obtained was very similar to the theoretical diffractogram of struvite, so much so that it can be considered pure struvite.

Below is a diffractogram of each of the situations studied. Those corresponding to the highest percentage of P recovery, that is, those with the highest pH, have been shown.

Situation 1: WW not concentrated Mg:P Ratio 1.2:1

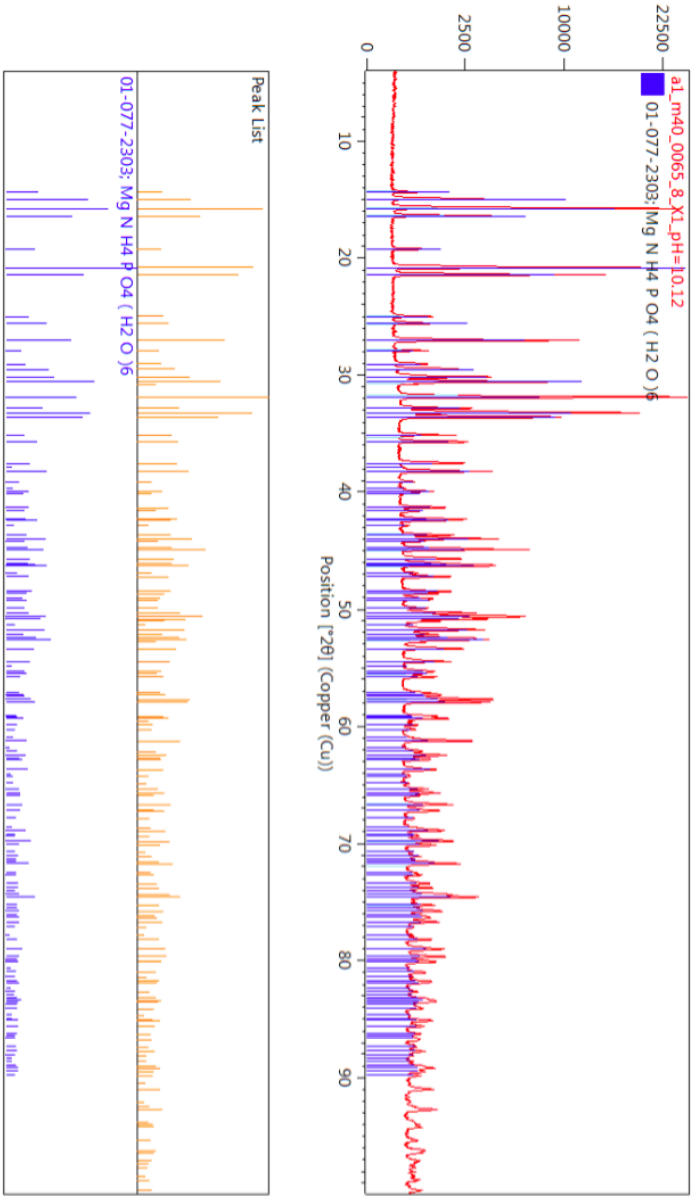


Figure 9. X-Ray diffraction Situation 1 pH= 10.12

## Situation 2: WW concentrated x 2 Mg:P Ratio 1.2:1

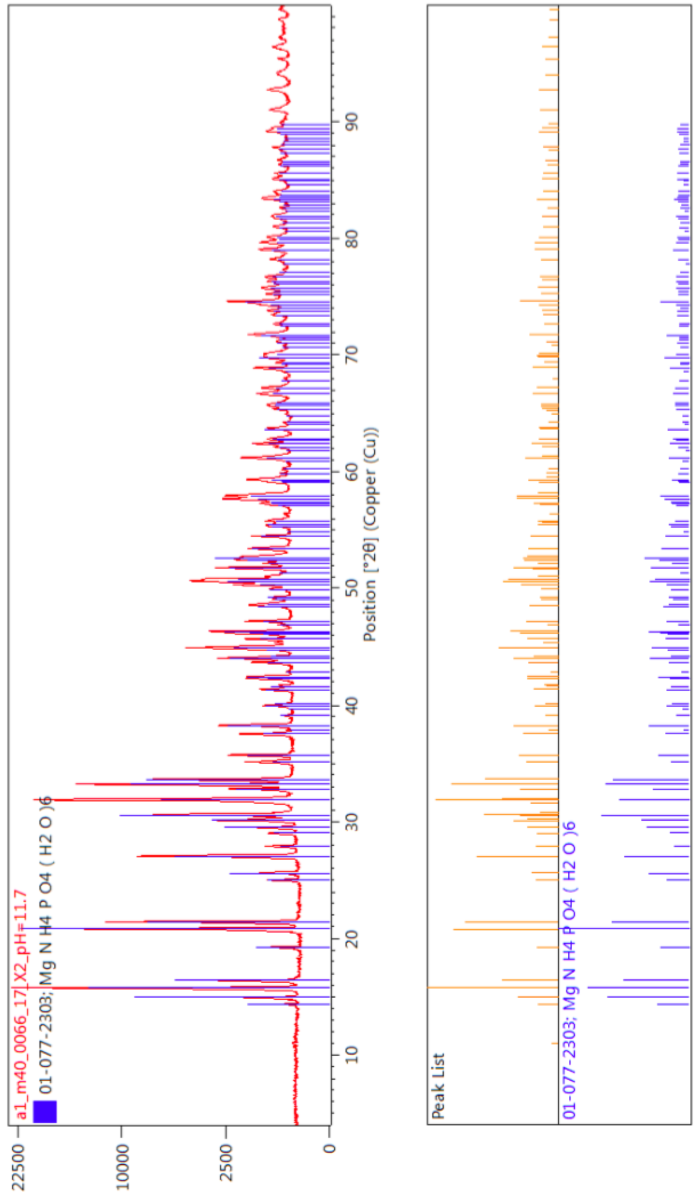


Figure 10. X-Ray diffraction Situation 2 pH=11.7

Situation 3: WW concentrated x 4 Mg:P Ratio 1:1

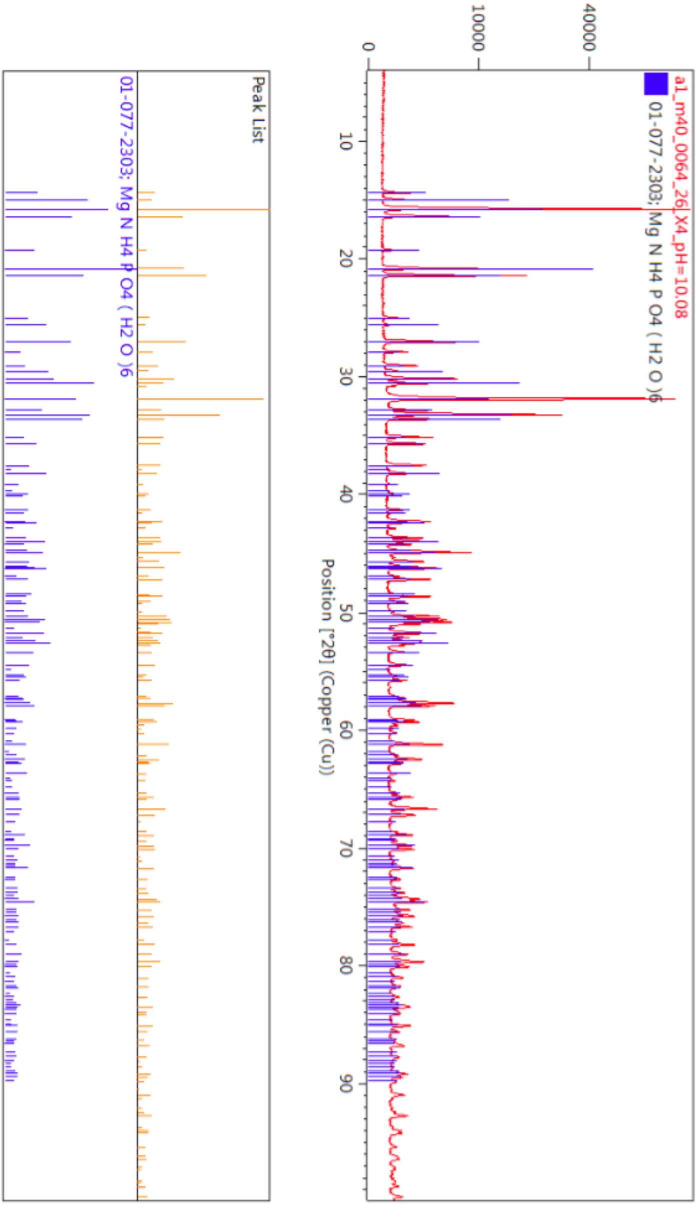


*Figure 11. X-Ray diffraction Situation 3 pH=10.08*

Hence, it is verified that the best results, that is, the highest percentage of P recovered as struvite, is obtained for the highest pH and for the most concentrated solutions. Achieving up to a percentage of P recovered of 99.74% as pure struvite.

The results obtained did not coincide totally with the bibliography or with the results obtained at the computational simulations.

In the bibliography we observed that the pH range in which the struvite precipitated was from 7 to 11.5 but that the best results were in the pH range from 7.5 to 9. In the results obtained in this project it is observed that the best results are obtained with the highest pH: Situation 1 pH 10.8, Situation 2 pH 11.69 and Situation 3 pH 10.05.

On the other hand, at the computational simulations it was observed that at high pH values, the precipitate was formed in addition to struvite of minerals such as $MgPO_4$, hydromagnesite or huntite. In the case of huntite, it can be attributed to the fact that the salts containing Ca were not added.

# 5. FUTURE WORK

As a continuity to the work performed so far, it would be interesting to carry out the following studies:

- Comparative study between the cost associated to implement a FO stage and the cost saving achieved by treating lower WW flow.
- The same study with other type of WW like industrial WW in order to compare the results obtained.
- Repeating the experiments on a pre-industrial scale to study if its possible to implement the crystallization stage studied in a real WWTP.
- Study of the shape of the crystals obtained.

# CONCLUSIONS

During the project, the problems caused by the presence of P in WW, the current state of the P reserves and the process of P recovery as struvite and the parameters that affect it were studied.

Then, a research of real WW compositions, computational simulations of the process studied step by step and laboratory-scale experiments were performed.

The conclusions achieved are as following

- The elimination of P from WW is necessary due to it is one of the causes of eutrophication problems.
- The natural sources of P are non-renewable and limited, due to this an alternative of renewable sources is urgent.
- The most common method of P recovery is through production of struvite precipitates by crystallization.
- Uncontrolled precipitation of struvite in WWTP causes problems in the facilities.
- The presence of Ca prevents the precipitation of P as struvite, therefore, it is necessary to introduce a pretreatment stage in the process to eliminate it.
- The FO stage is beneficial due to in addition to reducing the flow of water to be treated, the amount of P recovered increases.
- The parameters that affect the struvite precipitation are: temperature, stirring, pH, Mg:P ratio, N:P ratio and presence of Ca. Although in this project only pH, Mg:P ratio and presence of Ca was studied.
- The highest percentage of P recovered corresponds to the highest pH and the most concentrated solutions.
- It is possible to recover almost all P present in a solution as struvite (99.74%) from a real municipal WW following the next steps: elimination of Ca, concentrate WW through FO stage, adding Mg as $MgCl_2$ until Mg:P ratio are equal to 1:1 and adding NaOH until pH value of 10.05.

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# ACRONYMS

(P) Phosphorus

(FO) Forward osmosis

(WW) Wastewater

(WWTP) Wastewater treatment plant

(VM) Visual Minteq ver. 3.3

(OLI) Oli Studio (Stream analyzer) v. 9.5

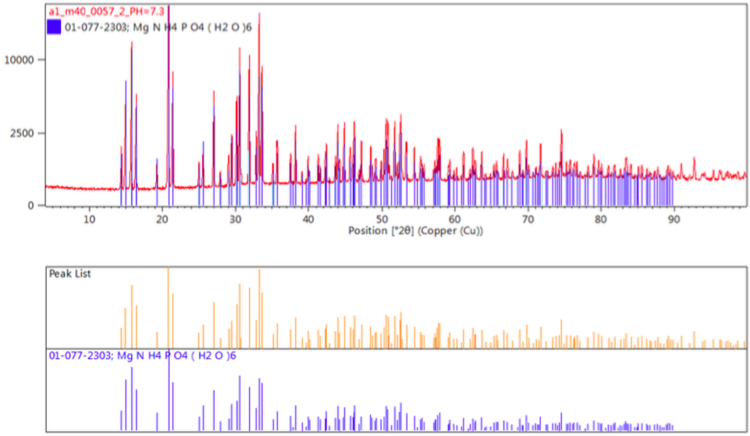
(IPC-OEC) Inductively coupled plasma – Optimal emission spectrometry

# APPENDICES

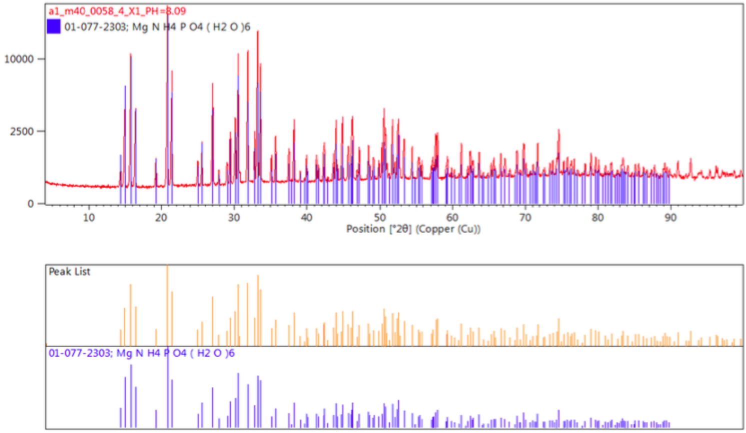
# APPENDIX 1: DIFFRACTOGRAMS

## Situation 1: WW not concentrated Mg:P Ratio 1.2:1

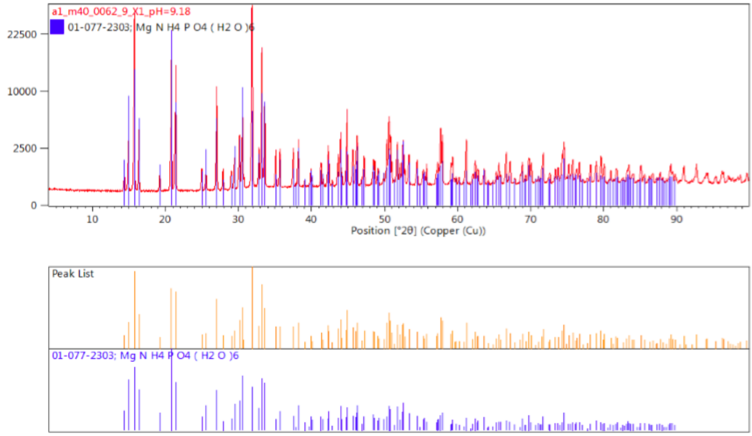
### pH=7.3



### pH=8.09

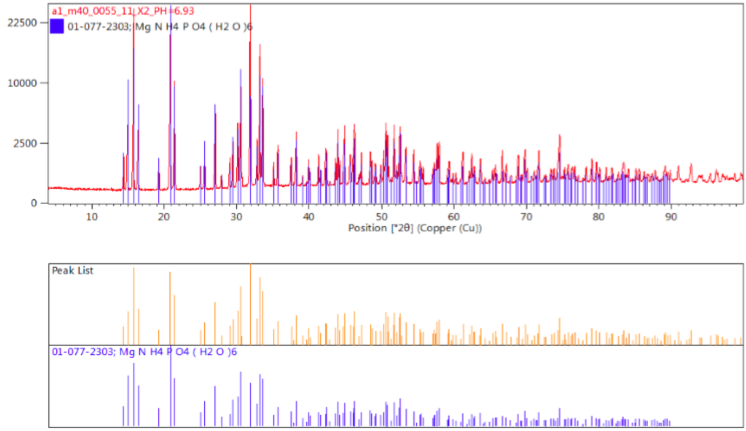


pH=9.18

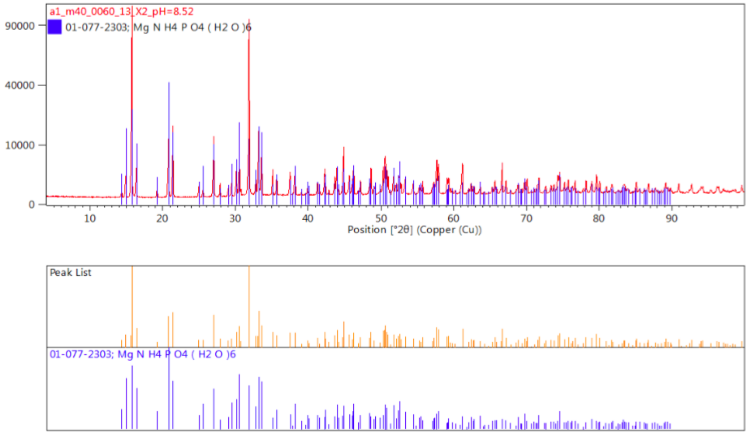


## Situation 2: WW concentrated x 2 Mg:P Ratio 1.2:1

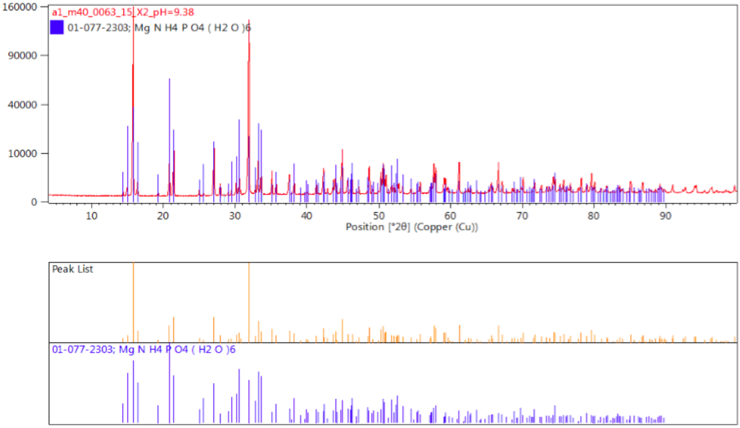
pH=6.93



pH=8.52

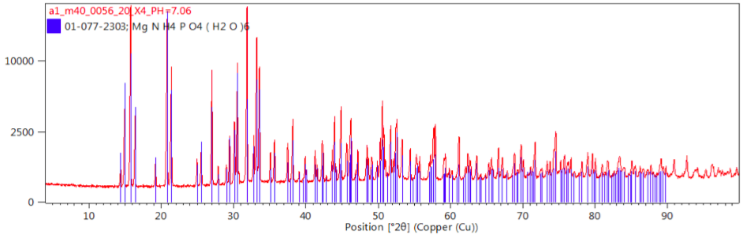

a1_m40_0060_13_X2_pH=8.52
01-077-2303; Mg N H4 P O4 ( H2 O )6
90000
40000
10000
0
10
20
30
40
50
60
70
80
90
Position [°2θ] (Copper (Cu))
Peak List
01-077-2303; Mg N H4 P O4 ( H2 O )6

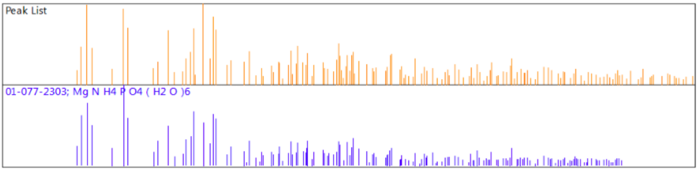
pH= 9.38


a1_m40_0063_15_X2_pH=9.38
01-077-2303; Mg N H4 P O4 ( H2 O )6
160000
90000
40000
10000
0
10
20
30
40
50
60
70
80
90
Position [°2θ] (Copper (Cu))
Peak List
01-077-2303; Mg N H4 P O4 ( H2 O )6

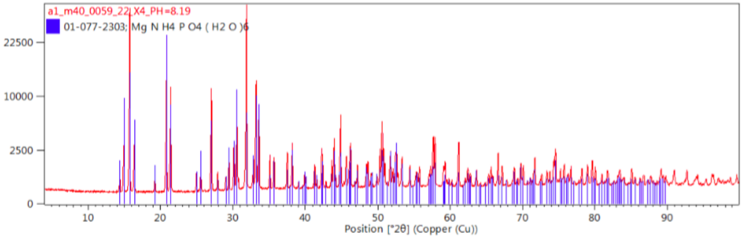
## Situation 3: WW concentrated x 4 Mg:P Ratio 1:1

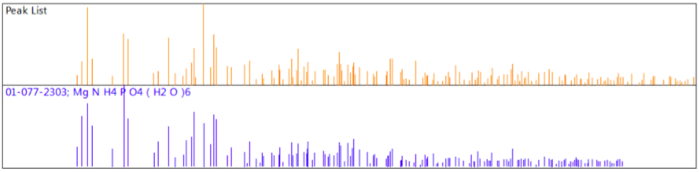
pH=7.06



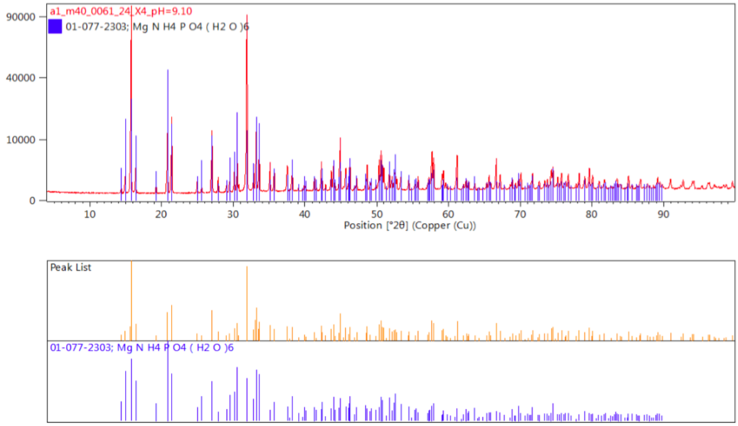


pH=8.19





pH=9.10


a1_m40_0061_24_X4_pH=9.10
■ 01-077-2303; Mg N H4 P O4 ( H2 O )6
90000
40000
10000
0
10
20
30
40
50
60
70
80
90
Position [°2θ] (Copper (Cu))
Peak List
01-077-2303; Mg N H4 P O4 ( H2 O )6