Treball de Fi de Grau

Grau en Enginyeria Química

Phosphate recovery using calcium zeolite in ultrafiltration pilot plant.

MEMORIA

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ABSTRACT

One of the most important ecological problems is the eutrophication, this process consist in the uncontrolled growing of algae and phytoplankton, which can destroy entire aquatic ecosystems. The reason of this process is the excess of nutrients, as for example, phosphate coming from human activities.

This project focus on the study of synthetic zeolites capacity to absorb phosphate from wastewater. Zeolites are porous minerals of the alumina-silicates family with high capacity of cations exchange. They can be natural or synthetic and present a tetrahedral structure that can include alkali or alkaline earth metals, those metals can improve the capacity to absorb determinates contaminants. The zeolite used for this work is a calcium zeolite (Ca-Ze) obtained from a synthetic sodium zeolite (NaP1). The NaP1 is produced using fly ashes as raw material, by hydrothermal process.

The objective of the project is to evaluate: the elimination of phosphate, the equilibrium and kinetic data, using agitated reactors, and the integration of the sorption process with a separation process, using ultrafiltration membrane in different operating conditions. The evaluated operation conditions are designed to simulate the treatment of residual waters coming from industries, households and agricultural fields.

Other experiments as kinetic, isotherms and point zero charge are done to characterize the zeolite used in the ultrafiltration plant and to make a comparison with other zeolites and adsorbents used for phosphate removal.

Analysis results of phosphate loaded samples give information about the phosphate adsorption mechanisms and the adsorption capacity in different working conditions. The formation of calcium-phosphate minerals, brushite, is the principal phenomena during adsorption, it is favoured by low pH as seen in the results.

The analytical techniques used are UV-visible spectrophotometry for phosphate analysis, ionic chromatography for the analysis of different ions presents in the water, X ray diffraction for zeolite sample analysis.

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1. **Glossary**

SETRI: Group on Techniques for Separation and Treating Industrial waste

FA: Fly Ashes

Ca-Ze: Synthetic zeolite modified with calcium

WWII: Second World War

mgP-PO$_4$: milligram of phosphate.

NaP1-NA: Synthetic sodium zeolite, also called **NaP1 and Na-Ze**

K-LB: Potassium zeolite, obtained using fly ashes from Los Barrios.

K-TE: Potassium zeolite, obtained using fly ashes from Teruel.

BOD: Biological Oxygen Demand

BOD$_5$: Biological Oxygen Demand expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20 °C

CIP: Common Intersection Point

p.e.: Population equivalent

P: phosphorus

PAO: Polyphosphate Accumulator Organism

PZC: Point of Zero Charge

XRD: X-ray Diffraction

UF: Ultrafiltration

MF: Microfiltration

NF: Nanofiltration

RO: Reverse osmosis

Re: Reynolds number

CSTR: continuous stirred-tank reactor

PAZ: Powder Activated Zeolite

TMP: Trans Membrane Pressure

Qt: Capacity adsorption

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Q$_P$: Flux of permeate.

SEM-EDS: Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy

2. **Preface**

2.1. **Origin of the project**

This final degree dissertation is part of the research project "Valorisation of by-products from industrial effluents: integration of membrane technologies in the separation, concentration and purification steps ("waste to product") developed by the SETRI group of the Chemical Engineering Department of Superior Technical School of Industrial Engineering of Barcelona. One of the challenges of study is the recovery of nutrients from wastewater (phosphates and ammonium) using adsorbent materials coming from different sources. The objective is to identify materials that allow the removal of nutrients from water to achieve the regulatory levels and at the same time can be valorised to use it for improve quality of agricultural and forest soils.

2.2. **Motivation**

The phosphate reserves are concentrate in very small areas of the planet, the use of this mineral increase every year because is fundamental for the fertilizer production. A growing population need more fertilizers and exploit those resources more and more. The phosphate reserve will have a long live even in the actual situation, and is precisely the low cost of phosphate that cause problems to ecosystem stability. The excessive use of phosphate give eutrophication problems and have big environmental impact in the mining zones. The recovery of phosphates can be a solution to palliate the eutrophication and reduce the mining exploit.

The use of industry by-products for the phosphate recovery is a new way to revalorize wastes, the coal combustion industry generates fly ashes (FA) which disposal is generating in given cases environmental management problems if not adequately treated. Fly ashes have been shown good adsorption properties and they can be used for phosphate recovery. Additionally, have been shown suitable to synthesized zeolites with also good phosphate sorption properties when converted to Ca(II) forms.

The work to be carried out is to validate the performance of calcium activated zeolites as sorption technology to remove phosphate from aqueous solutions and to integrate them in a hybrid process pilot using ultrafiltration as membrane separation technology. Experiments using a pilot sorption by powder zeolites- ultrafiltration plant needs to be evaluated as a new technology in phosphate recovery.

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3. Introduction

3.1. Objectives of the project

The aim of this project is the evaluation, using experimental methodologies, of the phosphate adsorption capacity of a synthetic zeolite obtained using fly ash from coal fired power plants.

This zeolite was modified to obtain a calcium zeolite (Ca-Ze) and it was used in an ultrafiltration a pilot plant to simulate in a scale condition a real depuration plant.

Beside this, the zeolite was characterized using kinetic and batch experiments, and a comparison with other adsorbents was done to know if the adsorption capacity of our zeolite is in the line of the other adsorbents nowadays used.

3.2. Scope of the project

- Know-how of actual technologies of phosphate recovery.
- Identification of adsorbents for phosphate recovery.
- Experimental work in laboratory to evaluate the equilibrium and kinetic parameters of adsorbents.
- Experimental work in laboratory to determinate the capacity of Ca-Ze to eliminate and recover phosphate in a simulated situation using an ultrafiltration pilot plant.
- Evaluation of experimental results and conclusions
- Economic evaluation.

Are not included in the scope of the project:

- Economic evaluation of the implementation of a real plant for wastewater treatment.
- Environmental impact of studied technology.

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4. State of the art.

Nowadays the control and elimination of dangerous contaminants in wastewaters, is one of the most important research fields for industries, governments and other entities related with environmental protection and conservation. One of the growing problem around the world is the eutrophication of aquatic ecosystems such lakes, bays, rivers and even large oceanic zones. One way to palliate eutrophication process is the elimination of phosphate from waste water. During the WWII, due to the lack of natural phosphate, precipitation methods were developed and applied to recover phosphate from water. In 1950's governments around the world establish that the phosphate concentration have to be imitated and this methods were implemented to reach the imposed levels. The chemical precipitation is still the most extended method to recover phosphates, but recently biological methods were applied successfully. Other methods are in developed as for example crystallization, invers osmosis and adsorption, the method studied in this work.

4.1. Zeolites.

Zeolites are porous minerals pertaining at the family of alumina-silicates. The Swedish geologist Alex Fredrik Cronstedt was the first to observe that when heated zeolites release steam, this phenomena occur because zeolites contain water in their structure. In 1756 he call those minerals zeolites, in geek "boiling stones" (*"zeo"* to boil and "*lithos"* stone).

Zeolites were believed to be rare minerals that occur in basaltic stones, therefore they were a non-exploitable resource, and for 200 years, after their discovery, their study was limited at academic area. In 1850 more than 20 different type of zeolite were classified. Their properties were well known, 1840 Damour observed that crystals of zeolite could be reversibly dehydrated without changes in their morphology. In 1858 the German chemic Eichhorn showed the reversibility of ion exchange on zeolite minerals. In 1927 Leonard described the use of X-ray diffraction for zeolite identification, and in 1950's yields of zeolite were discovered in sedimentary deposits in western United States. More deposit were discovered over the world and start their exploit for commercial uses as an adsorbent, pozzolanic cement and concrete and for use in agricultural soils.

The first synthetic zeolites were discovered in 1862 by St. Clarie Deville who synthetize levynite by hydrothermal synthesis. But was not until 1948 when was reported the first definitive synthesis of zeolite and was produced the first zeolite without natural homologue the ZK-5. Between 1949 and 1954 R.M. Milton and D.W. Breck develop the A, X and Y zeolite types, commercialized by Linde of Union Carbide.

Nowadays more than 200 different types of zeolite are classified and there are used is very different fields: as catalyst in cracking and hydrocracking, can facilitate acid-catalysed reactions, such as isomaration and alkylation, are used for water softening in detergents (approx. 80% zeolite production), or for odour control in pet litters. [5]

The first investigations on synthetic zeolites obtained using fly ashes were done by Höller and Wirsching [6]. Fly ashes have similitudes with some volcanic materials, as said before

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zeolites were firstly found in volcanic rocks, therefore FA were studied for the synthesis of zeolites. In books and papers can be found information about the methods for synthesis of zeolites using FA, for example using hydrothermal conversion in alkaline medium [7], microwave or molten salt assisted hydrothermal synthesis [8], or melting methods [9].

In the last years, FA zeolites are the focus of numerous investigations as adsorbents of anions and cations presents in the water. There are studies on adsorption of heavy metals [10], ammonium [11] [12], phosphates [13] and simultaneous adsorption of ammonium and phosphates [14] [15] in wastewaters, with positives results. Many studies are made to find FA zeolites for phosphate removal, for example Chen et al. [16] and Onyango [13] report better capacity of FA zeolites in front of FA without treatment. The most important link is between calcium and phosphate followed by iron link.

4.2. Zeolites structure

Zeolite structure is composed of tetrahedra of alumina (AlO_4) and silica (SiO_4) interlinked by oxygen atoms. They have a relatively open, three-dimensional crystal structure, if Al is incorporated into the silica framework then the +3 charge of Al make it negatively charged, and requires the presence of extra framework cations for example alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium). The composition of zeolites can be described by equation 4.1:

$$M_{n/2}^{m+}O \cdot ySiO_2 \cdot Al_2O_3 \cdot wH_2O \qquad \textbf{Equation 4.1}$$

The extra framework cations give rise to the rich ion-exchange capacity of zeolites, the representation of the basic building block, the tetrahedron, is shown in figure 4.1.
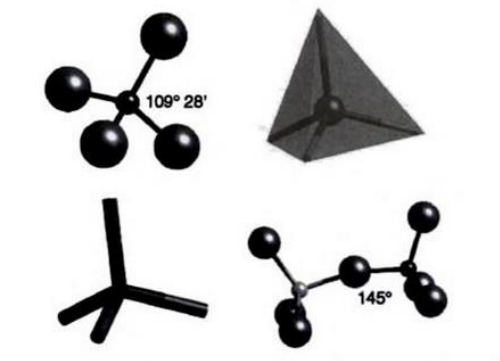
Figure 4.1: Zeolite basic unit, tetrahedron. *Handbook of Zeolite Science and Technology*

Zeolites form with many different crystalline structures, which have large open pores (sometimes referred to as cavities) in a very regular arrangement and roughly the same size as small molecules. An example of the different structures is shown in figure 4.2.
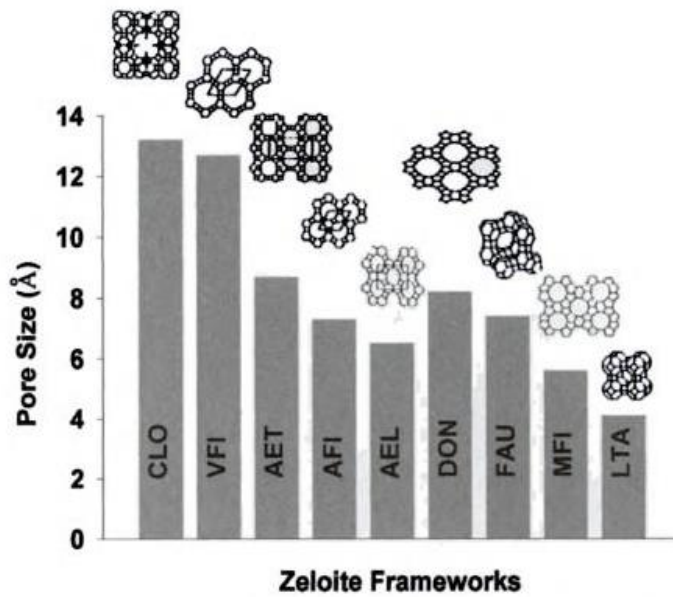
Figure 4.2: Comparison of pore size of different frameworks *Handbook of Zeolite Science and Technology*

Zeolites are very stable solids with high melting points, ~700 ºC in case of low silica zeolites and ~1300 ºC for completely siliceous zeolites. Two important properties are a) their open, cage-like, framework structure to trap molecules in their structure and reject molecules bigger than pore dimensions; b) the inclusion of extra framework cations exchangeable confering the ion-exchange properties. In the last years the synthesis of zeolites bring the possibility to create specific frameworks with controlled pore dimensions and the inclusion in the structure of determinate cations. In the book *"Atlas of Zeolite Framework Types"*, 176 different structures are described. [1]

An example is the zeolite with code GIS, the mineral gismondina, which include, the NaP1 ($Na_6Al_6Si_3O_{10} \cdot 12H_2O$), the synthetic zeolite modified and used in this work.
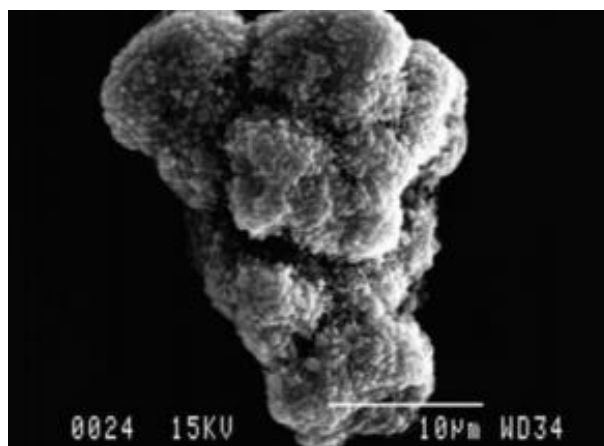
Figure 4.3: SEM image: synthetic zeolite NaP1 produced using FA. Narcea Querol et al. 2007

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The ion exchange and water retention properties are useful to prepare slow time release fertilizers, or improvements of soil quality. A study demonstrate that the addition of zeolite, resulted in a marked improvement in the soil's ammonium retention capacity. In these project will be investigated the capacity of phosphate recovery from waste waters using different type of synthetic zeolites and the possible application in agriculture. [2], [3], [4], [19]

4.3. The phosphorous cycle

Phosphorous cycle unlike other bio-geological cycles have no gaseous phase. The phosphorus cycle start in phosphoric rocks, due the action of tectonic movement and erosion, phosphoric rock are exposed to the elements. Rain dissolve the phosphoric rock and the rivers transport the dissolved phosphate to lakes, flooded areas, and oceans. The phosphate sedimentation create new deposits of phosphoric rock and after millions of years tectonic movements will expose again the rocks and the cycle start again.

This is the natural cycle, but nowadays human activity have to be included. The phosphoric rock is treated to obtain phosphate and this phosphate is used in industry and agriculture. Even if developed countries had limited or prohibited to discharge of wastewaters into rivers, lakes and oceans, in developing countries still do that. The phosphate that come from agriculture normally arrive filtrating into the subterranean waters and then arrive to the superficial waters.
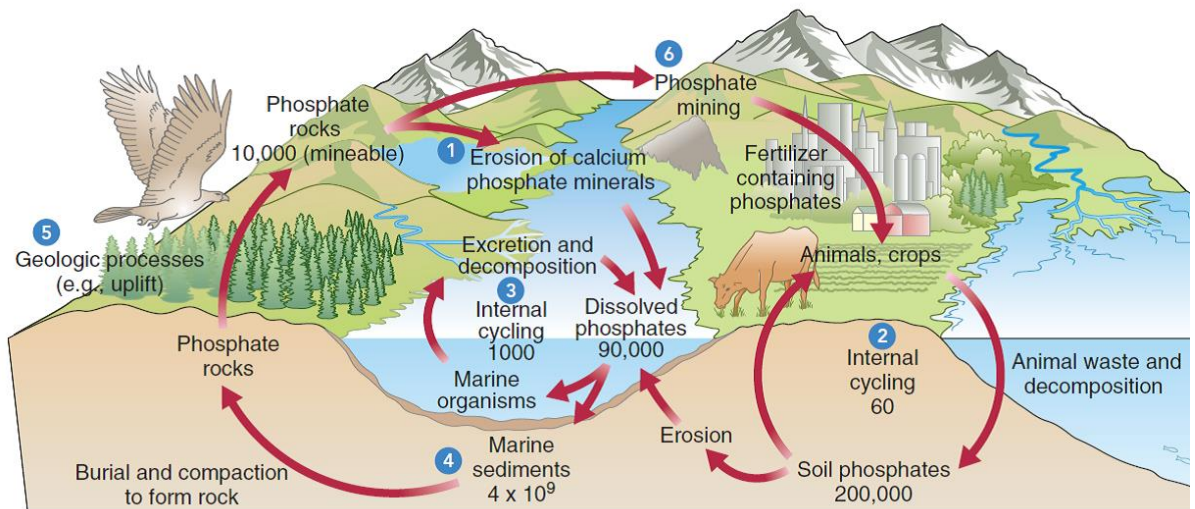
Figure 4.4: Phosphate cycle. Flows (10^{12}g P / year) (Solomon, Berg and Martin, 2010).

4.4. The problem of phosphate

Phosphorus, is used by all the living organisms on earth, is incorporated in nucleic acids and ATP. Phosphorous nitrogen and potassium, are the tree most important compounds for plants growing and phosphorus is considerate a limiting agent. Phosphate represents the 0.076% of the earth's crust, is the 11th most abundant element on earth and the 13th in

water. The most common form is apatite [$Ca_5(PO_4)_3(F,Cl,OH)$], it represent the 95% of all the phosphoric rocks. [19]

The human activity and specially agriculture need phosphate. The industry of fertilizer use around the 85% of all the phosphate produced in the world, the 5% to prepare detergents and the rest for other products. The excessive use of fertilizers can contaminate the water near the fields, if crops don't use all the fertilizer it filter into the soil and arrive to the sub terrain waters or the rivers and lakes near.

Phosphate used as a surfactant agent in detergents, contain high levels of phosphate and the growing population had increased the organic phosphate because only the 2% of ingested phosphorus is assimilated. Due that households wastewaters can contain a 70% of orthophosphates (figure 4.6), organic phosphate and polyphosphates ($P_3O_{10}^{-5}$ o $P_2O_7^{-2}$)
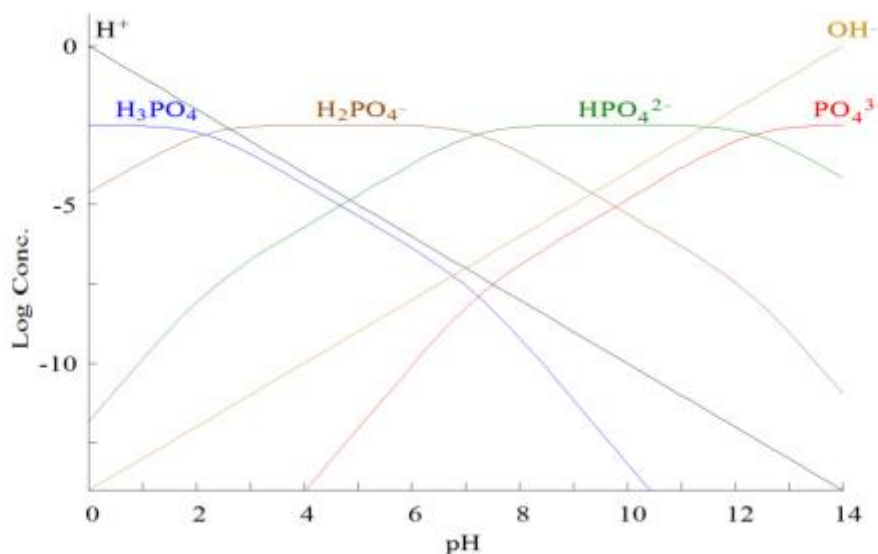
Figure 4.6: Orthophosphate Log C. diagram. Total PO_4^{3-} $3.2 \cdot 10^{-3}$ M, "Estudi de la recuperació de fosfats d'aigües residuals amb zeolites sintètiques"

4.5. Eutrophication

The term eutrophication come from the geek and means good nutrition is associated to the excess, natural or anthropogenic, of nutrients like nitrogen and phosphate into and ecosystem (normally aquatic). Potassium, Nitrogen and Phosphate are the tree basic compounds for plants grown and phosphate is considered a limiting agent, for example in water the relation N:P is normally 16:1. [18]That is why the presence of phosphate in wastewaters, coming from human activity are the responsible of innumerable cases of eutrophication around the world.

The high concentration of phosphate can cause an uncontrolled growing of water flora (from microscopic algae and plankton to macroscopic algae or water plants). The algae may keep out the light and when they eventually die, they are decomposed by bacteria which consume oxygen in this process. The water may become temporarily anoxic (hypoxia) which may be toxic to aquatic life. Some studies demonstrate that a concentration of 0.02 mgP-PO_4/l in

water can be dangerous for some aquatic ecosystems. [17]

European Union directive 91/271/CEE define eutrophication as an increase of nutrients in water, specially nitrogen and/or phosphate that produce an accelerated grown of vegetal species with undesired effects on the equilibrium between living organisms in water and the quality of the water. [20]

4.6. Phosphate legislation

The European legislation 91/271/ECC, require the recollection, using a collecting system, and appropriate treatment of wastewater in agglomerations with more than $2x10^3$ p.e. (Population Equivalent), a secondary treatment is obligatory in those agglomerations. A more advanced treatment is needed in agglomerations with more than 10^4 and 10^5 p.e. For those cases the amount of phosphate cannot be higher than 2 and 1 mgP-PO_4/l for each case. The minimum reduction for both cases is the 80% of the amount of phosphate. Normally the EU and USA, states had established the limit to 1 mgP-PO_4/l. The terms used in this abstract of Directive 91/271/ECC are described in Article 2:

> - 'Agglomeration' means an area where the population and/or economic activities are sufficiently concentrated for urban waste water to be collected and conducted to an urban waste water treatment plant or to a final discharge point.
>
> -'Collecting system' means a system of conduits which collects and conducts urban wastewater.
>
> -'1 p.e. (population equivalent)' means the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60 g of oxygen per day.
>
> -'Primary treatment' means treatment of urban waste water by a physical and/or chemical process involving settlement of suspended solids, or other processes in which the BOD_5 of the incoming waste water is reduced by at least 20 % before discharge and the total suspended solids of the incoming waste water are reduced by at least 50 % .
>
> -'Secondary treatment' means treatment of urban waste water by a process generally involving biological treatment with a secondary settlement.
>
> -'Appropriate treatment' means treatment of urban waste water by any process and/or disposal system which after discharge allows the receiving waters to meet the relevant quality objectives and the relevant provisions of this and other Community Directives. [20]

## 4.7. Phosphate wastewater treatment technology

The wastewater treatment is actually done in special structures with the objective of remove the major quantity of contaminants present in the residual waters. A primary treatment is applied, in this case the eliminated pollutants are organic and inorganic small particles by

combination of sedimentation or gravity settling, chemical coagulation, or filtration. In secondary treatment is eliminated the BOD (Biological Oxygen Demand), it is eliminated by biological process. After this treatments wastewaters still contain phosphates and nitrogen and even other contaminant that cannot be eliminated with normal treatments. An advanced treatment is need to eliminate them and normally is an extension of secondary treatment. For phosphate elimination the most common method is the chemical precipitation, developed in the 1950's, the Biological Phosphate Removal is now implemented successfully and but other methods are in use and development as for example adsorption, membranes for advanced filtration, ion exchange, and reverse osmosis.

## 4.8. Phosphate removal by chemical precipitation

Chemical precipitation is the most used method to eliminate phosphates from wastewaters. It was firstly implemented in Swiss in the 1950s, is a reliable method and none significant changes have been acted in years. Is not an economic method because chemical precipitants have to be used but the efficacy justify the price. It consist in the addition of a Al, Fe or Ca coagulant salts where the insoluble phosphate salts that can be separated by sedimentation. Anionic polymers can be added to help the formation of flocks to easily separate solids.

Calcium: It is usually added in the form $Ca(OH)_2$. At pH values about 10, the excess calcium ions presents in wastewater react with the phosphate precipitating hydroxyapatite:

$$10\ Ca^{2+} + 6\ PO_4^{3-} + 2\ OH^- \leftrightarrow Ca_{10}(PO_4)*6(OH)_2\ (s)$$
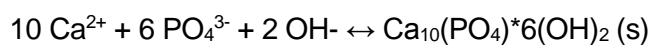
Aluminium and Iron:

Aluminium or hydrated aluminium sulphate is widely used precipitating phosphates and aluminium phosphates ($AlPO_4$). The basic reaction is:

$$Al^{3+} + HnPO_4^{\ 3-n} \leftrightarrow AlPO_4(s) + nH^+$$
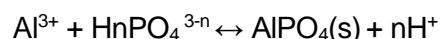
The efficiency of coagulation falls as the concentration of phosphorous decreases. In practice, an 80-90% removal rate is achieved at coagulant dosage rates between 50 and 200 mg/l. Dosages are generally established on the basis of bench-scale tests and occasionally by full-scale tests, especially if polymers are used. Aluminium coagulants can adversely affect the microbial population in activated sludge, especially protozoa and rotifers, at dosage rates higher than 150 mg/l.

Ferric chloride or sulphate and ferrous sulphate also known as copperas, are all widely used for phosphorous removal, although the actual reactions are not fully understood. The basic reaction is:

$$Fe^{3+} + HnPO_4^{3-n} \leftrightarrow FePO_4(s) + nH^+$$
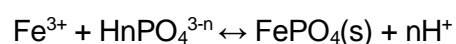
Ferric ions combine to form ferric phosphate. They react slowly with the natural alkalinity and so a coagulant aid, such as lime, is normally add to raise the pH in order to enhance the coagulation. [21]

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The coagulants can be introduced in different stages of the treatment, before primary treatment, due the elimination will be done in the primary treatment tank. In the aeration tank or in the flux before secondary treatment, eliminating phosphates in secondary treatment stage. Or finally can be added in a tertiary treatment. In the picture below are shown the schemes of the tree possibilities.
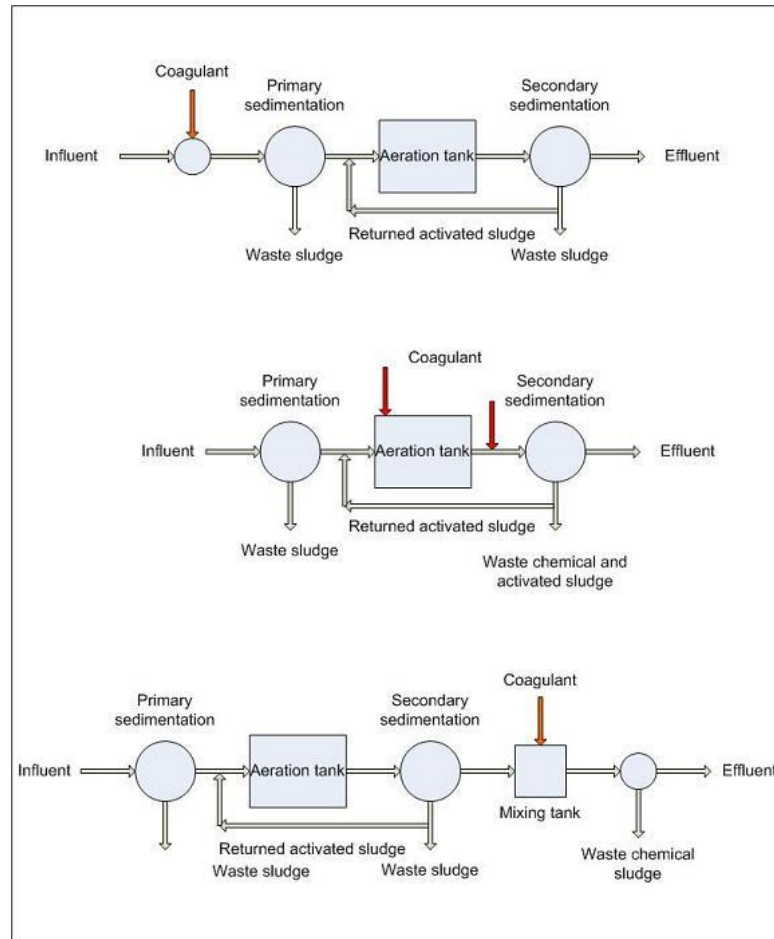
Figure 4.7: introduction of coagulant in the different stages.

4.9. Biological process of phosphate removal

Over the past 20 years, several biological suspended growth process configurations have been used to accomplish biological phosphorous removal. The most important are shown in the following picture.
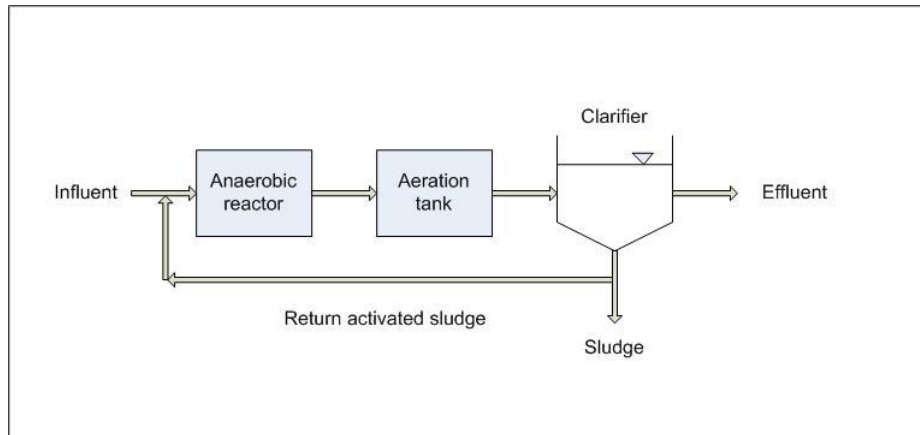
Figure 4.8: Scheme of biological treatment plant.

The principal advantages of biological phosphorous removal are reduced chemical costs and less sludge production as compared to chemical precipitation.

To precipitate phosphorous are used microorganisms, called Phosphate Accumulating Organisms (PAO). In the anaerobic reactor PAO accumulate phosphorous in polyphosphate form for their metabolic grown. The retention time in the anaerobic tank is about 0.5-1 hour and its contents are mixed to provide contact with the return activated sludge and influent wastewater. In the aerobic zone the PAO release the accumulated polyphosphate in orthophosphate form. The concentration of phosphate in the effluent water is normally around 0.1 mgP-PO$_4$/l. [21]

4.10. Sorption technologies of phosphate removal

The adsorption is a physic-chemical phenomenon based on the interaction between molecules of gas or liquid with the surface of a liquid or solid. The physical adsorption is based on Van der Waals forces between the atoms of adsorbate and the surface of adsorbent. In chemical adsorption the molecules or atoms of the adsorbate are joined to the surface of the adsorbent by chemical bond as for example covalent bond.

The materials chosen for adsorption processes have to present the largest possible surface area to maximize the interaction between the adsorbate and the adsorbent. Materials with a big specific surface such as activated carbon, zeolites or mineral clays are normally used. [22]

The phosphate removal using adsorption, even if is not commercially implemented, is a new important field of research. Many studies have proven that adsorption can eliminate high percentage of dissolved phosphate. An emerging trend is the use of industry byproducts, for example fly ashes and synthetic zeolites obtained using those FA. Metal oxides are used too, the alumina (AlO$_3$) and iron oxide (III) (Fe$_2$O$_3$) were used with good results. [23], [24].

## 4.11. Other methods for phosphate removal

Other investigations, with the common objective of phosphate removal, are carried out by

investigation laboratories and universities. For example Nihal Bektaş et al. used electro-coagulation to remove phosphate from wastewater. Ebbers et al [24] tried to recover phosphates using electro-dialysis.

4.12. Ultrafiltration

In the recent years, separation process using barriers and other solid agents have increased because the progress in the fabrication of selective adsorbents and membranes. Membranes can separate streams in different ways, by chemical potential (Osmosis), concentration difference (Dialysis), voltage/current (Electro dialysis) and pressure (MF, UF, NF, RO).

In the separation process a liquid feed containing two or more components pass through a semipermeable barrier (membrane). The components are partially separated obtaining two flows: Permeate, that part that does pass through the membrane and retentate, which do not pass through the membrane.
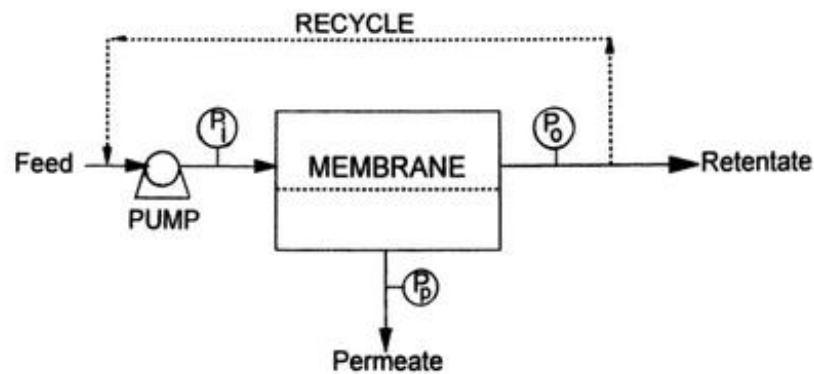
Figure 4.9: scheme of pressure membrane separation process

Is important to note that in MF, UF, NF and RO membranes the separation is done by a physical process, the separation capacity depends on the pore dimension, smaller pores allow to separate smaller particles. In ultrafiltration the dimension of the pore can vary from 0.001 to 0.02 µm and allow to separate macromolecules. [25]

Membrane Separations
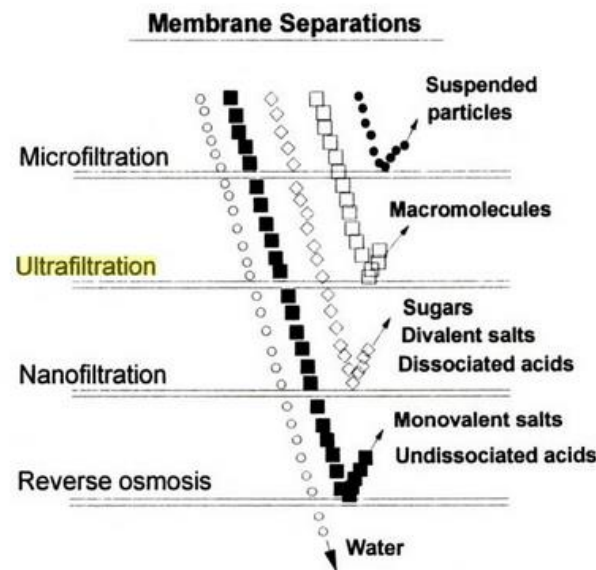
Figure 4.10: Pressure driven membrane separation characteristics

In the figure are shown the different separation capacity of the pressure-driven membranes.

Ultrafiltration membranes are used in very different fields: alimentary industry separation process like juice concentration and clarification and milk purification, pharmaceutical industry, wastewater and drinking water treatments and for laboratory grade manufacturing. That because those membranes do not alter the properties of the separated streams. [26]

4.13. Hollow fibre membrane

Hollow fiber membranes start their development in the 1960s, in 1969 DuPont commercialized the first aramid polymer hollow fiber. Other companies followed and developed their own technologies, Dow Chemical Company and Toyobo create cellulose triacetate polymer membrane. A hollow fiber membrane is a capillary having an inside diameter of less than 25 µm and an outside diameter of less than 1 mm. The fibers are normally grouped into a bundle, which can contain tens of thousands of fibers or, in the case of RO membranes, several millions.

Hollow fibers offer advantages in front of flat-sheet or tubular membranes, they have a higher productivity because of the high packing density and the large surface area. They are self-supporting, it means they can be simply plotted into a standard size tube without other supports. In case, for example, of UF tubular membranes they need to be assembled using spacers and porous supports [26].

The hollow fiber can be assimilated to a tube due can be applied the fluid-dynamics roles. The flow regime can be determinate by Reynolds number (Re), the laminar or turbulent regime affect the mass transfer, of it is turbulent the mass is randomly distributed across all the fiber surface improving the separation. Re formula is:

$$Re = \frac{\rho \cdot V \cdot L}{\mu} = \frac{v \cdot L}{\nu}$$

Equation 4.1

Where:

- V is the mean velocity of the object relative to the fluid (m/s)
- L is a characteristic linear dimension, (m)
- µ is the dynamic viscosity of the fluid (Pa·s or N·s/m² or kg/(m·s))
- v is the kinematic viscosity (v = µ/ ρ) (m²/s)
- ρ is the density of the fluid (kg/m³).

The flow rate of the inlet of the fiber can be determinate using the formula:

$$Q = V \cdot A = V \cdot \pi \cdot \left(\frac{D}{2}\right)^2$$

Equation 4.2

Where:

- Q is the flow rate of the fluid (m^3/s)
- A is a the area of the transversal tube section, (m^2)
- D is the diameter of the tube (m)
- V is the speed of the fluid (m/s)

Knowing the flow rate of one of the outlet fluxes (permeate or retentate) can be known the other by difference.

5. Adsorption equilibrium models

The adsorption equilibrium could be described by model isotherms that show the ratio between the absorbed amount of a substance and remaining in solution when is reach the equilibrium. The isotherm describes the capacity to retain a substance from aqueous media to solid in determinate conditions of temperature and pH. Langmuir and Freundlich models are extensively applied using the sorption capacity data as described by equation 5.1:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m_s}$$
<div align="right">**Equation 5.1**</div>

Where:

Q_e (mg/g) is the capacity of adsorption in the equilibrium.
C_0 and C_e (mg/dm^3) are the initial concentration and the concentration at equilibrium in the solution.
V (dm^3) is the solution volume.
m_s (g) is the mass of adsorbate.

5.1. Langmuir isotherm

The isotherm is based on the hypothesis that the adsorption process occur in one layer and assumes that this adsorbent has an homogeneous surface, due that all the adsorption points are identical and equivalent. Langmuir model is described by equation 5.2 [32]

$$Q_e = \frac{K_L \cdot Q_m \cdot C_e}{1 + K_L \cdot C_e}$$
<div align="right">**Equation 5.2**</div>

Where:

Q_m (mg/g) is the maximum adsorption capacity.
K_L (dm^3/mg) is the Langmuir adsorption constant.
C_e (mg/dm^3) is the concentration at equilibrium.

The linearized form of the Langmuir isotherm is represented by the equation 5.3:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L \cdot Q_m}$$
<div align="right">**Equation 5.3**</div>

The values of the parameters Q_m and K_L are adjusted using the lineal regression of the representation C_e/Q_e function C_e. As can be seen in Equation 5.3, Q_m is the invers of the slope of the lineal representation and K_L is the product of the slope and y-intercept.

5.2. Freundlich isotherm

Freundlich isotherm describe non homogeneous and multilayer adsorbents with different adsorption capacity in each point of the surface. This isotherm is widely used in liquid-solid

adsorption.[32] And it is described by equation 5.4:

$$Q_e = K_F \cdot C_e^{1/n}$$

Equation 5.4

Where:
K_F ($mg^{1-1/n} \cdot dm^{3n} \cdot g^{-1}$) is Freundlich adsorption constant.
n is the parameter of intensity of Freundlich (n>1 represents a favourable adsorption).
C_e (mg/dm^3) is the concentration at equilibrium

The linearized form of Freundlich isotherm is the equation 5.5:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Equation 5.5

The values of the parameters K_F and n are adjusted using the lineal regression of the representation $\ln(Q_e)$ function $\ln(C_e)$. As can be seen in equation 5.5, n is the invers of the slope of the lineal representation and K_L is the exponential of y-intercept. [34]

5.3. Kinetic models for solid-liquid adsorption

The kinetic model give the possibility to know the evolution of the adsorption capacity (Q in mg/g) in function of the time (t in s). The basic equation of kinetic is:

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m_s}$$

Equation 5.6

Q_t is the adsorption capacity at a time t, C_0 and C_t are the initial concentration and the concentration at time t. V is the volume of the solution (dm^3) and m_s is the mass of the adsorbent (g).

5.3.1. Pseudo first order kinetic model

The pseudo first order model was introduced by Lagergren in 1898, he presented a model for the adsorption of oxalic acid and malonic acid onto charcoal. Lagergren's kinetics equation may have been the first one in describing the adsorption of liquid-solid systems based on solid capacity. In order to distinguish kinetics equation based on concentration of solution and adsorption capacity of solid, Lagergren first order rate equation has been called pseudo-first order.[35]

The equation of the model have been widely used for adsorption in liquid solutions, the equation 5.7 is the pseudo first order model.

$$\frac{dQ_t}{dt} = k_1 \cdot (Q_e - Q_t)$$

Equation 5.7

Where k_1 is the speed constant of pseudo 1st order, Q_t and Q_e (mg/g) are the adsorption capacities in the time t and at the *equilibrium*. The t is the time since the adsorption starts. The differential equation can be solved applying initial conditions. $Q_t = 0$ at time 0 (t=0), $Q_t = Q_t$ at time t. In this conditions the equation is:

$$\ln(Q_e - Q_t) = \ln(Q_e) + k_1 \cdot t \qquad \textbf{Equation 5.8}$$

The *ln(Q_e-Q_t)* can be represented in function of *t,* the regression curb obtained give k_1 as the pendent of the curb and Q_e as the exponential of the y-interception.

5.3.2.   Pseudo second order kinetic model

This case is similar to the pseudo 1st order, but in the pseudo 2nd order equation the chemical adsorption is considered a limiting stage of the adsorption process. The equation is very similar to the pseudo 1st order equation:

$$\frac{dQ_t}{dt} = k_2 \cdot (Q_e - Q_t)^2 \qquad \textbf{Equation 5.9}$$

If the same condition of the pseudo 1st order are considered the differential equation can be expressed as follow:

$$\frac{t}{Q_t} = \frac{1}{k_2 - Q_e^2} + \frac{t}{Q_e} \qquad \textbf{Equation 5.10}$$

Representing *t/Q_t* as function of *t/Q_e*. The regression curb give Q_e as the inverse of the pendent and k_2 can be found using y-intercept.

5.3.3.   Elovich kinetic model

This is a model based on chemical adsorption, it was firstly introduced to describe the exponential decrease of the adsorption capacity when the surface of the adsorbent is covered by de adsorbate. This model is widely used for gas-liquid systems but is useful for liquid-solid systems too. It can be employed for modelling chemisorption on heterogeneous surfaces. The equation of the Elovich model is:

$$\frac{dQ_t}{dt} = a \cdot e^{-b \cdot Q_t} \qquad \textbf{Equation 5.11}$$

The parameter *a* is related with the adsorption speed (mg/(g·s)), parameter *b* is the desorption constant (g/mg), *t* and Q_t are the same parameters of the pseudo 1st and 2nd order models.

Imposing the initial conditions: Q_t = 0 at time 0 (t=0), Q_t = Q_t at time t. The equation can be solved as follow:

$$Q_t = \ln(a \cdot b) + b \cdot \ln t \qquad \textbf{Equation 5.12}$$

Representing *Q_t* as function of *ln(t).* The regression curb give *b* as the pendent and *a* can be found using y-intercept.

5.4. Acid-base properties of adsorbents.

The point of zero charge (PZC) describes the condition when the electrical charge density on the surface of an adsorbent is zero. To determine the PZC is applied the CIP (common

intersection point) method to the potentiometric curbs of the adsorbent. The surface charge is calculated by the equation 5.13:

$$b = C_a - C_b + [H^+] - [OH^-]$$

Equation 5.13

The parameters of the equation are: b (mol/g) is the consumption of hydroxide ions, C_a and C_b are the respective concentration of acid and base (mol/dm^3); $[H^+]$ and $[OH^-]$ are the concentrations of protons and hydroxide measured by pH for a determinate volume of solution and weight of zeolite.

6. Materials and methodology

6.1. Cleaning and preparation of laboratory materials and set-ups.

Every time is needed to prepare all the utensils for an experiment before start, all the plastic and glass material have to be cleaned using firstly tap water and then distillated water, is very recommended to not use soap for the cleaning because it contain phosphate that can interfere with the experimental. If it is needed can be used low concentrated hydrochloric acid to do the first cleaning, the material is submerged in the solution for 24 hours and then cleaned using distillated water. When cleaned, tools, can be dried in the hoven, for plastic material is recommended to put a maximum temperature of 60 ºC.

6.2. Calcium zeolite preparation

In this process the objective is the transformation of sodium zeolite in calcium zeolite, which mean the substitution of sodium (Na^+) by calcium (Ca^{2+}) in the structure.

For the experiment are needed: 2 l beaker, Ca^{2+} 0.5 M solution using $CaCl_2 \cdot H_2O$ as reagent, Milli-Q water, balance, pH meter (pH METER GLP22 Crison), magnetic agitation (Heidolph MR Hei-Tec), vacuum system, Büchner funnel and Kitasato.

Firstly 250 grams of Na-Ze are weighted and putted into the beaker, then 1 liter of the $CaCl_2$ solution is added, before start agitation is needed to measure the pH and take a sample. The agitation time is approx. 1 hour and the agitation speed 500 rpm. When it is time agitation stops and leave the solution to stand for at least 5 minutes, then can be taken a second sample and a new pH measure. Done this using the vacuum system all the liquid have to be separated from solid. The solution is thrown in the filter trying not to lose solid. The zeolite trap in the filter is cleaned and returned in the beaker using Milli-Q water, 1 liter Milli-Q water have to be used for clean filter, beaker walls and refill the beaker. The beaker with the zeolite and Milli-Q water return to the magnetic agitation for 10 minutes. After that is filtered again to remove the water, when filtration finish the paper filter is cleaned using the calcium chloride solution and as done before is used for clean the beaker walls and refill the beaker.

Again is taken one sample and pH measure, and start agitation for one hour more. This process have to be repeated five times more to convert Na-Ze to Ca-Ze.

Finished the 5 cycles all the zeolite is filtered and have to be dried in the hoven at a maximum temperature of 50 ºC. When the powder is dry is weighted to know how much quantity was lost during the process.

6.3. Ultrafiltration pilot plant

One of the main challenges of this project is the integration of the sorption using a stirred tank reactor with a zeolite separation step using ultrafiltration membrane modules. This

configuration set-up was used to simulate the implementation of the process at full scale level on wastewater treatment plants. In figure 6.1 it is shown the scheme of the pilot plant.
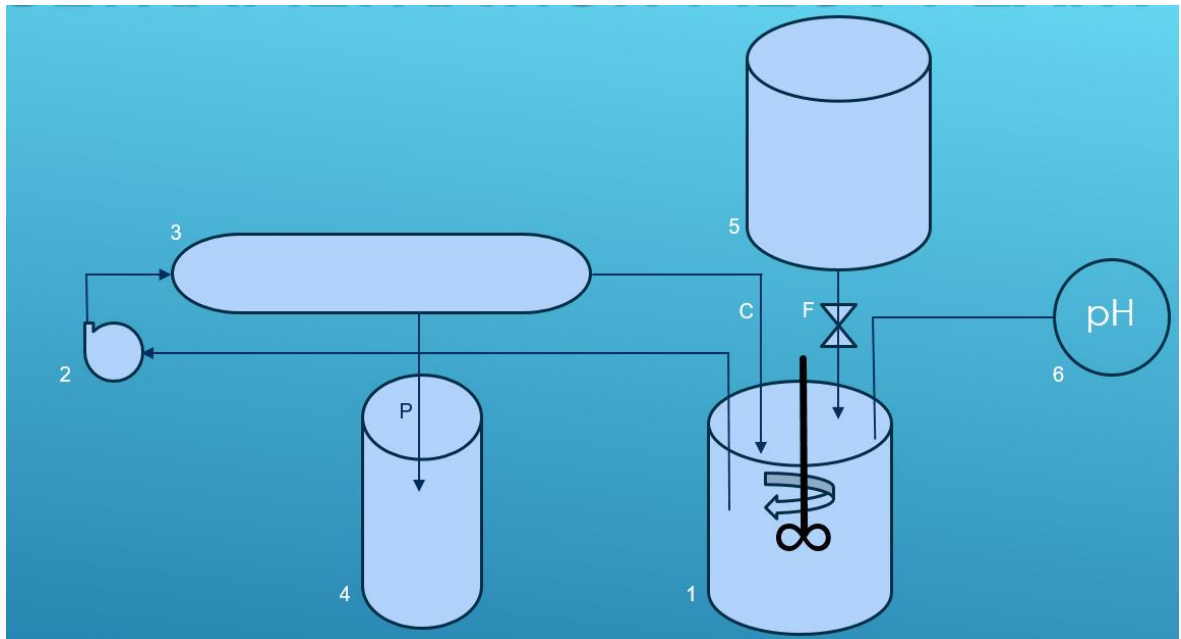
Figure 6.1 Pilot plant scheme

The sorption-membrane separation pilot plant is composed by the following main components:

1. Continuous stirred tank reactor (CSTR) of 40 l capacity, agitation speed up to 1000 rpm, normal working speed 350-400 rpm.
2. Peristaltic pump with flow control.
3. Ultrafiltration membrane module.
4. Permeate tank, stored permeate is used for back wash when experiment is finish.
5. Buffer tank, two are used, when the shown in figure is near to finish the other is used for refilling.
6. pH meter for control of pH experiments.

6.3.1.   Mass balance of the ultrafiltration pilot plant

The total amount of phosphate retained by the powder activated zeolite $m(PO_4)_{PAZ}$ can be calculated using equation 6.1. From figure 6.1 can be obtained the equations to evaluate the terms of the equation.

$$m(PO_4)_{PAZ} = m(PO_4)_C + m(PO_4)_0 - m(PO_4)_P - m(PO_4)_T$$ **Equation 6.1**

Where:
$m(PO_4)_{PAZ}$: amount of phosphate retained by the powder activated zeolite.
$m(PO_4)_C$: amount of phosphate in concentrate stream.

$m(PO_4)_0$: initial amount of phosphate.
$m(PO_4)_P$: amount of phosphate in permeate stream.
$m(PO_4)_T$: amount of phosphate in CSTR stream.

The flow rate of the CSTR outlet stream is given by the pump settings and is known. The permeate flow rate is during the operation of the pilot plant. The concentrations of phosphate for each stream are given by the samples analysis.

The amount phosphate in the stirring tank is calculated using equation 6.2:

$$m(PO_4)_T = V_T \cdot C_T$$
$$\textbf{Equation 6.2}$$

Where V_T is the volume of the CSTR and C_T concentration phosphate in the CSTR.

The amount of phosphate in the concentrate, and the amount in permeate are calculated by the equations 6.3 and 6.4:

$$m(PO_4)_C = m_{Ci-1} + Q_{Ci} * \Delta t_i * \frac{C_{Ci}+C_{Ci-1}}{2}$$
$$\textbf{Equation 6.3}$$

$$m(PO_4)_P = m_{Pi-1} + Q_{Pi} * \Delta t_i * \frac{C_{Pi}+C_{Pi-1}}{2}$$
$$\textbf{Equation 6.4}$$

Where:
m_{Ci}: is the previous amount of phosphate in the stream C, the initial value is the amount in the CSTR.
m_{Pi}: is the previous amount of phosphate in the stream P, the initial value is 0 due the permeate stream at time 0 is 0.
Q_{Ci}: is the stream of the concentrate in the time i. (ml/s)
Δt_i: is the difference of time between two samples. (s)
C_{Ci}: is the concentration in the concentrate stream sample at time i."
C_{Ci-1}: is the concentration of the previous concentrate sample.
C_{Pi}: is the concentration in the permeate stream sample at time i."
C_{Ci-1}: is the concentration of the previous permeate sample.

Evaluating the equations 6.3 and 6.4 can be calculated the phosphate accumulated in the system as:

$$m(PO_4)_{acc.} = m(PO_4)_C - m(PO_4)_P$$
$$\textbf{Equation 6.5}$$

Finally is calculated the phosphate removal efficiency (%) of the Ca-Ze.

$$Ef(\%) = \left(1 - \frac{C_{Pi}}{C_{Ci}}\right) \times 100$$
$$\textbf{Equation 6.6}$$

6.3.2. Operation conditions

In each tank a solution of phosphate was prepared by using an analytical grade of sodium triphosphate as a source of phosphate by dissolving an appropriate amount in tap water. The desiderated concentration was 10 mgP-PO$_4$/l, for the tree deposits. After preparing, the concentration of solutions were measured by spectrophotometric measurements.

Once the concentrations have been measured 100 g of calcium zeolite were added to the CSTR and the buffer tank of 40 l was connected to a floating gate system to refill the CSTR when water level was lower than 33 cm (approx. 40 l).

The operation of the pilot plant is regulated by peristaltic pump that take water mixed to calcium zeolite from CSTR to ultrafiltration membrane module. The permeate stream is stored in a deposit of 20 l and it is used for backwash when it was required. The concentrate stream is recirculate into the CSTR.

Along the experiments samples from the different streams and tank were collected for being analyzed. In table 6.1, a summary of the different experiments performed and the conditions and specific parameters to be studied are described.

Experiment	A, standard conditions	B, effect of pH	C, effect of flow rate
Absorbent	Ca-Ze	Ca-Ze	Ca-Ze
pH	8±0.2	9±0.2	8±0.2
Conditions changes	Initial conditions to allow the comparison with the other experiments	pH control setup that pump NaOH 0.5 M to the CSTR if needed	Pump speed settings were changed to increase the flow rate
[PO$_3^{4-}$] (mgP-PO$_4$/l)	10	10	10
PAZ (g)	100	100	100
Agitation (rpm)	320-350	320-350	320-350
Flow rate (l/min)	1.16	1.16	1.4
Water in CSTR (l)	40	40	40

Table 6.1: Description of the conditions of the different experiments

6.3.3. Kinetic evaluation of phosphate adsorption with Ca-zeolites

Experiments to determine the adsorption kinetic and identify the required times for maximum phosphate removal were carried out.

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For these experiments a solution of 10 mgP-PO$_4$/l a 1 l beaker and 2.5 g of calcium zeolite were used. The phosphate concentration and the weight used were chosen to reproduce the same conditions of the pilot plant tank.

Every 30 min in the first three hours, and then every 24 hours till the solution arrives to a concentration lower than 1.5 mgP-PO$_4$/l a sample was taken. When concentration was lower or equal to 1.5 mgP-PO$_4$/l as considered that one cycle is ended and the beaker was refilled and phosphate was added to reach again 10 mgP-PO$_4$/l

6.3.4.   Phosphate adsorption Isotherms

The objective of this experiments is study the adsorption in the equilibrium using a constant mass of adsorbents and different concentration of adsorbates. In this stage additionally to Ca zeolite (Ca-Ze), four additional sorbents were used:
a) A sorbent containing hydrated iron oxide (Bayoxide)

b) A sorbent rich in calcium, clinker from a cement industry mainly conformed by calcium silicate, tricalcium aluminate and calcium aluminoferrite.

c) Two Ca and K activated zeolites (K-LB, K-TE) produced from two different fly ashes.

The study is done using 20 ml tubes, fixing pH at 8 and at room temperature (22-24 ºC). The mass used in the experiments is 1 mg for each adsorbent (Bayoxide, Clinker, K-LB, K-TE, Ca-Ze) and the volume of adsorbate is 10 ml. Depending on the nature of the sorbent and their calcium content the phosphate concentration range used was modified accordingly..

For Bayoxide and Clinker samples the concentration ranged from 10 to 1000 mgP-PO$_4$/l, for K-LB and K-TE from 500 to 8000 mgP-PO$_4$/l and for Ca-Ze from 5 to 100 mgP-PO$_4$/l. The phosphate solutions were prepared using NaH$_2$PO$_4$·2H$_2$O.

The pH is fixed using 0.05 to 1 M HCl and NaOH solutions.

After equilibration times of 24 hours, pH was measured the solid is separated from liquid phase. The solutions were analyzed to determine the phosphate concentration using UV-visible spectrophotometry, part of the solution is stored in case chromatography analysis is needed and the solid is stored in eppendorf tubes for XRD analysis.

6.3.5.   Determination of the Point of zero charge of phosphate adsorbents.

The point of zero charge describes the condition when the electrical charge density on the surface of an adsorbent is zero and is determined by potentiometric methods.

Samples of 0.2 g or 0.125 g depending of the adsorbent were mixed with 25 ml or 10 ml of: a) deionized water, b) 0.01 M NaCl and c) 0.05 M NaCl. Measures of the initial and equilibrium pH were taken. To determine the point of zero change.

7. Analytical methodologies.

7.1. Spectrophotometry analysis of phosphate

For spectrophotometric analysis the samples have to be prepared making a solution of 5 ml containing: 3.5 ml of the sample, 1 ml of reagent (Vanadate-Molybdate) and 0.5 ml of Milli-Q water.

To take the sample is recommended a micropipette of 5 ml and for reagent and MilliQ water one of 1 ml. The reagent Vanadate-Molybdate react with phosphate changing the colour of the water from transparent to yellow. To make the reagent Vanadate-Molybdate two solution have to be prepared:

Solution A: Dissolve 25 g ammonium molybdate, $(NH_4)Mo_7O_{24} \cdot 4H_2O$, in 300 ml Milli-Q water; a 500 ml beaker and a magnetic agitator can be used for the preparation, to dissolve completely the solid are needed approx. 15 minutes.

Solution B: Dissolve 1.25 g ammonium metavanadate, NH_4VO_3, by heating to boiling in 300 ml Milli-Q water, a 500 ml beaker and a magnetic agitator can be used for the preparation, is strongly recommended to do the solution in a fume hood because gases are released during the process.

Cool solution B, put it in a 1 l volumetric flask and add 330 ml of concentrated HCl, the HCl is a corrosive acid that release irritant vapour, protection have to be wearied (gloves, glasses, lab coat) and have to be manipulated in a fume hood. The reaction between solution B and HCl is exothermic, before adding solution A is need to wait solution B + HCl is cooled.

When solution B, HCl and solution A are mixed dilute to 1 l. [29]. The reagent was stored into an opaque bottle and not exposed to light.

7.2. Ion-exchange chromatography analysis

Ion analysis was performed using a Thermo Scientific Dionex ICS-1100 (for anions) and the Thermo Scientific Dionex ICS-1000 for cations: Samples are taken from an automatic bench. The eluent used are: 3.9 ml Methanesulfonic acid for cationic resin and a solution of 0.134 g $NaHCO_3$ and 0.954 g of Na_2CO_3.

Figure 7.2 Thermo Scientific Dionex ICS-1100 and Thermo Scientific Dionex ICS-1000.

7.3. X-ray diffraction (XRD)

The phase purity and crystallinity of the Hap powder were analyzed by X-ray diffraction with λ CuKα radiation (λ= 1.54056 Å)) at a scanning rate time of 19.2 and 57.6 s, steep angle of 0.015° and 2θ in range of 4-60°. The average crystallite size long c-direction of Hap powder was calculated from (002) reflection in XRD pattern, using Sherrer's equation (Equation 7.1 [30], [31]):

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$
Equation 7.1

Where τ (nm) is crystallite size, K is the shape factor (K = 0.9), λ is the wavelength of the X-ray (λ = 0,15406 nm for CuKα radiation), β is the full width at half- maximum (FWHM) (rad) of the peak along (002) direction and θ is the Bragg's diffraction angle.

8. Results and discussion

8.1. Chemical and mineralogical characterization of adsorbents

Two different fly ashes, from two coal thermal power stations were used to prepare the Ca and Ca-K zeolites. One is situated in Andorra (Teruel) and it is using lignite to produce a nominal power of 1050 MW. The other station is situated in Los Barrios (Cádiz) it is using a bituminous coal with a nominal power of 567 MW. Both fly ashes were used to synthesized Ca, and K zeolites as described elsewhere [34]

From XRD diffractogram it can be seen the presence of crystalline phases in the Teruel (K-Te) and Los Barrios (K-LB) modified fly ashes and in the synthetic calcium zeolite. The common crystalline species are *quartz* (SiO_4) and *mullite* ($Al_6Si_2O_{13}$) those minerals can be normally found in coal fly ashes and are a source of Si and Al for zeolite synthesis. In K-TE is present an third mineral, of zeolite group, *merlinoite* ($K_5Ca.2(Al_9Si_{23}O_{64})\cdot24H_2O$. In K-LB are present the *perlialite* ($K_9NaCaAl_{12}Si_{24}O_{72}\cdot12H_2O$) and *merlinoite* zeolites. The presence of a crystalline phase containing K mean that the conversion of FA to K-FA is efficient.

In the calcium zeolite are present the silica and alumina-silica minerals *quartz* and *mullite*, the mineral *garronite* ($NaCa_2.5(Si_{10}Al_6)O_{32}\cdot14 H_2O$) and *calcite* ($CaCO_3$).
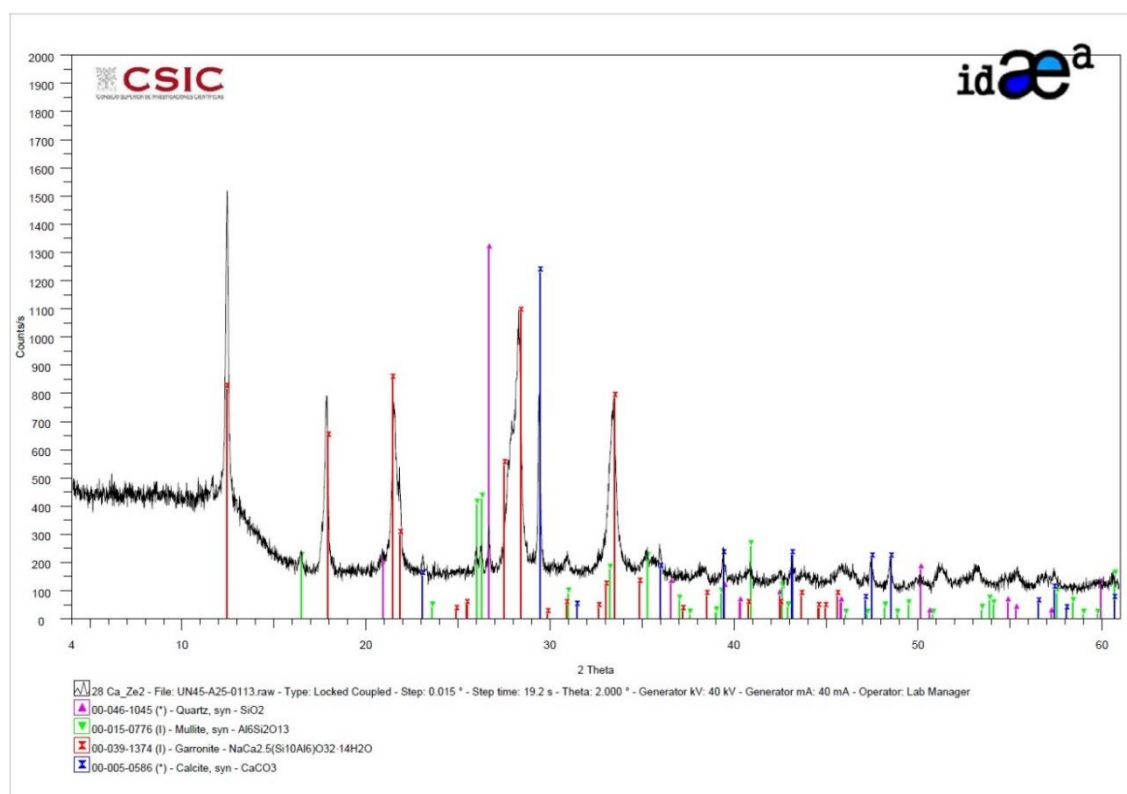

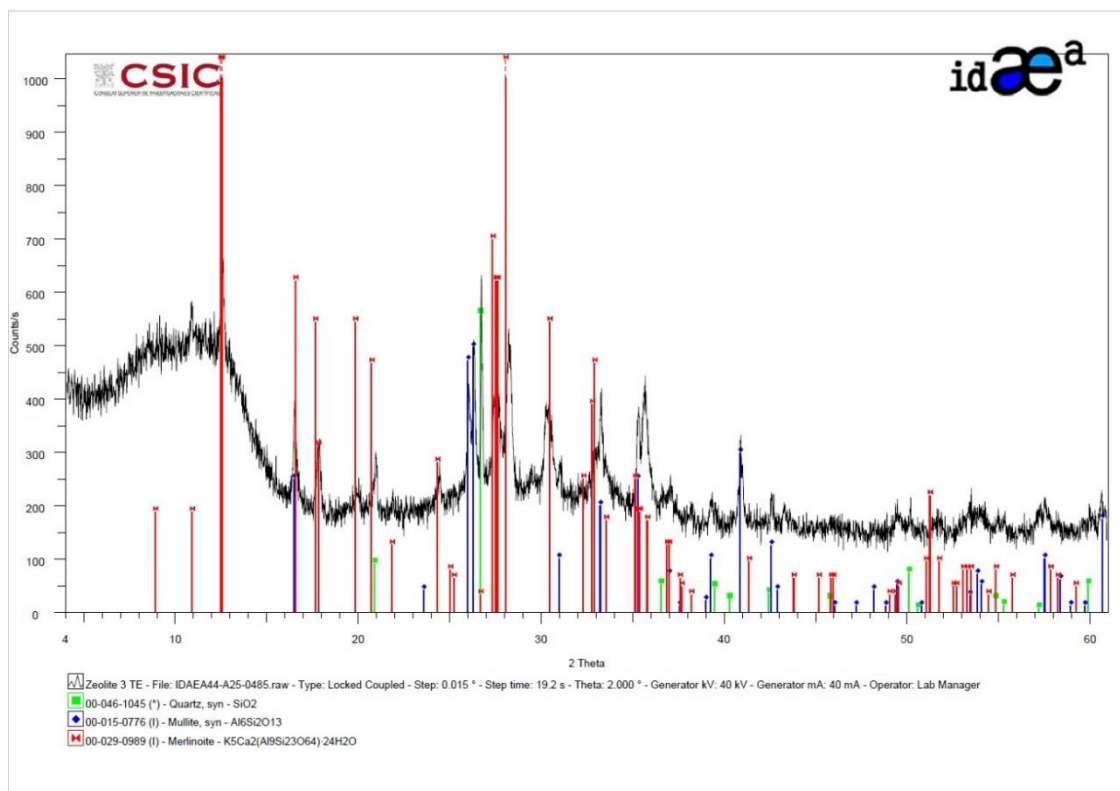**Figure 8.1**: Calcium zeolite XRD

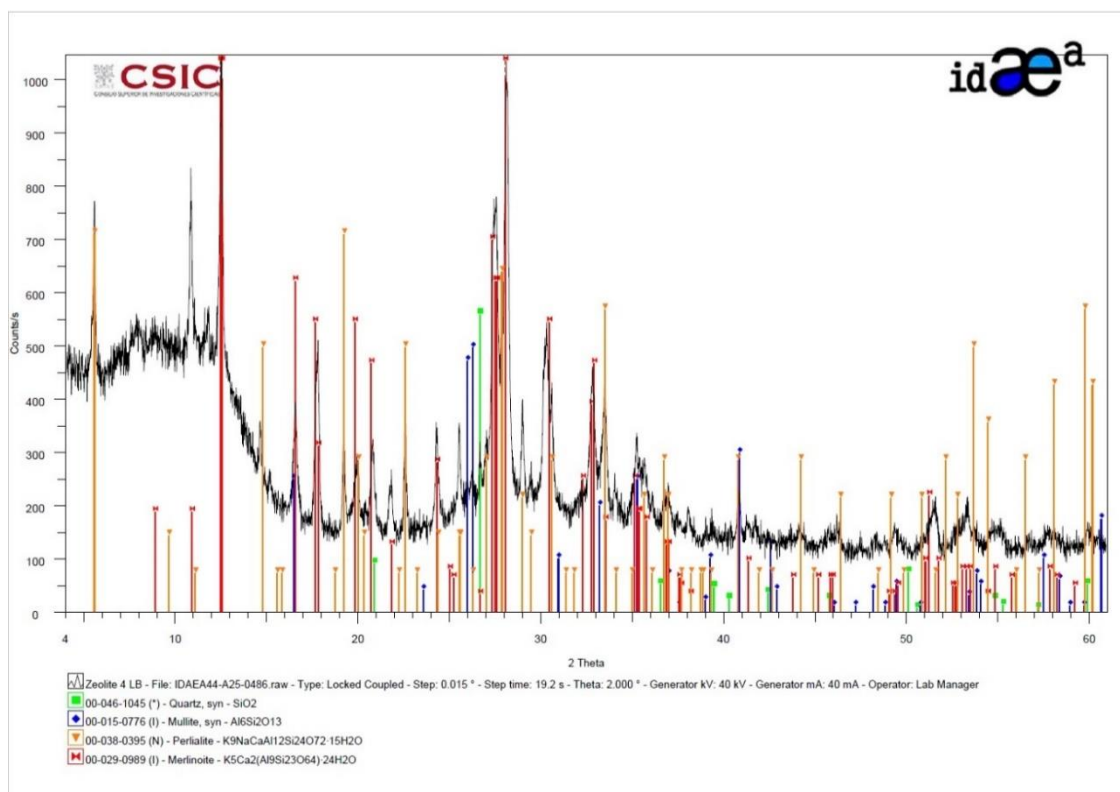**Figure 8.2**: K-TE fly ash XRD
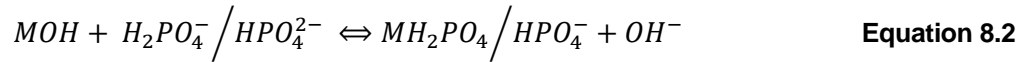

Figure 8.3: K-LB fly ash XRD

When zeolites and FA are in a phosphate solution different mechanism are involved in the

phosphate elimination such as ion complex equilibrium, precipitation and physical adsorption. Those mechanisms can be affected by the structure of zeolite or FA and by the pH of the solution. The postulated mechanism are [34]:
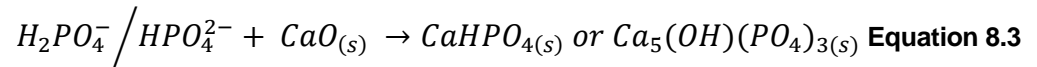
a) Complex with group $\approx MOH_2^+$ on surface.

$$MOH_2^+ + H_2PO_4^- \Big/ HPO_4^{2-} \iff MH_2PO_4 \Big/ HPO_4^- + H_2O \qquad \textbf{Equation 8.1}$$
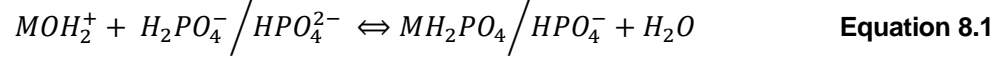
b) Complex with group $\approx MOH$ on surface.

$$MOH + H_2PO_4^- \Big/ HPO_4^{2-} \iff MH_2PO_4 \Big/ HPO_4^- + OH^- \qquad \textbf{Equation 8.2}$$

c) Formation of Calcium phosphate minerals with the Ca^{2+} present in the zeolite structure (e.g. $CaO_{(5)}$).

$$H_2PO_4^- \Big/ HPO_4^{2-} + CaO_{(s)} \rightarrow CaHPO_{4(s)} \; or \; Ca_5(OH)(PO_4)_{3(s)} \; \textbf{Equation 8.3}$$

d) Formation of Calcium phosphate minerals with the Ca(II) who occupy the places of ion exchange of the zeolite structure.

$$\cong (ZO^-)_2 Ca^{2+} + H_2PO_4^- + 2K^+ \rightarrow 2 \cong ZO^-K^+ + CaHPO_{4(s)} + H^+ \; \textbf{Equation 8.4}$$
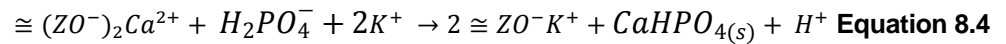
Analysis of samples after the adsorption experiments with K-LB and K-TE FA detected the presence of brushite ($CaHPO_4$) (Equation 8.4). In figure 8.4 is shown an example of XRD difractogram of K-LB and KTE zeolites after adsorption experiments with phosphate solutions.
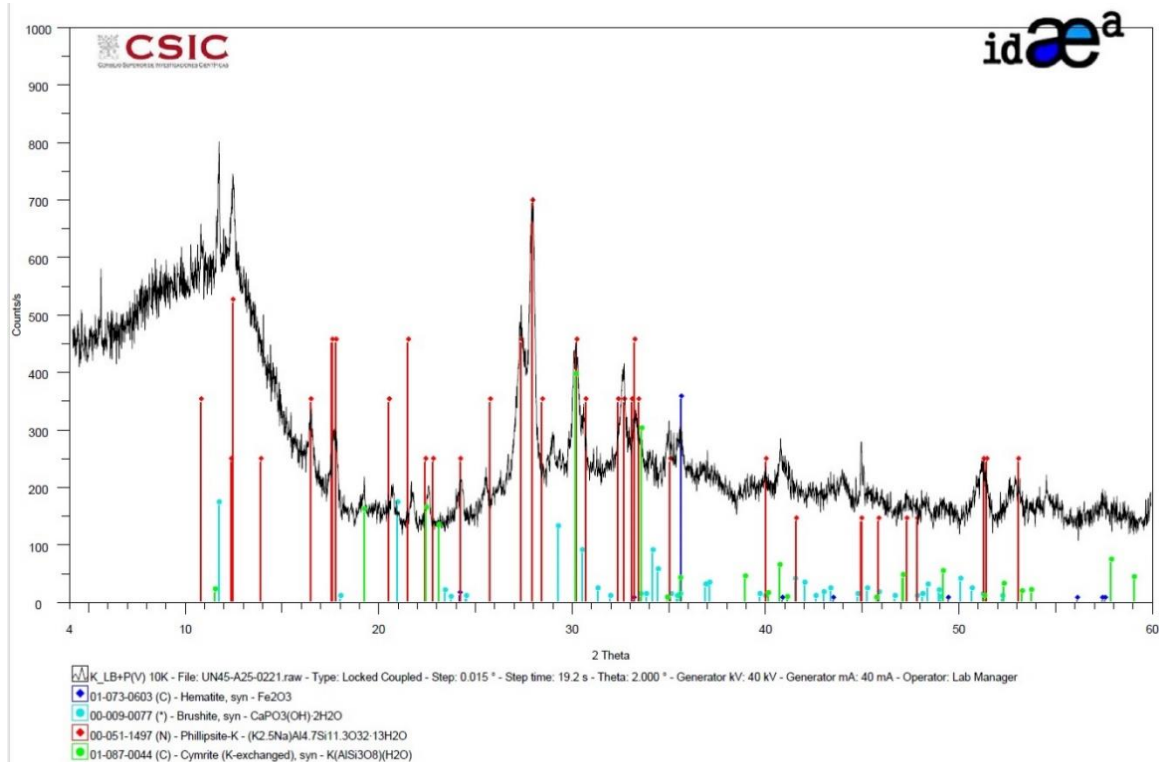
Figure 8.4: K-LB fly ash XRD, after 24 h in P solution 10.000 mgP-PO4/l

8.2. Point of zero charge

Figures 8.5-8.8 show the evolution of the ΔpH as a function of the equilibrium pH for the different solids studied. Analysis of this functions identifying the pH corresponding to ΔpH equal to zero was used to determine the point of zero charge (PZC). The modified FA, K-LB and K-TE, have a PZC around pH 9.25 and 9.3 respectively, the calcium modified zeolite (Ca-Ze) has a PZC around 6.1 and the hydrated ferric oxide adsorbent (Bayoxide) has a PZC around 7.6. The PZC of the clinker sample was not determined as the high basicity provided by the sample did not provide the required pH range to determine the PZC.

 The PZC is the point where the charges on the surface are balanced and give a neutral total charge. For the pH values lower than PZC the global surface charge is positive and for values higher than PZC the global surface charge is negative.
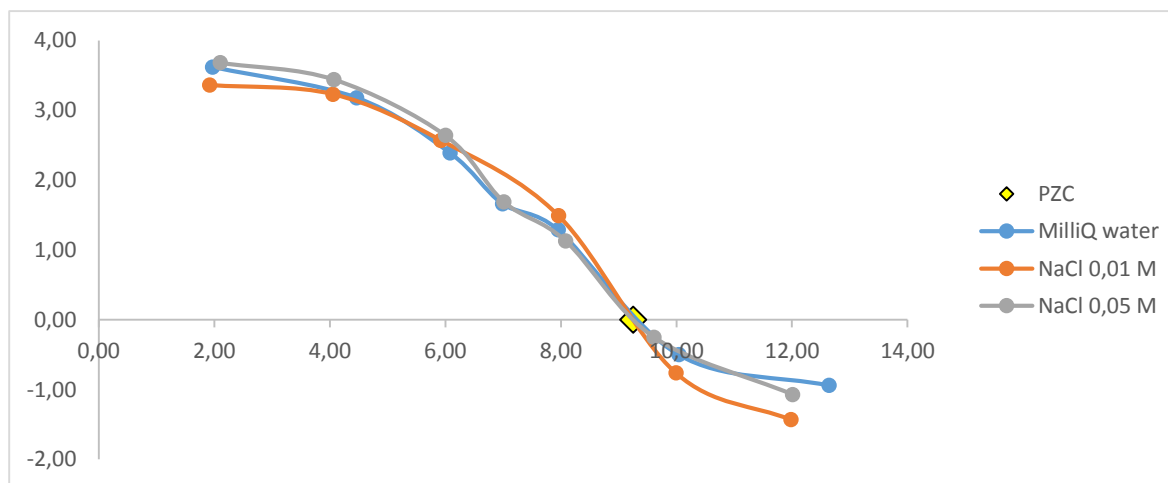
Figure 8.5: K-LB fly ash PZC
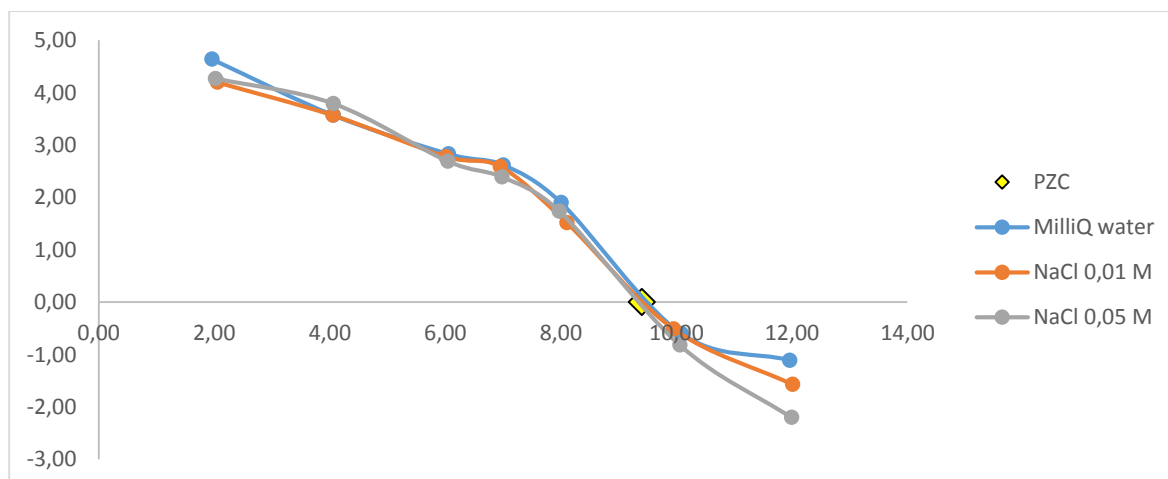
Figure 8.6: K-TE fly ash PZC
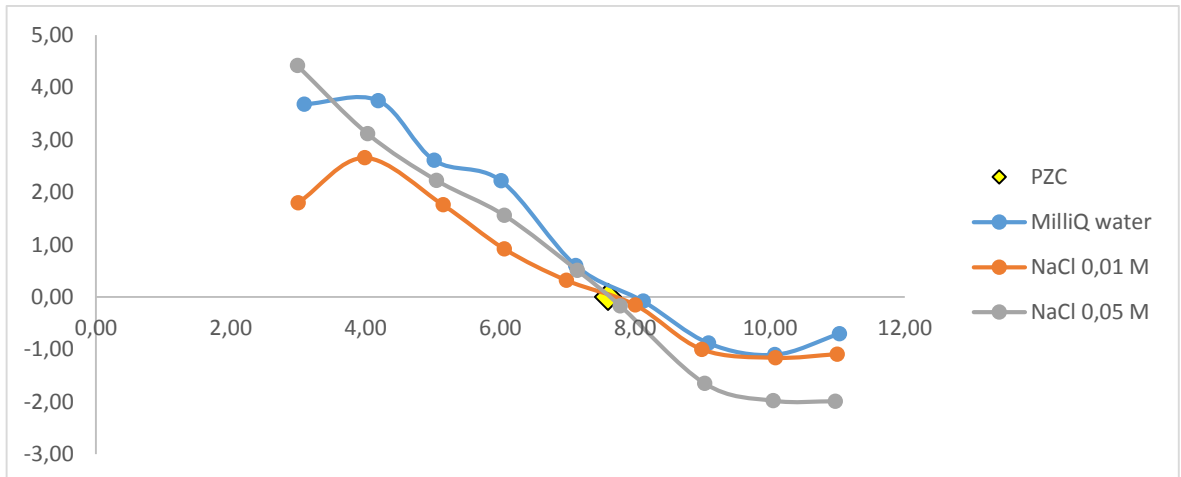
Figure 8.7: Bayoxide PZC
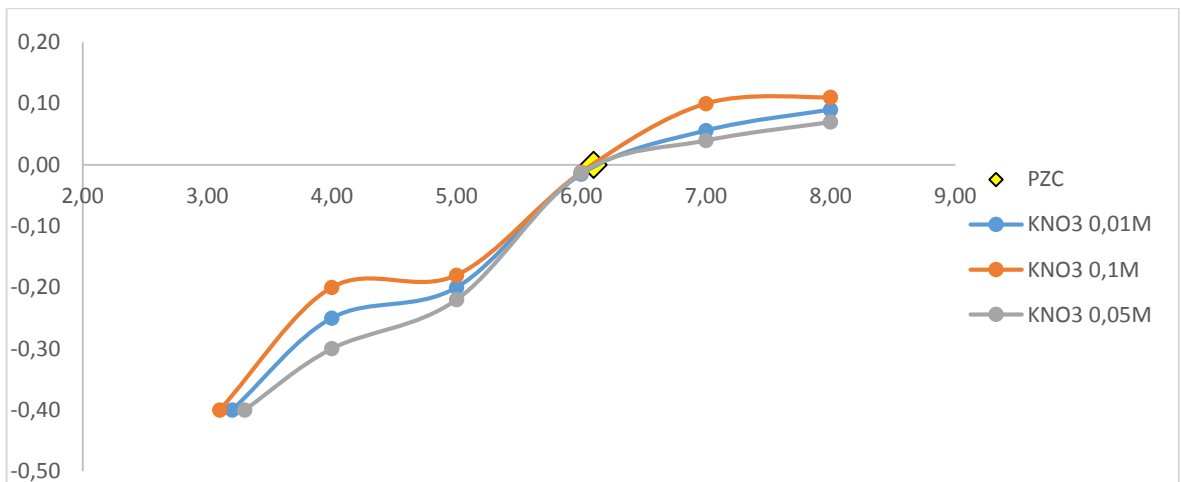
Figure 8.8: Ca-Ze PZC [34]

8.1. Phosphate equilibrium isotherms

Figures 8.9-8.12 shown the phosphate equilibrium sorption data in the for sorption isotherms (Qe vs. Ce) for Ca-Ze, K-LB, K-TE, Bayoxide and Clinker adsorbents. The experiments were done at the same pH conditions to guarantee a more objective comparison.
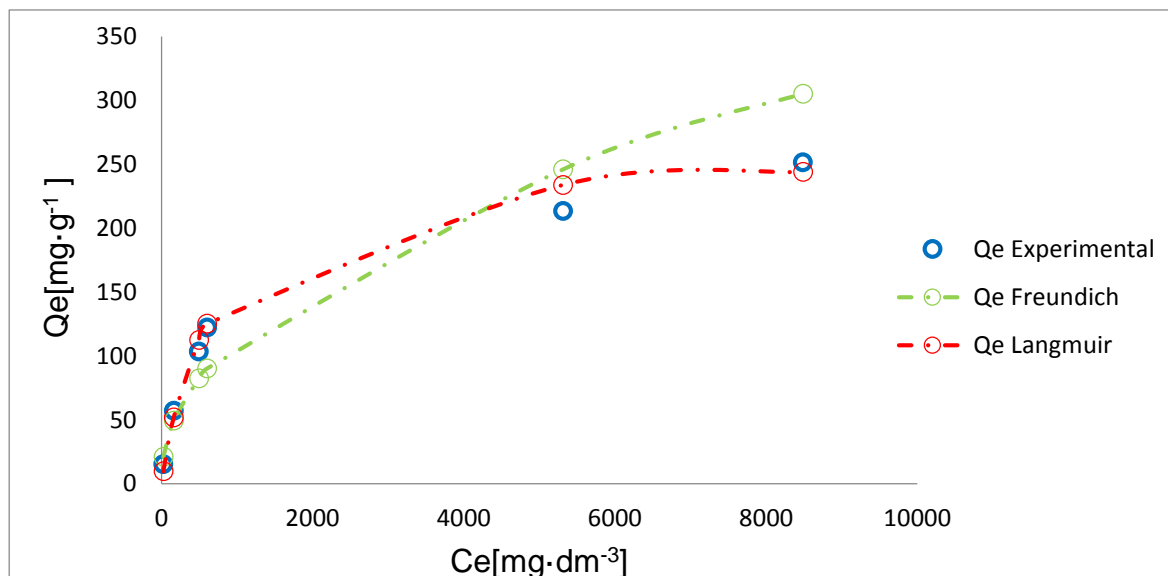
Figure 8.9: Adsorption isotherms for K-LB FA, pH 8.
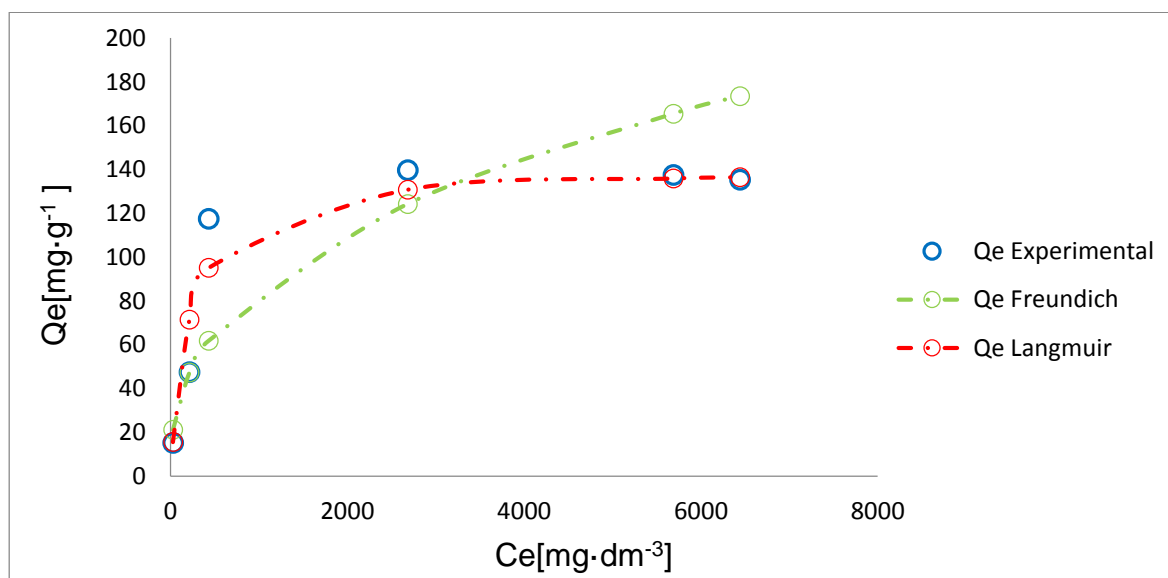
Figure 8.10: Adsorption isotherms for K-TE FA, pH 8.
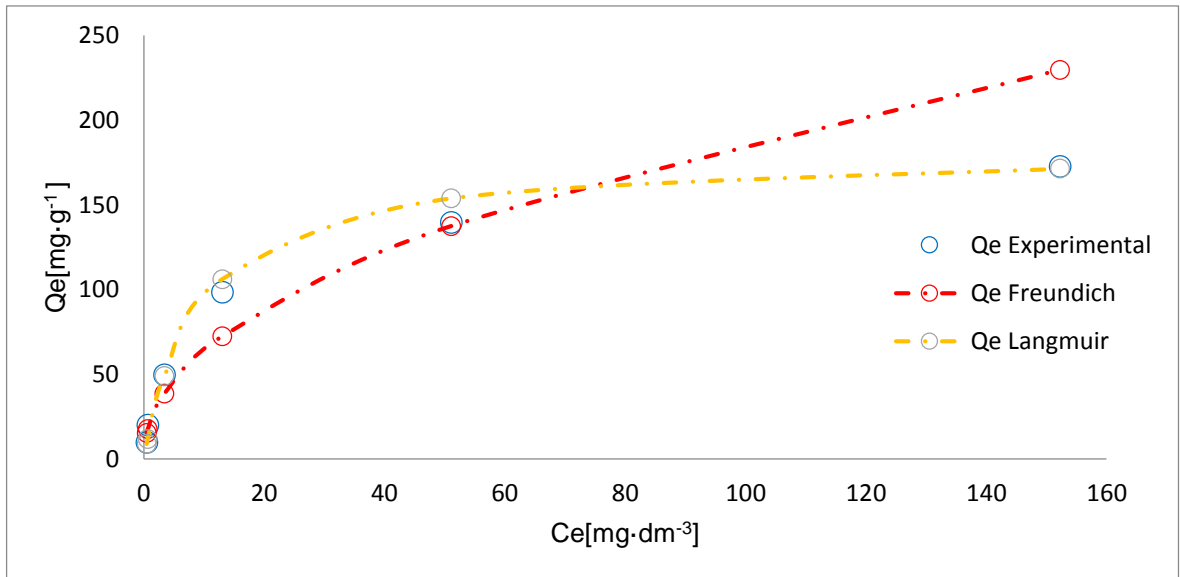
Figure 8.11: Adsorption isotherms for Clinker, pH 8.
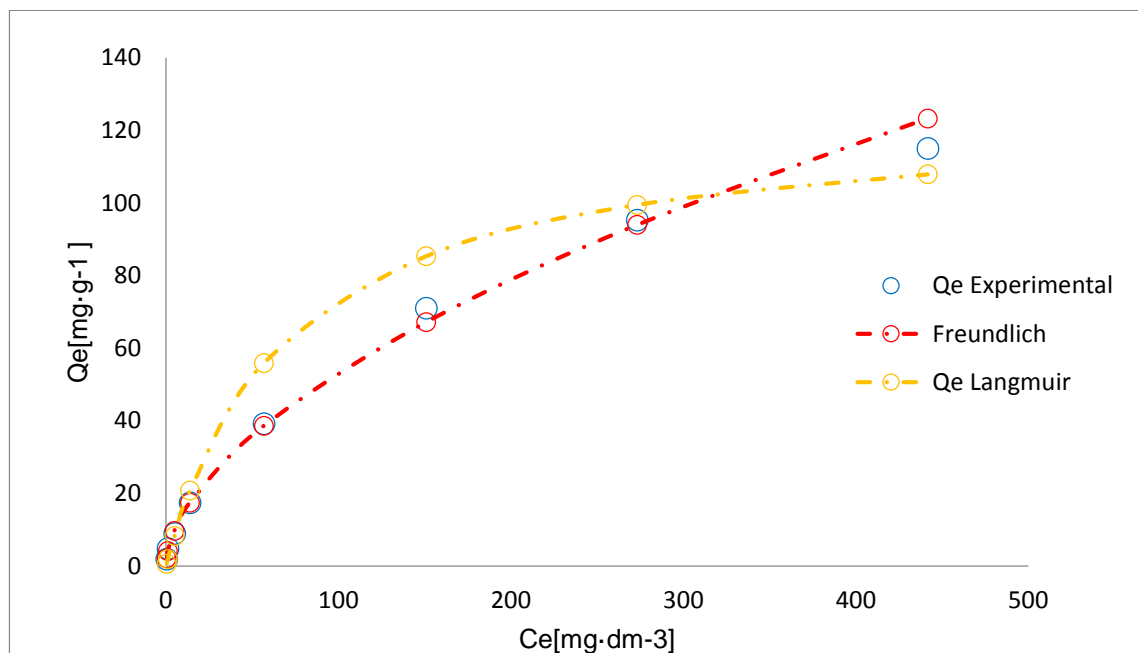
Figure 8.12: Adsorption isotherms for Bayoxide, pH 8.

K-TE, K-LB and Clinker adsorption data are well described by the Langmuir isotherm and while data for Bayoxide are well described by the Freundich isotherm. Regression coefficients for the isotherms and the sorption equilibrium constants of the different adsorbents are reported in table 8.1.

Isotherms models	Langmuir			Freundich		
Adsorbent	Qm	KL	R²	KF	n	R²
K-LB	263.2	0.0	0.99	4.7	2.2	0.94
K-TE	140.8	0.0	1.00	6.1	2.6	0.84
Clinker	181.8	0.1	1.00	21.7	2.1	0.93
Bayoxide	125.0	0.0	0.95	3.9	1.8	1.00
Ca-Ze	194.0	0.0	0.98	10.0	3.0	0.82

Table 8.1: Table of result Langmuir vs. Freundlich of the adsorbents.

In table 8.1 can be seen the adsorption capacities of each adsorbent are compared with the Ca-Ze previously determined [34]. The adsorbent with the highest sorption capacity for phosphate was K-LB, with a 30% higher than for Ca-Ze, and 45% higher that K-TE. Although the K-LB zeolite has higher phosphate sorption capacity due to fact that Ca-Ze was produced in higher scale, a 100 kg batch was produced, this zeolite was used along the project.

8.2. Sorption kinetic evaluation of Ca-Ze

Figure 8.13, shows the variation of the phosphate concentration in solution of three consecutive sorption cycles simulating the expected conditions of the sorption-separation experiments for a 10 mgP-PO_4/l solution at pH 8±2.
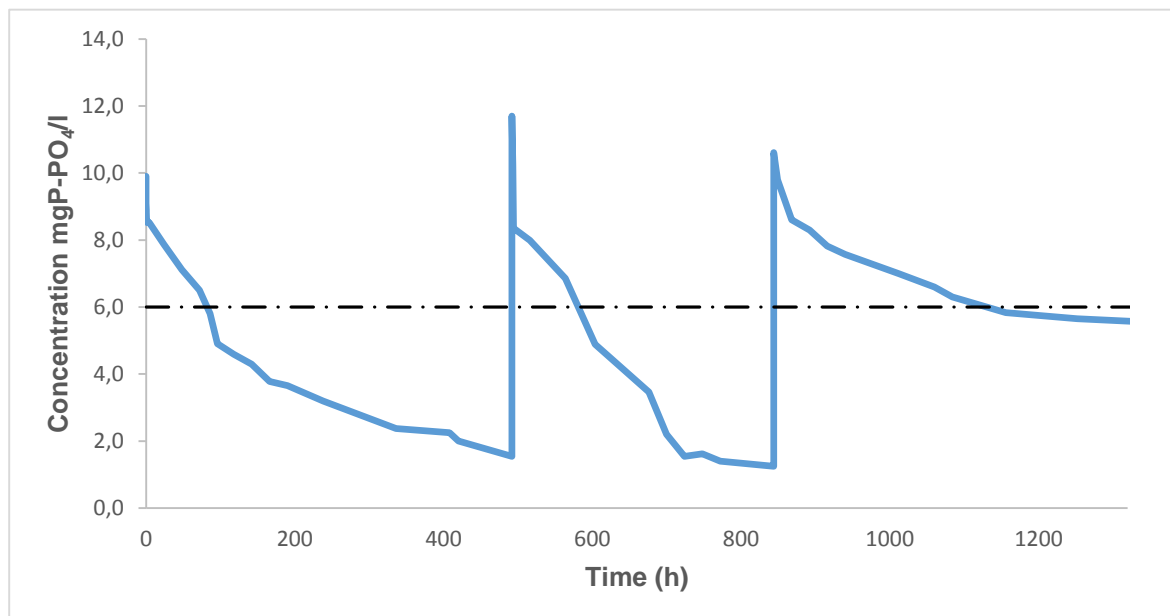
Figure 8.13: Kinetic study for Ca-Ze, evolution of concentration during the tree sorption cycles.

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As can be seen for the firsts two cycles a reduction of 80% of the initial phosphate concentration was achieved, although the first cycle need a higher time to reach this point, in the third cycle the zeolite reach saturation as could be seen. The concentration in solution decrease up to 6 mgP-PO$_4$/l and then it was maintained constant. The variation of the phosphate loadings with time of each experiment were used to study the kinetic parameters using the models described in section 5.3.

The first cycle follow a pseudo first order model and the second and third a pseudo second order model as can be seen in the table 8.2. Although the first cycle can be modeled using pseudo second order, the graph of this model seem to have a better fit than the pseudo first order graph. In the figure below are shown the graphs of results for each cycle and the table with the model's fit results.
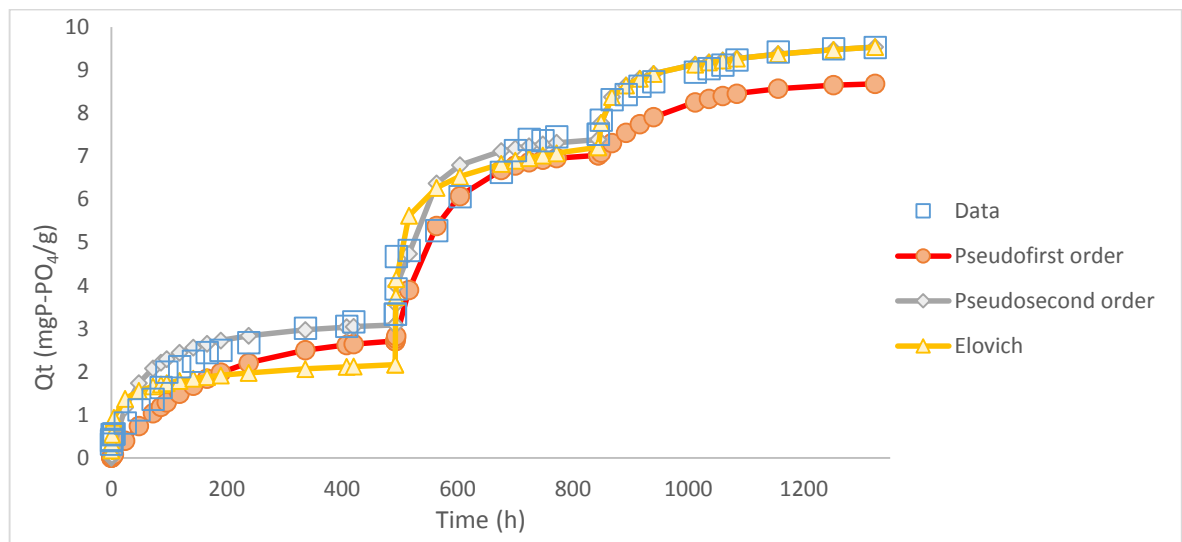
Figure 8.14: Kinetic models for the tree cycles

Cycle 1										
PSEUDOFIRST ORDER			**PSEUDOSECOND ORDER**				**ELOVICH**			
ln (Qe-Qt)= ln Qe -kt			t/Qt = 1/[kQe^2] + t/Qe				Qt=a+b·ln(t)			
Pendent	-1,7E-06	Qe	2,8	Pendent	0,3	Qe	3,37	Pendent	0,3	a	0,01
y-intercept	1,0	K	1,7E-06	y-intercept	4,8E+04	K	1,8E-06	y-intercept	-1,6	b	0,26
R2	0,99	Qe'	3,3	R2	0,95			R2	0,82		
Cycle 2										
PSEUDOFIRST ORDER			**PSEUDOSECOND ORDER**				**ELOVICH**			
ln (Qe-Qt)= ln Qe -kt			t/Qt = 1/[kQe^2] + t/Qe				Qt=a+b·ln(t)			
Pendent	-3,7E-06	Qe	4,4	Pendent	0,1	Qe	7,7	Pendent	0,6	a	0,26

y-intercept	1,5	K	3,7E-06	y-intercept	7033,0	K	2,4E-06	y-intercept	-1,1	b	0,59
R2	0,91	Qe'	7,5	R2	0,99			R2	0,84		
Cycle 3											
PSEUDOFIRST ORDER				PSEUDOSECOND ORDER				ELOVICH			
ln (Qe-Qt)= ln Qe -kt				t/Qt = 1/[kQe^2] + t/Qe				Qt=a+b·ln(t)			
Pendent	-2,1E-06	Qe	1,7	Pendent	0,1	Qe	9,6	Pendent	0,4	a	7,8E+04
y-intercept	0,5	K	2,1E-06	y-intercept	2798,9	K	3,9E-06	y-intercept	4,0	b	0,4
R2	0,94	Qe'	9,5	R2	1,00			R2	0,96		

Table 8.2: Table of results of the different regression models and cycles.

Analysis of the regression results indicate that the pseudo second order model provides the better description for the three cycles and was selected for further calculations. According to the selected model the phosphate sorption capacity (Qt) reach the maximum value of 9.5 mgP-PO$_4$/g.

8.3. Integration of sorption and zeolite separation using Ultrafiltration membranes

In this part will be presented the results obtained in the pilot plant. Experiments lasted in most of the case up to 60 hours and were developed in 6 hours runs per day. The objective of the preliminary validation of the system was the comparison of the phosphate removal capacity in different conditions. A defined plan according to the duration of the TFG was developed. The conditions of experiments are lied down in the table 8.3.

Experiment	A	B	C
Absorbent	Ca-Ze	Ca-Ze	Ca-Ze
pH	8±0.2	9±0.2	8±0.2
[PO$_3^4$] (mgP-PO$_4$/l)	10	10	10
PAZ (g)	100	100	100
Agitation (rpm)	320-350	320-350	320-350
Flow rate (l/min)	1.16	1.16	1.4
Water in CSTR (l)	40	40	40

Table 8.3: Details of the experimental operation conditions for the removal of phosphate using CSRT-UF set-up conditions.

8.3.1. Effect of pH in phosphate removal by Ca-Ze

In this experiment is studied the influence of pH in phosphate removal by Ca-Ze. The

conditions can be seen in table 8.3 experiments "A" and "B". In the experiment "A" the pH value is 8±0.2 and is defined by the presence of bicarbonate in the model solution. In experiment B the pH is fixed 9±0.2 using a NaOH 0.5 M solution and an automatic pH control system to ensure the pH value.

The influence of pH in phosphate sorption capacity (Qt) and efficiency for a 10 mgP-PO$_4$/l solution are shown in the figures 8.16 and 8.17.
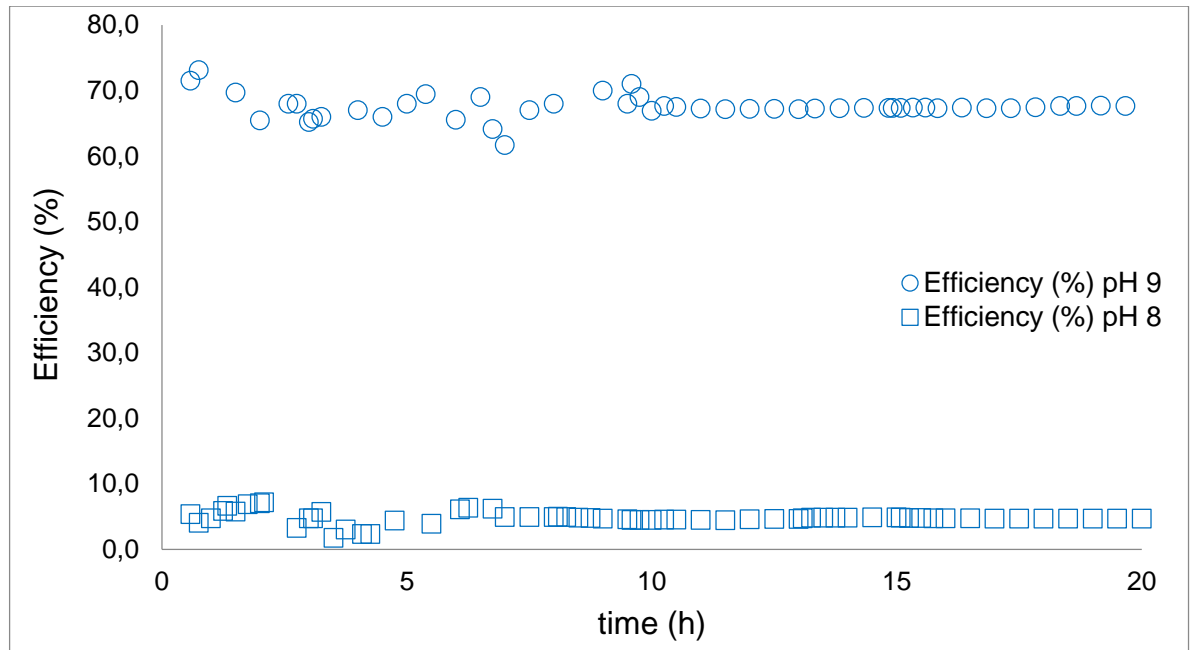
Figure 8.16: Graph of efficiency (%) vs t(h) at pH 8 and pH 9
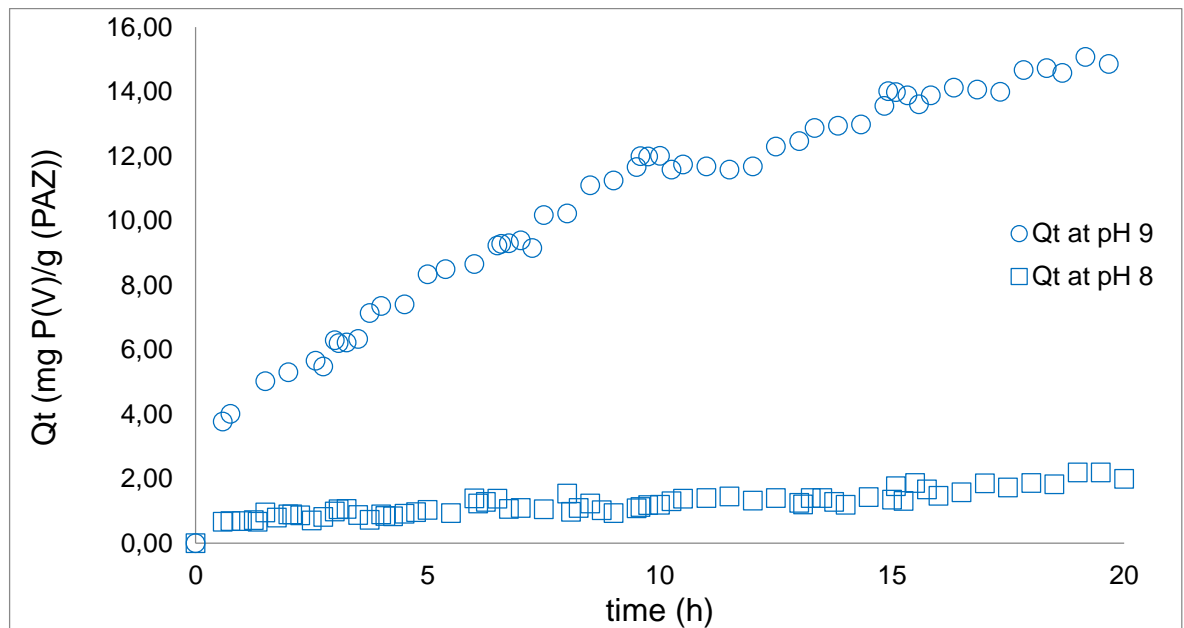
Figure 8.17: Variation of Qt (mg P(V)/g PAZ) versus t (h) at pH 8 and pH 9.

The Ca-Ze sorption capacity after 20 hours of filtration cycles reach a value of 1.7±0.3 mg P(V)/g PAZ at pH 8, corresponding to an efficiency of 5±1% and a value of 14±0.5 mg P(V)/g PAZ at pH 9, corresponding to an efficiency of 70±3%.

In figure 8.18 is shown the XRD analysis of Ca-Ze samples collected at the end of UF experiment.
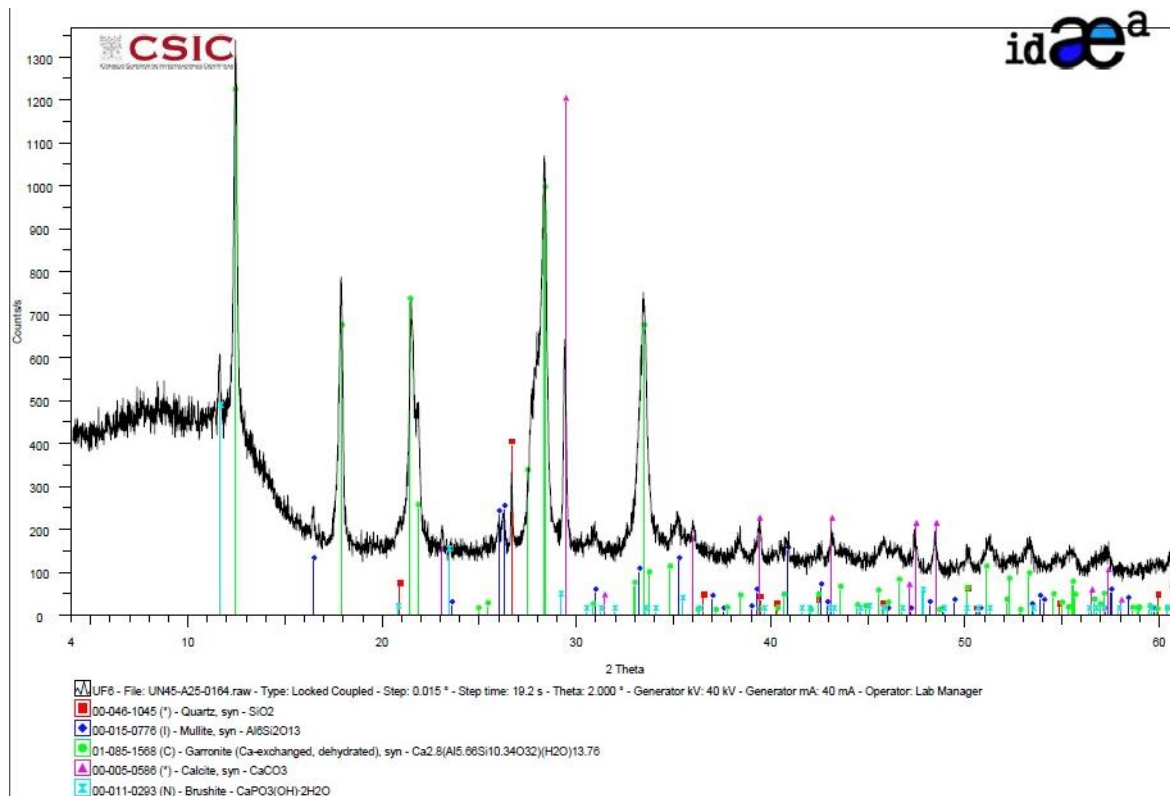
Figure 8.18: XRD of Ca-Ze after UF experiment A.

In the samples at pH 8 where identified the presence of brushite, however it was not detected any mineral phase of calcium phosphates in samples at pH 9. An SEM-EDS analysis (data not shown) of pH 9 samples identified the presence of amorphous particles containing P, Ca and O on Ca-Ze. A reasonable hypothesis can be the formation of amorphous forms of calcium phosphate minerals that cannot be detected by XRD.

8.3.2. Effect of the flow rate in phosphate removal by Ca-Ze.

The influence of flow rate in phosphate removal by Ca-Ze. Was evaluated by experiments "A" and "C". In the experiment "A" with a flow rate of 1.2 l/min, was used according to previous experiments [34], while in experiment "B" the pump speed was at 1.4 l/min.

The influence of the flow rate in phosphate sorption capacity (Qt) and efficiency for a 10 mgP-PO$_4$/l solution are shown in the figures 8.19 and 8.20.
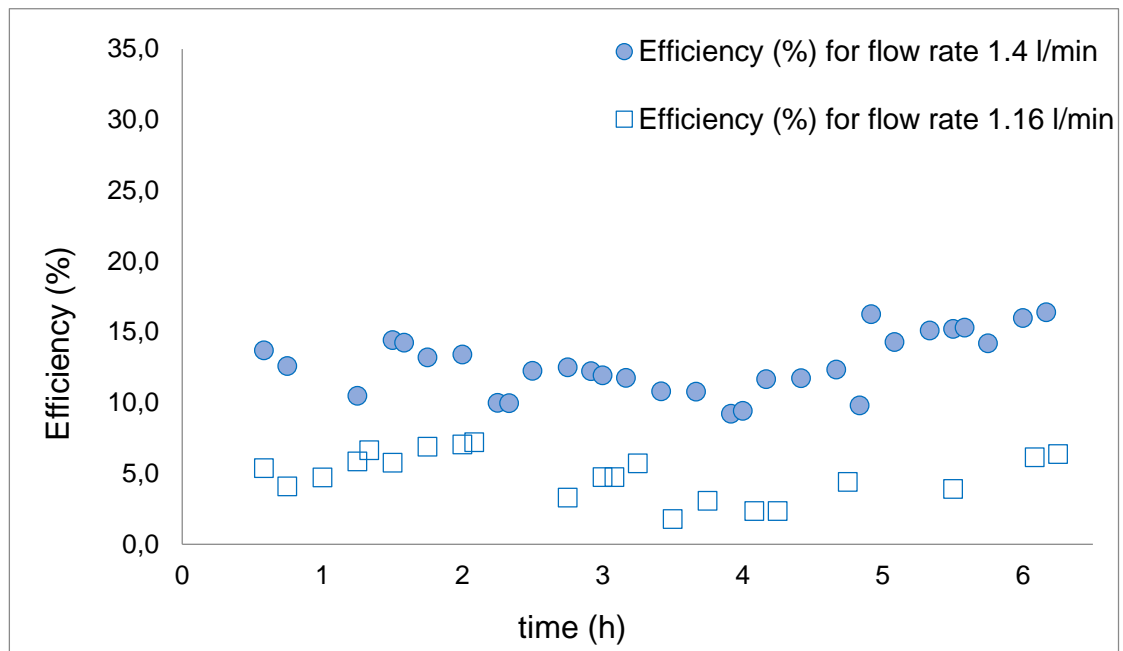
**Figure 8.19:** Graph of efficiency (%) vs t(h) for the different flow rates
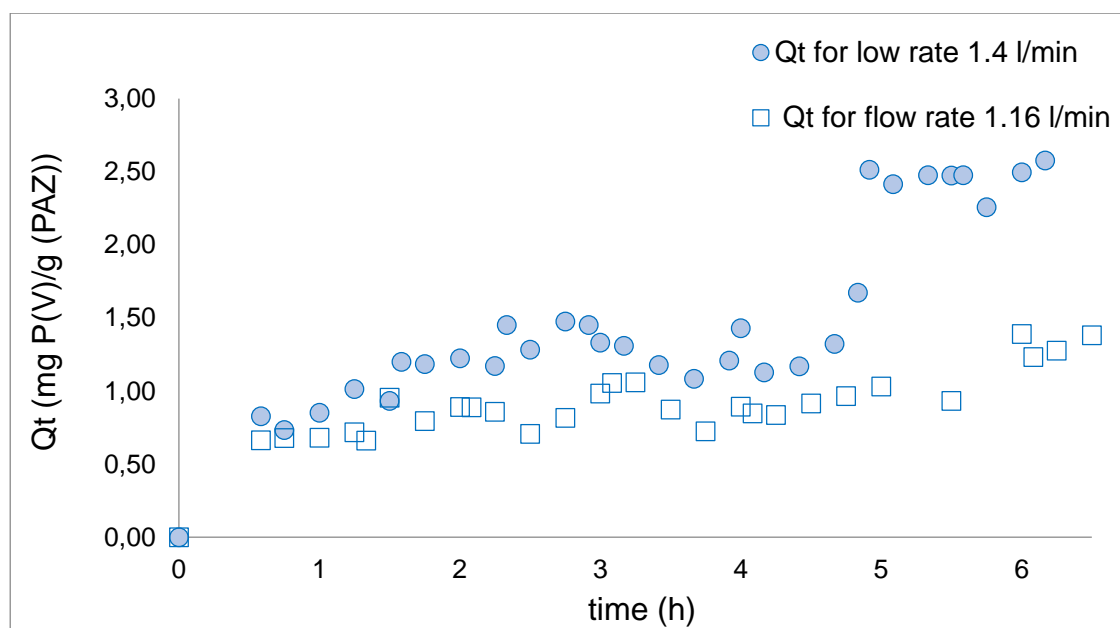
Figure 8.20: Graph of the Qt (mg P(V)/g PAZ) vs t (h) for the different flow rates.

The Ca-Ze sorption capacity after 6.3 hours of filtration cycles reach a value of 1.2±0.2 mg P(V)/g PAZ with a flow rate of 1.2 l/min, corresponding to an efficiency of 6±1% and a value of 2.58±0.3 mg P(V)/g PAZ with a flow rate of 1.4 l/min, corresponding to an efficiency of 15±1%.

The total filtration time was only 6.3 hours due to the fact that the increase of flow rate increased the trans membrane pressure (TMP).

Trans membrane pressure is calculated using the median of the lower and higher values given by the manometer in the sample acquisition time. As can be seen in the figure 8.21, the TMP of experiment C present higher values than the TMP in experiment A. The number of cycles in experiment C is 7 and in experiment A 5 for the same filtration time, and the cycles of experiment C present the same duration not as experiment A where every cycle is longer than the previous.

Figure 8.21: Evolution of TMP (bar) during the filtration time of experiments A and C
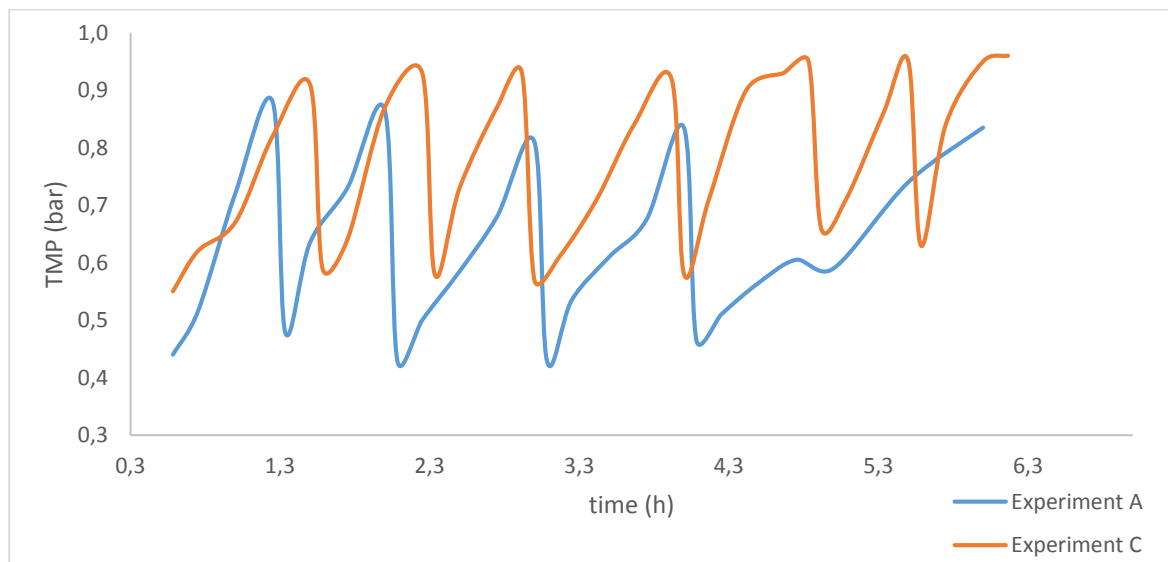
The TMP grows because during the operation the deposition of zeolite on the surface fibers causes the membrane fouling due to cake layer formation. The layer of zeolite does not penetrate the fibers and the fouling is reversible and it was removed by backwash cleaning step using permeate. The operations of backwash wear carried out once the TMP reach values near 0.8±0.1. The layer of zeolite forms faster with the increased flow rate and as can be seen in figure 8.21, the initial values after backwash and plant starting are higher in experiment C than experiment A as the final values.

8.3.3.   Permeate production

In figure 8.22 is shown the flow rate of the permeate obtained in the three experiments. The values of permeate flux (Q_P) are similar for the experiments A and B. For the experiment C can be seen that the Q_P is lower even if flow rate is increased. The explanation is that the increased flow rate favored the fouling of the membrane that cause a fast decrease of Q_P.
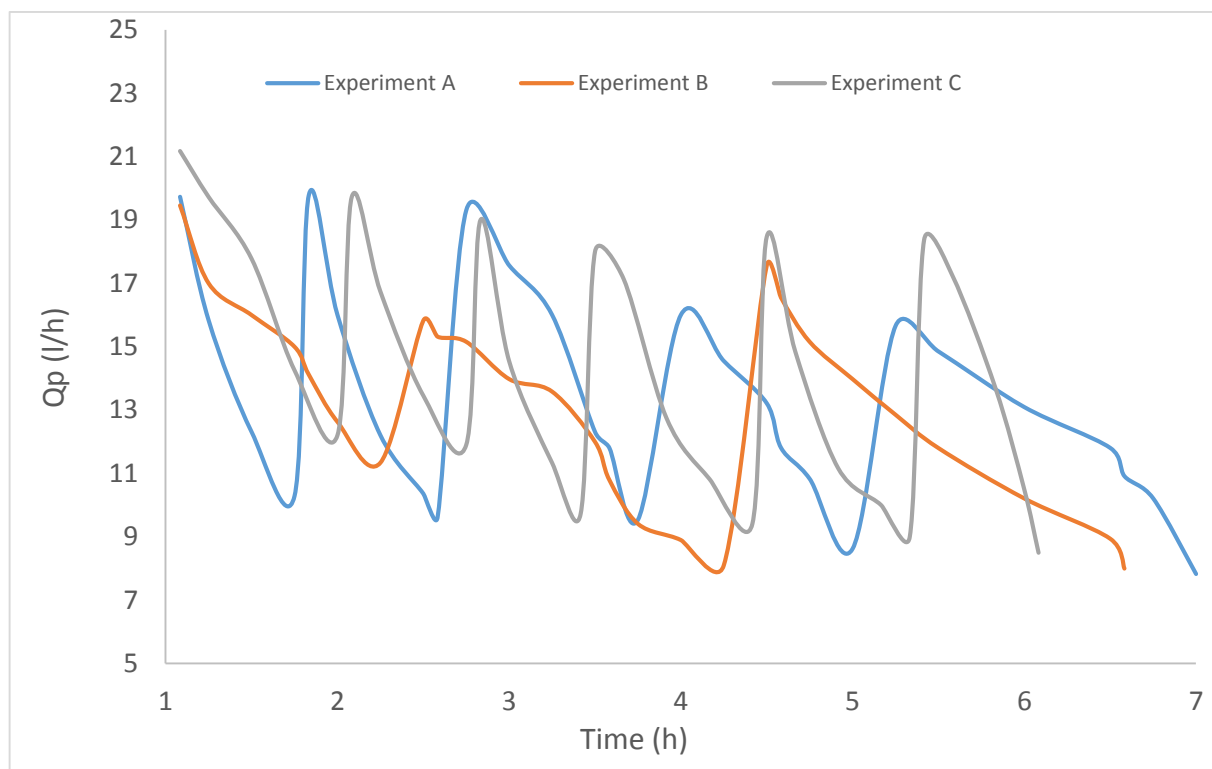
Figure 8.22: Fluxes evolution for the UF experiments A, B and C

9. Conclusions

From the results of this experimental study on the evaluation, using experimental methodologies, of the phosphate adsorption capacity of a synthetic zeolite obtained using fly ash from coal fired power plants the following conclusion could be drawn:

XRD analysis show that the conversion of the sodium zeolite in Ca-Ze and the Los Barrios and Teruel fly ashes in the potassium form was efficient.

The equilibrium isotherms show that phosphate adsorption by zeolites follow the Langmuir model and the sorption capacity of the calcium zeolite Ca-Ze is the more adequate for the sorption experiments using the hybrid system incorporating UF.

The kinetic evaluation in the low phosphate concentration range shows a good phosphate sorption rate for continuous stirred tank reactors..

The studies of sorption and zeolite separation by ultrafiltration show better performance in the phosphate removal kinetics.

The increase of pH from 8±0.2 to 9±0.2 have very positive effects increasing the phosphate removal efficiency up to 70%. Although at these pH values the charge on the Ca_Ze surface is negative and according to this the phosphate adsorption be not be favored the precipitation of calcium phosphates, as brushite and hydroxyapatite, is thermodynamically and kinetically favored and then the phosphate removal is improved.

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10. Environmental impact of the project

This project look to reduce the environmental impact of phosphates, but during the experiments and analysis chemicals were used to prepare solutions of phosphates, colorimetric reagents, etc., paper, glass, gloves and other laboratory materials were waste. All the residues have to be eliminated correctly.

One contaminant is phosphate, it is the waste studied and standard solution were prepared for the experiments, from low concentration (1 mg/l) to high concentrations (15.000 mg/l), sometimes this solutions contain others like HCl or NaOH for pH control. The phosphate solution can contain other contaminants such as nitrates and sulphates, because of the acid o basic nature of the waste those are stored in acid-base waste containers.

The colorimetric reagent for UV-Vis spectrophotometry is made using vanadium and molybdenum, those are heavy metals and are dangerous for the environment, and they had to be stored in apposite heavy metal waste container.

The eluents used in ionic chromatography and samples waste are stored automatically by the chromatograph into an apposite container.

The glass wastes have to be stored in a container for the safety of the cleaning personnel, pieces of glass can be dangerous when manipulated and may have dangerous substances on the surface because are used for laboratory experiments.

Other wastes like paper that not contain contaminants can be throw in normal waste.

All the hazardous wastes are treated by an authorized company that recycle, eliminate or store it correctly.

Another impact to consider is the use of natural resources as water, to clean and prepare solutions, and fuels used to generate electrical energy for the equipment.

Those are negative impacts to the environment but at list this project focus on the environments' conservation and protection. In a global look this project have a positive impact because the research will allow to reuse hazardous contaminants such as phosphate and fly ashes. The elimination of phosphates from water will palliate the eutrophication process and the use of adsorbents will eliminate the sludge produced by precipitation methods and the chemicals needed for. The zeolite can be used directly as a slow release fertilizer, due are not needed more chemical transformations to recycle the phosphate. The reutilization of phosphate means less extraction, and the reduction of mining and chemical transformation, reducing the emissions causing greenhouse effect.

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11. Economic study

In this part are related the costs of laboratory materials, reagents, equipment and personnel for the realization of this project.

The BOM is detailed in table 11.1. Almost all the materials were present in the laboratory before, because were used by other students and teachers in the past, but in this BOM are related all thinking in a new starting project.

Item	Unit cost (€/un.)	No. Units	Cost (€)
Volumetric flask 25 ml	9,21	6	55,26
Volumetric flask 50 ml	9,72	6	58,32
Volumetric flask 100 ml	12,26	8	98,08
Volumetric flask 250 ml	16,47	2	32,94
Volumetric flask 500 ml	21,78	2	43,56
Volumetric flask 1000 ml	24,11	1	24,11
Volumetric flask 2000 ml	37,33	1	37,33
Volumetric flask 5000 ml	113,02	1	113,02
Beaker 50 ml	2,47	4	9,88
Beaker 100 ml	2,54	1	2,54
Beaker 250 ml	2,77	2	5,54
Beaker 500 ml	3,13	2	6,26
Beaker 1000 ml (PP)	2,81	1	2,81
Vial 20 ml	0,25	63	15,75
Test tubes 10 ml (250)	20,00	4	80,00
Reagent bottle 1000 ml	3,21	1	3,21
Petri dish (20)	66,16	1	66,16
Kitasato	35,91	1	35,91
Filter paper (100)	1,46	1	1,46
Magnet	2,28	2	4,56
Parafilm	25,75	1	25,75
Micropipette 1 ml	90,00	1	90,00
Micropipette 5 ml	110,00	1	110,00
Micropipette 10 ml	150,00	1	150,00
Micropipette tips (200)	20,00	5	100,00
Syringe 10 ml (100)	9,19	10	91,90
Filters 20 µm	0,68	1000	680,00
Sample rack	7,50	3	22,50
Safety goggles	7,37	1	7,37
Lab coat	19,20	1	19,20

Gloves box	4,99	1	4,99
Waste container	12,79	1	12,79
		Total:	2011,2

Table 11.1: BOM of laboratory needing.

In the next table are detailed the costs of reagents used during experimental and analysis, such as eluents for ionic chromatography, colorimetric reagent for UV-Vis spectrophotometry and salts to prepare solutions.

Reagent	Unit cost	No. Units	Cost
NaH2PO4·2H2O (500 g)	24,49	1	24,49
HCl (1 l)	11,86	1	11,86
NaOH (500 g)	16,89	1	16,89
CaCl2 (500 g)	27,79	1	27,79
NaCl (500 g)	14,62	1	14,62
Na2CO3 (500 g)	19,40	1	19,40
Na2SO4 (500 g)	24,29	1	24,29
NaHCO3 (500 g)	25,07	1	25,07
CH3SO3H (250 ml)	73,40	1	73,40
(NH4)6Mo7O24·4H2O (100 g)	50,40	1	50,40
NH4VO3 (50 g)	33,40	1	33,40
Milli-Q	1,00	150	150,00
			471,61

Table 11.2: BOM of laboratory reagents.

The equipment's cost has to be calculated using the repayment period, due the cost is calculated in base of the initial investment, time in use and time needed to return the investment. Spanish law establish a maximum payback period for the different equipment. For the laboratory equipment the maximum % amortized /year is 10% in a maximum period of 20 years and for informatics systems 33% in a maximum period of 6 years.

The amortised cost is calculated using equation 11.1:

$$(amortised\ cost) = \frac{(equipment\ cost)\ x\ (time\ in\ use)}{repayment\ period}$$ **Equation 11.1**

The % amortized is calculated using equation 11.2:

$$\%amortised = \frac{(amortaised\ cost)\ x\ (time\ in\ use)}{(equipment\ cost)}$$ **Equation 11.2**

The equipment cost is calculated in reference to reference prices.

Equipment	Equipment cost (€)	Repayment period (years)	Time in use (years)	amortised cost (€)	% amortised/year
Spectrophotometer	6000	15	10	4000,0	6,67
Automatic sample rack	2500	15	2	333,3	6,67
Chromatograph	24000	15	2	3200,0	6,67
Computer	700	5	2	280,0	20
			Total amortised:	7813,3	

Table 11.3: Amortised costs of equipment.

The personnel cost are calculated considering that the work into the laboratory is done by: clean service, who keep clean the laboratory, technicians, who do the experiments and collect the data, project manager who coordinate the operations and do data discussion.

Personnel	Salary (€/h)	Time (h)	Cost (€)
Cleaning	15,00	80	1200,00
Technicians	35,00	800	28000,00
Project manager	52,00	30	1560,00
		Total:	30760,00

Table 11.4: Personnel costs.

Another cost is water and is estimated in 250€ and electrical energy 300€.

To all this costs is needed to calculate the duties and taxes, in table 11.5 is shown the results.

The insurance for the personnel is called in Spain "seguridad social" (SS) and is 32%. The value-added tax (VAT) is 21% for materials, energy and equipment and 10% for water.

Costs		VAT (%)	Insurance (SS) %	Costs + VAT or SS
amortised cost (€)	7813,3	21	N/A	9454,1
Lab. Materials cost (€)	2011,2	21	N/A	2433,6
Reagent cost (€)	471,6	21	N/A	570,6
Water cost (€)	250,0	10	N/A	275,0
Energy	300,0	21	N/A	363,0
Personnel cost (€)	30760,0	N/A	32	40603,2
			Total cost:	53699,5

Table 11.5: Total costs.

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13. Bibliography

[1] Introduction to Zeolite Molecular Sieves Escrito por Jiri Cejka,Herman van Bekkum,A. Corma,F. Schueth

[2] mindat; http://www.mindat.org/min-4395.html

[3] "Using Zeolites in Agriculture"; Frederick A. Mumpton; Department of the Earth Sciences State University College.

[4] J. V. Smith, "Structural classification of zeolites," *Mineral. Soc. Am. Spec. Pap. 1. Int. Mineral. Assoc. Pap. Third Gen. Meet.*, 1963.

[5] P. A. Jacobs, E. M. Flanigen, J. C. Jansen, and H. van Bekkum, *Introduction to Zeolite Science and Practice*, 2nd ed. Elsevier Science, 2001.

[6] N. Moreno, X. Querol, F. Plana, J. M. Andres, M. Janssen, and H. Nugteren, "Pure zeolite synthesis from silica extracted from coal fly ashes," *J. Chem. Technol. Biotechnol.*, vol. 77, no. 3, pp. 274–279, 2002. New Developments in Zeolite Science and Technology editado por Y. Murakami,A. Iijima,J.W. Ward

[7] N. Moreno, X. Querol, C. Ayora, C. F. Pereira, and M. Janssen-Jurkovicová, "Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters," Environ. Sci. Technol., vol. 35, no. 17, pp. 3526–3534, 2001.

[8] C. Y. Pathak, D. Roy, and S. Das, "Utilization of fly ash byproduct in synthetic zeolites," World J. Civ. Eng. Constr. Technol., vol. 1, no. 1, pp. 2–11, 2014.

[9] D. Ruen-ngam, D. Rungsuk, R. Apiratikul, and P. Pavasant, "Zeolite formation from coal fly ash and its adsorption potential." J. Air Waste Manage. Assoc., vol. 59, no. 10, pp. 1140–1147, 2009.

[10] K. S. Hui, C. Y. H. Chao, and S. C. Kot, "Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash," J. Hazard. Mater. vol. 127, no. 1–3, pp. 89–101, 2005.

[11] R. Juan, S. Hernández, J. M. Andrés, and C. Ruiz, "Ion exchange uptake of ammonium in wastewater from a Sewage Treatment Plant by zeolitic materials from fly ash," J. Hazard. Mater. vol. 161, no. 2–3, pp. 781–786, 2009.

[12] M. Zhang, H. Zhang, D. Xu, L. Han, D. Niu, B. Tian, J. Zhang, L. Zhang, and W. Wu, "Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method," Desalination, vol. 271, no. 1–3, pp. 111–121, Apr. 2011.

[13] M. S. Onyango, D. Kuchar, M. Kubota, and H. Matsuda, "Adsorptive removal of

phosphate ions from aqueous solution using synthetic zeolite," Ind. Eng. Chem. Res., vol. 46, no. 3, pp. 894–900, 2007.

[14] B. Zhang, D. Wu, C. Wang, S. He, Z. Zhang, and H. Kong, "Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment," J. Environ. Sci., vol. 19, no. 5, pp. 540–545, Jan. 2007.

[15] H. Huang, D. Xiao, R. Pang, C. Han, and L. Ding, "Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined

[16] J. Chen, H. Kong, D. Wu, Z. Hu, Z. Wang, and Y. Wang, "Removal of phosphate from aqueous solution by zeolite synthesized from fly ash.," J. Colloid Interface Sci., vol. 300, no. 2, pp. 491–7, Aug. 2006.

[17] http://www.iseca.eu/en/science-for-all/what-is-eutrophication

[18] V. Smil, "Phosphorus in the environment: Natural Flows and Human Interferences," Annu. Rev. Energy Environ., vol. 25, no. 1, pp. 53–88, 2000.

[19] A. Paytan and K. McLaughlin, "The oceanic phosphorus cycle," Chem. Rev., vol. 107, no. 2, pp. 563–576, 2007.

[20] "European directive 91/271/CEE."

[21] http://www.lenntech.com/phosphorous-removal.htm#ixzz3evAszlDF

[22] Principles of Adsorption and Reaction on Solid Surfaces Escrito por Richard I. Masel

[23] S. Yeoman, T. Stephenson, J. N. Lester, and R. Perry, "The removal of phosphorus during wastewater treatment: a review." Environ. Pollut. vol. 49, no. 3, pp. 183–233, 1988.

[24] B. Ebbers, L. M. Ottosen, and P. E. Jenssen, "Electrodialytic treatment of municipal wastewater and sludge for the removal of heavy metals and recovery of phosphorus," Electrochim. Acta, 2015.

[25] Separation process principals Henley,Seader,Roper and Ultrafiltration and Microfiltration Hanbook Munir Cheryan

[26] Micellar Enhanced Ultrafiltration: Fundamentals and applications Sirshendu De, Sourav Mondal

[27] HOLLOW-FIBER MEMBRANESI. Moch Jr. I. Moch and Associates Inc., Wilmington, Delaware, USA

[28] Análisis químico cuantitativo tercera edición Daniel C. Harris editorial Reverté

[29] American Public Health Association, American Water waorks Association, Water Environmental Federation. 1999

[30] Squire's Fundamentals of Radiology Escrito por Robert A. Novelline,Lucy Frank Squire 6th edition

[31] X-Ray Diffraction: A Practical Approach. Escrito por C. Suryanarayana,M. Grant Norton first edition 1998, ISBN 978-1-4899-0148-4 (ebook)

[32] K.Y. Foo, B.H. Hameed / Chemical Engineering Journal 156 (2010) 2–10.

[33] Pham et al., 2013.

[34] Mahrez 2015.

[35] Citation review of Lagergren kinetic rate equation on adsorption reactions YUH-SHAN HO a) School of Public Health, Taipei Medical University, Taipei (Taiwan) b) Bibliometric Centre, Taipei Medical University - Wan-Fang Hospital, Taipei (Taiwan)