

## Summary

Phosphorus is a limited global resource; current studies have to be focused mainly on its recovery rather than its disposal. Thereby, the operational lifespan of this resource would be extended and in turn the phosphorus resources can reduce their depletion. Nowadays, wastewater represents a breakpoint of this cycle, in our daily activity. Even though legislation rules the maxim concentration of phosphate in the effluents, it is not required its recovery, and there it lies the interesting line of work.

Aiming at the development of phosphorus recovery technology from the wastewater, it was investigated the sorption behaviour of phosphate ( $\text{PO}_4^{3-}$ ) by sorbents like fly ash and synthetic zeolites. Furthermore, with the loaded zeolite can have the potential use as a low cost fertilizer, since the sorbed phosphate can be released to the soil.

On the other hand, for this project a sorbent was previously synthesized by enhanced the original synthetic zeolite named Na-P1 to its calcium form, expecting an improvement of the new sorbent (Ca-Ze) in terms of the sorption capacity.

Divided into two parts this project would achieve the following objectives. Firstly, the study of the mechanism involved in the sorption process to remove the phosphate from aqueous solution by the sorbents above mentioned. Finally, the second objective was establish the settings of the working conditions for the experimentation on a hybrid sorption-ultrafiltration pilot plant, where the sorbent with best sorption feature was tested.

Experiments carried out were designed to study the behaviour between sorbent and sorbate (phosphate) under different conditions. Batch experiments were carried out under conditions of pH 8, typical of treated waste water and considering two sources of phosphate. Kinetics experiments were performed using two sources of phosphate, and two different aqueous matrix; Mili-Q and tap water.

The obtained data was fitted by the Langmuir and Freundlich sorption models to establish the equilibrium. On the other hand, kinetics data were fitted by the pseudo first order, pseudo second order and Elovich models. The characterisation of the sorbents was carried out by XRD and SEM/EDAS techniques, before and after the sorption process.

Moreover, as the second part of this project the best sorbent found during the equilibrium and kinetic experiment was then tested in a hybrid sorption-ultrafiltration pilot plant. Where more realistic conditions were set and tested with the aim of setting the suitable working conditions of the elements involved in the system.



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## 1. Glossary

- B Fly ash from Los Barrios
- Ca\_Ze Synthetic zeolite riche in calcium
- EQ Equation
- Fig. Figure
- Hap Hydroxyapatite
- Na-P1 Synthetic zeolite riche in sodium
- SEM/EDS Scanning electron microscopy / Energy Dispersive X-ray Spectroscopy
- T Fly ash from Teruel
- ppm Part per million
- XRD X-Ray diffraction



## 2. Preface

### 2.2. The project start

This Final Degree Project is part of a PhD thesis ongoing in the Chemical Engineering Department of the “Escola Tècnica Superior d’Enginyeria Industrial de Barcelona”. It is focused on the removal and recovery of phosphate and ammonium from wastewater effluents through zeolites, synthesized from fly ash and pre-treated with sodium hydroxide.

### 2.3. Motivation

As part of a long journey through my degree on Chemical Engineering, this project is the sum up of this hard work. Where people encountered along this road awakened in me the motivation to face any problem, even those impossible at first sight. In view of that every small contribution is important in itself, and therefore every small step walked approaches us to the final solution.

Earth is our planet, so though it can hold all of us it is our duty to manage it properly. Natural resources are finite. Phosphorus is an example, since is essential for live. But in this case the difficulty arises from the nature of phosphorus and the amount of its reserves.

This project is a further step in the field of recovery of nutrients and specifically phosphorus, which is found in wastewater treatment plant effluents. In order to do that, some materials were evaluated for its sorbent properties and its potential application as low cost fertilizer.

Materials such as fly ash and synthetic zeolites, this latter made from the former, were studied to finally select one candidate, which was studied in a pilot plant, where a combined system of sorption and ultrafiltration was tested and setting.



## **3. Introduction**

### **3.1. The aims of project**

Under this project would be reached the understanding of phosphate sorption process by fly ash and synthetic zeolites.

To that end, several experiments were conducted to study and determine different parameter for the equilibrium and kinetic between sorbent and sorbate for the working condition established.

The final aim in this project was establish the working condition for a hybrid sorption-ultrafiltration pilot plant, where the best sorbent found was tested.

### **3.2. The scope of the project**

This project is part of a much wider objective, which its objective is the recovery of phosphate and ammonium from waste water by wastewater effluents through zeolites, synthesized from fly ash and pre-treated with sodium hydroxide.

As part of this wider project, the phosphate sorption will be studied by fly ash and synthetic zeolites.

Finally establish the working condition for a hybrid sorption-ultrafiltration pilot plant, where the best sorbent found was tested.



## 4. State of art

### 4.1. Phosphorus

There are 14 essential plant nutrients and phosphorus (P) is one of them. As a limiting nutrient that is, its different forms stimulates the growth of aquatic plants, even more than nitrogen as their ratios are typically 16:1 in aquatic systems (Wendling et al. 2013).

The plants most often absorb the phosphorus in the form of orthophosphate, such as ionic forms of  $(\text{H}_2\text{PO}_4)^-$ , at pH below 7, and sometimes as  $(\text{HPO}_4)^{2-}$ , in alkali soils. Phosphorus is often referred to as the “energizer” since it helps to store and transfer energy, such as the adenosine triphosphate or ATP molecule, during photosynthesis. It is also part of the genetic material of all cells-DNA and RNA.

Phosphorus can be found in two forms in water bodies basically, dissolved and particulate, though when both are dissolved they can change easily from one form to another very quickly.

Dissolved phosphorus is small enough to pass through a 0.45  $\mu\text{m}$  filter and includes phosphorus forms like: soluble reactive phosphorus and soluble organic compounds that contain phosphorus. While particulate phosphorus is big enough not to pass through 0.45  $\mu\text{m}$  filter and usually is incorporated into particles of soil or as part of algae and small animals that are suspended.

#### 4.1.1. Phosphorus as phosphate forms

Municipal and industrial wastewater discharges contain the higher amount of phosphorus susceptible to be recovered nowadays (Kõiv et al. 2010). Phosphorus more usual forms are orthophosphate and polyphosphate. However the orthophosphate form is mainly present in in the phases shown in Fig. 4.1.

Although orthophosphate is more common as part of life, it is the phosphate form which can be more easily removed from wastewater, and thereof be used as for making fertilizers by different techniques.

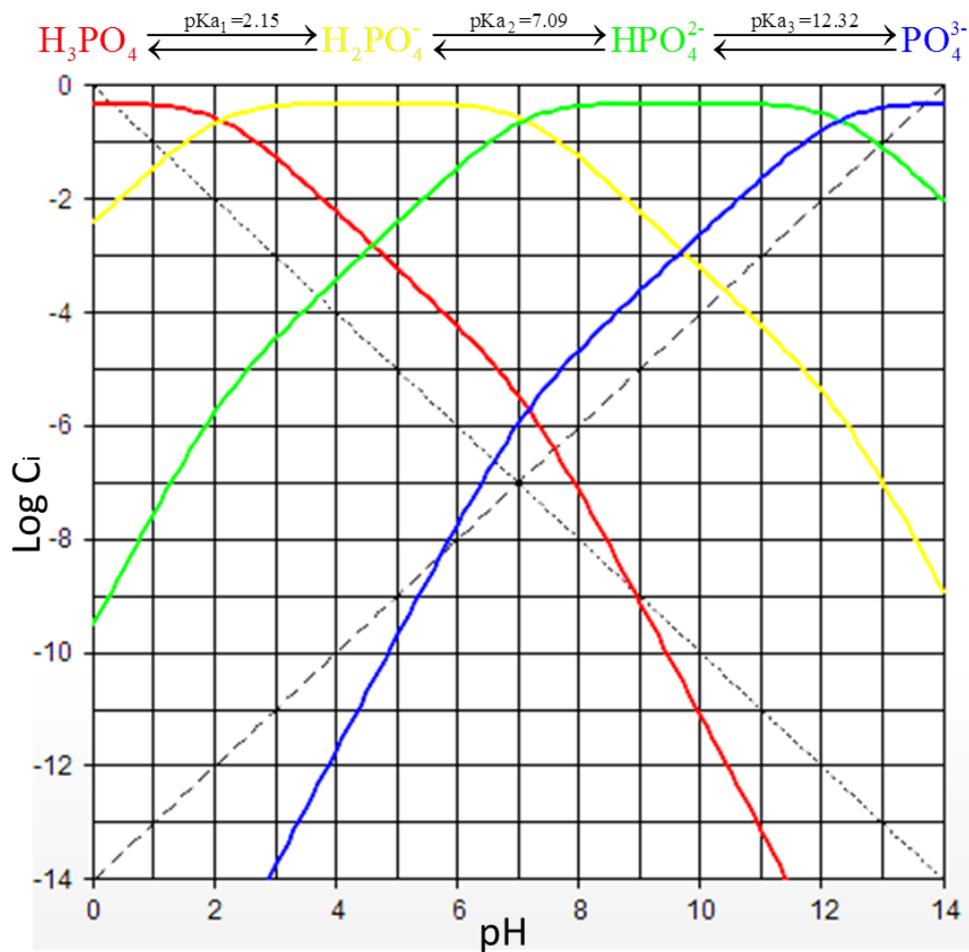


Fig. 4.1. pH diagram of the species of orthophosphates in aqueous solution.

#### 4.1.2. Phosphorus as solid forms

The most common mineral of phosphorus is apatite. Apatite is a family of minerals, where the fluoapatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ , is the most common. Also it is the main source of the phosphorus required by plants.

In the same apatite it is found apatito-(CaOH), also called hydroxyapatite or Hap (chemical composition  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ), which represents around 80% of total phosphorus in human being as part of bones and teeth. Moreover, in the same family it is found brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) the precursor of the Hap, with much better possibilities to be a fertilizer than Hap since this latter is more difficult to dissolve under natural conditions.

## 4.2. Phosphorus concerns

Phosphorus is a limited and scarce resource on Earth. The supply of phosphorus is running out (Franklin D. Roosevelt (May 20, 1938). 64 - Congress on Phosphates for Soil Fertility). Almost 90% of estimated reserves are located in five countries: Morocco (the first global – exporter), China, South Africa, Jordan and the United States.

The phosphorus cycle begins with phosphorus rocks, which is released by the rainwater in a solution of phosphate. This solution nourishes the soil and plants can incorporate phosphorus from it. Then, the animals eat the plants incorporating its phosphorus, finally it will be returned to the soil again, either by plants and animals through its decomposition material and/or depositions. Otherwise, phosphorus ends in the seas and oceans, where the cycle to return to earth could take millenniums.

Moreover, since phosphorus cannot be manufactured synthetically (Yuan, Pratt, and Batstone 2012) and the need in agriculture is increasing a technological solution must be developed. This solution must necessarily involve the recovery of phosphorus instead of mere its disposal, as its importance in the industry of fertilizer can report profit, as well as an environmental benefits.

On the other hand, overuse of fertilizers has created the problem of elevated phosphorus in water bodies causing eutrophication. This is a well-known anthropogenic problem that is getting worse since the Earth's population is increasing along with its needs. Meanwhile, many lakes, artificial dam and stretches of rivers with backwaters have seen destroying their ecosystems by this problem.

The ideal stoichiometric nutrient ratio of Si:N:P is 16:16:1 in aquatic systems (Wendling et al. 2013) and when this ratio is been altered, by increasing its limiting resources (like the availability of nitrogen and phosphate), microscopic algae begin to grow uncontrollably covering the surface of the water. This fact prevents sunlight from reaching the bottom of the water, which effects the growth of background algae. Less light means less photosynthesis and therefore oxygen levels decrease. Life dies and decomposition takes place, accelerating the diminution of oxygen until is found a lifeless environment. This happens mainly in dams and lakes, since they trap and accumulate nutrients, Ward & Stanford (1983) suggested that. On the other hand, the opposite problem can be also possible. Where the entrapment within reservoirs could lead to oligotrophication downstream, causing reductions in the biota (Benítez-Mora and Camargo 2014).

Anthropogenic inorganic forms of nitrogen and phosphate come mainly from fertilisers used in agriculture. Once the soil has absorbed the necessary nutrients, the remaining nutrients

are likely to be washed into the rivers and lakes by rainwater, reaching the water table and contaminating the water.

Moreover, nitrogen and organic phosphate come from domestic waste water. Nitrogen as urea basically ( $\text{CO}(\text{NH}_2)_2$ ), and phosphate as part of macromolecules like DNA, RNA, enzymes, vitamins etc. present in human and animal excreta. This latter is accentuated by intensive animal farming.

### 4.3. Phosphorus recovery and removal technologies

When phosphorous became a problem in the 1950's, several technologies were developed to remove it. Recently it became obvious that phosphorous is a limited global resource making that these studies focussed more on its recovery, to increase the operational lifespan of the resource.

Early studies about the removal of phosphorus involved the simple technique of chemical precipitation.

Many other removal techniques exist, but currently the most employed ones such as sorption, crystallization and biological, are used to concentrate the resource with potential formation of a product or by-product with high added value.

#### 4.3.1. Chemical precipitation

This technique is used in water treatments and it is based on the addition of a chemical in order to alter the physical state of dissolved and suspended solids thereby facilitating their removal by sedimentation (Physico-chemical process). Aluminium sulphate is the main chemical used and it works as a destabilizer or flocculent to improve an insoluble metallic phosphate salt: like ferric phosphate ( $\text{FePO}_4$ ), calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), hydroxyapatite (Hap) or apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) and struvite ( $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ). Where phosphate precipitated is removed through the sewage slugs.

Spanish legislation determines the potential use of sewage sludge on agricultural soils (Directiva 86/278/CEE of 12th of Jun) according to the concentrations of hazardous pollutants to human health. Many of the studies are focused on reducing the concentration of phosphorus before it finally becomes part of the sludge (Barat et al. 2011), because the vast majority ends up in landfills, or is used as alternative fuels or as part of construction materials. Where phosphorus still remains in the sludge it is not recovered and so cannot be re-used.

### 4.3.2. Biological removal / recovery

Different and varied microorganisms are used in order to consume the phosphorus present in waste water. As part of their natural cycle they need phosphorus to increase their population. And as part of their natural cycle they die and are collected as part of sewage sludge that can have many uses as fertilisers, combustibles or even material for construction.

This technique is not only used in urban sewage treatment plants, but also in abattoir wastewater. Industries must regulate the concentration of their effluents due to regulation. Then discharge must reach the limits defined by legislation and the same time can recover phosphorus present in the effluent. Much more interestingly, when the source of phosphorus is biological and reduces the cost of the recovery process (Ge and Batstone 2014).

As part of wastewater the phosphorus is under concentrations of  $10 \text{ mg P/dm}^3$ . Biological removal produces a sludge where phosphorus is much more concentrated, and the uses of this sludge are interesting as they can be solubilised in order to recover phosphorus as mineral product or even as fertilizer scattered directly on the soil (Yuan, Pratt, and Batstone 2012).

### 4.3.3. Sorption

Nowadays the most studied and interesting technique to recover the phosphorus is sorption. This could meet both the removal needs and the use for the phosphorus through a new line of products depending of the materials and technique used.

Sorption fundamentals, which will be further explained in Chapter 6, are basically separation techniques where a sorbent with suitable properties can trap/retain the phosphate in its surface structure. Many materials have been used for this purpose, like silica, ion exchange resins, clays and activated carbon among others. Much of these materials have an expensive cost and/or they cannot have any other use, so the phosphorus sorbed is just removed.

Zeolites, natural or synthetic, are potential sorbents that have received more attention in the last decades as they can hold phosphorus and other elements, like ammonium and potassium, from wastewater discharges (Johansson Westholm 2006). And furthermore some of the by-products obtained can be used as fertilizers (Luz and Bashan 2004), so the cycle of phosphorus is completed again in the plants.

In this regard, studies based on synthetic zeolites made from fly ash assess two interesting targets. Firstly, these synthetic zeolites can be made with selective proprieties to enhance the separation of the target ion. Secondly, the fly ash is a by-product of power plants, which would otherwise end up as filler material.



## 5. Generalities about fly ash and zeolites

Down below, a theoretical and global introduction about the sorbents used for this study.

### 5.1.1. Fly ash

Fly ash can have either natural or anthropogenic origin. Natural fly ash comes mainly from volcanic eruptions and deposited on the ground, whereas anthropogenic fly ash comes from the combustions facilities and is considered a priori a useless by-product.

The inorganic residues arising from coal combustion process are known as coal combustion by-products (CCBs in USA, or CCP in Europe). CCP are mainly considered as fly ash from the combustion in coal power plants. However, the fly ash term is used as a general speaking, since at list two classes of these ashes can be distinguished. Bottom ashes are the ones to reach the bottom of the boiler through falling down the airflow, and are mechanically removed. The term fly ash, by contrast, is referring to ash which is particles fine enough to ascend by flue gas and collected by the electrostatic or mechanical precipitator. However, other classifications can be applied according to other properties, such as its chemical composition.

#### 5.1.1.1. Fly ash chemical properties

What defines fly ash uses is its mineralogical composition, which depends on:

- a) Composition of coal and its source.
- b) Burning condition and temperature of the boiler.
- c) Boiler configuration.
- d) The particle size of coal.
- e) The gas cleaning equipment.

The proper characterization in terms of mineralogy and elemental composition, surface chemistry and reactivity is of great concern, but this is a high challenge, since as approximately 316 individual minerals and 188 mineral groups have been identified in various ash samples (Yao et al. 2015)(Wendling et al. 2013). Even thought, major components are metallic oxides with varying contents of unburnt carbon. The contents of principal oxides are usually in decreasing order:  $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CaO} > \text{MgO} > \text{K}_2\text{O}$ .

#### 5.1.1.2. Fly ash physical properties

Fly ash is a fine powder, where the particles are predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature, though the crystalline phase can

be found in fly ash that come from coal power plants, and depends on the temperature of combustion. The carbonaceous material is composed of angular particles, and depends if the coal used is bituminous or sub-bituminous. The sizes of these particles are in the range of 0.1 to 600  $\mu\text{m}$ . Other physical properties, as the specific gravity usually range from 2.1 to 3.0, while its specific surface area (BET) may vary from 170 to 1000  $\text{m}^2/\text{kg}$ . All these parameters are important to determine the reactivity of the fly ash and capacity to make a synthetic zeolite. The colour of fly ash can vary from tan to grey to black, depending on the amount of unburned carbon in the ash.

### 5.1.1.3. Fly ash uses

As already discussed, many uses can be found to turn fly ash in a new product with added value. Though all basically depends on their original composition.

The principal uses are explained in this section, though paying more attention to their applications as sorbent and as precursor of synthetic zeolites.

As solid they can be used as part of constructions materials like cement, road surface, ceramics products and filler material, though seldom by themselves on account of their chemical composition and reactivity, which may confer some incompatibilities.

Fly ash has been evaluated as sorbent material, in view of their characteristics to ion-exchange or just superficial sorption which is determined by their surface area configuration. In that direction fly ash can be part of additives for immobilization of pollutants in industrial and water treatment plants, so they can store toxic metals such as Al, Si, Fe, Ge, V, and Ni. Several other metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Hg}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{As}^{5+}$  and  $\text{Cs}^+$  can be removed from wastewaters by using fly ash precipitation and sorption mechanisms. In most cases, removal efficiency depends on metal concentration, pH and temperature. Likewise fly ash can be used as a sorbent for toxic substances in flow gas, like NOX and  $\text{SO}_2$ . Due to the higher stability of its principal component aluminosilicates, fly ash could also be employed as catalyst supports for various reactions.

Fly ash has similar compositions of natural fly ash and some volcanic material, the precursor of natural zeolites. Since the pioneering work of Holler and Wirsching (1985), many new studies have been undertaken and various ways have been developed to synthesize diverse types of zeolites.

Zeolite synthesis is based on the dissolution of Al–Si-bearing fly ash phases with alkaline solutions (mainly NaOH and KOH solutions) and the subsequent precipitation of zeolitic material (Querol et al. 2002). Three steps, namely dissolution, condensation and crystallization, exist in an alkali hydrothermal reaction for zeolite synthesis. The rate of the synthesis is influenced by the  $\text{Na}^+$  concentration in the alkali solution. However, two

obstacles are presented using the technique mentioned. Firstly the amount of mullite ( $Al_4+2xSi_2-2xO_{10-x}$  (where  $x \sim 0.4$ )) and quartz ( $SiO_2$ ) are considered to be inert and difficult to dissolve. So the resultant product is usually co-crystallized zeolites with original crystalline phases. The second issue which may happen is the formations of a cover of aggregates, like an egg white, in the central core of fly ash particles, a factor that lowers the efficiency of the synthesis of zeolite.

### 5.1.2. Zeolites

Zeolite can be defined in many ways, but the most accepted definition is to talk about aluminium-silicates with alkali elements as Na, K, Mg or Ca. With a complicated structure of inorganic polymer forming a crystal unit, based on the tetrahedral bonds between oxygen of  $AlO_4$  and  $SiO_4$ . In Fig. 5.1 is shown how the structural units are taking place in order to build the crystalline structure.

There are many ways to classify Zeolites, but can be distinguished two big families. Natural zeolites, which are minerals like: clinoptilolite, mordenite, erionite or phillipsite, and then synthetic zeolites. Which are made from fly ash by and hydrothermal crystallization. Shape, size, pore size hold, canal network distribution, volume and distribution of cell and the availability for cations are some of many ways that zeolites can be classified.

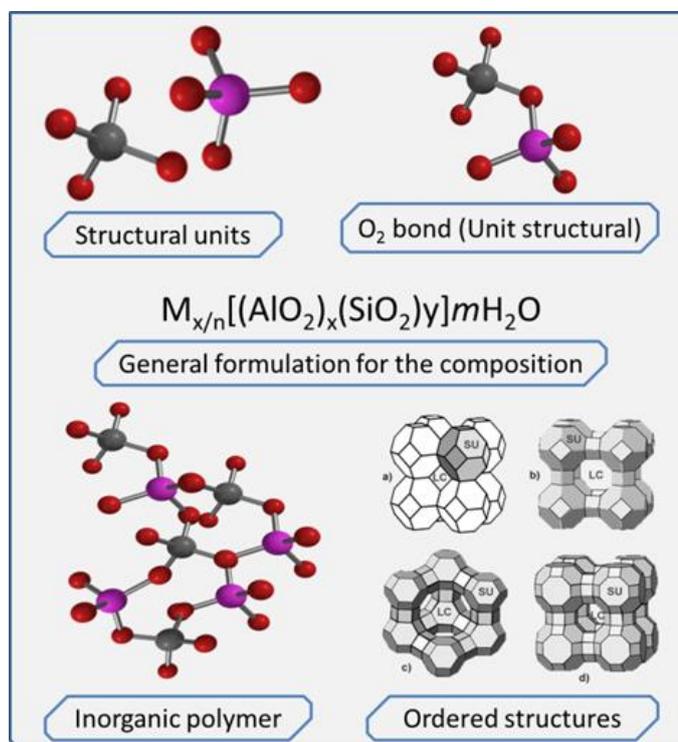


Fig. 5.1. Structure and nomenclature of zeolite.

### 5.1.2.1. Zeolites chemical properties

Two major chemical properties are relevant for zeolites. First one is catalysts. Their rich composition in metal oxides and ordered amorphous structure, with plenty of cavities, allow good contact between the medium to be catalysed and the zeolite activator in it. And as we already have mentioned, through the swapping between cations, we can conduct a specific reaction instead of another.

Much more important is their ion exchange capacity. The Si/Al-O structure is rigid, but cations can be exchanged by others, for this reason they are called exchangeable cations. Usually the new cation, with lower charge, takes the place of the tetrahedral cation with greater charge, this is known as isomorphs exchange. This swap raises the structural negative charge of the zeolite, so more cations can take the remaining spaces, while the water holds the zeolite electronegativity integrity. This property makes possible modifying as much the structure and sizes of the canals as the charge, and this significantly affects the kind and size of molecules that can be sorbed. So the sorption behaviour can be modified through a good selection of new cations that can meet our needs.

### 5.1.2.2. Zeolites physical properties

Zeolite and fly ash share physical properties, however through the modification that can be applied on zeolites, these properties can be enhanced. Like the internal structure and size pore and chemical composition.

### 5.1.2.3. Synthetic Ca-zeolite and phosphate recovery

It has been commented already that zeolites can be synthesised from fly ash. In this point, cations are exchanged for the cation provided for the alkali solution used. The most usually reactive expended is NaOH. Considering that sodium cations can be easily exchanged again for another cation of interest. This is possible because sodium cation is weak, though the structure zeolite has to conserve its integrity, for this reason others cation can take its place.

Furthermore, nowadays several studies are in line to synthesize zeolites rich in calcium (Moutsatsou et al. 2006) in order to succeed in obtaining products with potential use as fertilizer (Bansiwal et al. 2006). To this end the importance of calcium is crucial because together with phosphate can be obtained minerals such as HAP, struvite and brushite, thus incorporating both phosphorus and calcium in the same structure. It is both important elements in the formulation of the current agricultural fertilizers.

Studies carried out about sorption process between synthetic zeolites rich in calcium and phosphate, show that many mechanisms would be carried out simultaneously, where the equilibrium would be the one ruling them as result of the experimental conditions.

Precipitation and complexation are both mainly involved by equilibrium conditions where pH, temperature, species in solution, concentrations of these, the characterisation of the zeolite are the main parameters that eventually affects the equilibrium and therefore the products obtained. Nevertheless, physical sorption is related to the size of phosphate molecule and the size of pores in the zeolite, which could hold it. Likewise physical sorption has influence in the equilibrium process as the available concentration of phosphate change.

#### **5.1.2.4. Zeolites uses**

Some of the uses of zeolites have already been mentioned to explain some of its properties. These are some other specific applications:

- Dehydrating agents.
- Activators agents in some reactions.
- Filler material.
- Ion exchange.
- Sorbent agents.



## 6. Sorption

Sorption is a physical and chemical process by which one substance becomes attached to another. Specific cases of sorption are absorption, adsorption and ion exchange.

Throughout this project was used the term sorption to indicate the different mechanisms involved in the removal of phosphate. Given that sorption is a complex and difficult process to define, other mechanism as precipitation and complexation can be also take in consideration as mechanisms involved in this process. Since their resulting products can be sorbed by the sorbent.

Sorption is a surface phenomenon whereby gas or liquid molecules bind to the solid sorbent surface. In any material, all the bonding requirements of the material are filled by the other surrounding atoms. However, atoms on the surface are not fully surrounded and therefore can attract sorbate in order to reach the neutrality. The nature of the bonding depends on the details of the species involved, but the sorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding) and electric type.

Sorption of electric type falls squarely with the ion exchange and often called adoption exchange, a process whereby the ions of a substance were located on charged sites on the surface as a result of electrostatic forces. For ionic solids, these electrostatic forces are ruled by the charged sites, which are distributed on the surfaces of its channel network and can partially offset when spaced closely. This means that the capacity and selectivity of a given sorbent against two sorbates are ruled as much by the molecular size (radius solvation), which determines the order of preference, as by the charge of the ions, which is the determining factor in the exchange sorption.

The sorption that takes place due to van der Waals is called usually physical sorption or physisorption. In such case, the sorbate molecule is not fixed on specific place but rather is free to move within the interface. This sorption generally predominates at low temperatures.

On the other hand, if the interaction between sorbent and sorbate undergoes a chemical interaction, the phenomenon is called chemical sorption or chemisorption. The sorption energies are strong links located at the active sites of the sorbent and usually favoured at elevated temperature.

Moreover, the sorption separation is achieved by one of three mechanisms: steric, kinetic, or equilibrium effect. The steric effect is unique with zeolites and molecular sieves because of the uniform aperture size in the crystalline structure. In this case only small and properly

shaped molecules can diffuse into the sorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecules. A large majority of processes operate through the equilibrium sorption of mixture and hence are called equilibrium separation processes.

Zeolites have unique sorption properties, mainly because of their unique surface chemistry. The surface of the framework is essentially oxygen atoms, where the anionic oxygen atoms are more abundant and are much more polarizable than Al and Si cations. Thus, the interactions with the sorbate are mainly dominated by van der Waals forces.

The affinity between phosphorus with metallic ions, such as aluminium and iron (Kinouchi, Seino, and Takase 2012; Rafati et al. 2012), makes the zeolite a selective sorbent for phosphorus in aqueous solution. Moreover, zeolites can be enhanced by addition of other metallic ions such calcium, with which can also be achieved an interesting product such a fertilizers.

## **6.1. Sorption principles**

This chapter presents the different experimental configurations and the mathematical models used in this study introducing the theory, fundamentals and principles on which they are based. For the sorption at the equilibrium, two well know models were used Langmuir and Freundlich. On the other hand, Pseudo First Order, Pseudo Second Order and Elovich were the approaches used for the kinetic studies.

All models mentioned are mathematical representations, though they were empirically elaborated. Even though there is an error range they are widely used on different industrial fields. They are generic models so they can easily show pattern of overall sorption process.

### **6.1.1. Sorption at the equilibrium studies**

Equilibrium experiments determine the correlation between concentration in aqueous and solid phase once equilibrium is reached. This may be possible, as many models can be used to get a representation of sorption isotherms. The models used are presented as follows.

#### **6.1.1.1. Lineal isotherm**

Based on Henry's Law, this method allows a mathematical interpretation of the sorption process, where is being assumed a homogeneous sorption on the solid and directly proportional to the sorbate concentration present in the medium (Foo and Hameed 2010)

Mathematical equation is:

$$q_e = k \cdot C_e \quad \text{EQ ( 6.1 )}$$

Where:

- $q_e$ : quantity sorbed at the equilibrium ( $\frac{\text{mg}}{\text{g}}$ )
- $C_e$ : concentrations of the sorbate at the equilibrium ( $\frac{\text{mg}}{\text{dm}^3}$ )
- $k$ : sorption constant ( $\frac{\text{dm}^3}{\text{mg}}$ )

### 6.1.1.2. Langmuir isotherm

The Langmuir model assumes: an electrically homogeny solid surface and there is no interactions between neighbouring sorbed molecules. Where sorption takes place only in the active site points, which can take one and only one molecule and have the same affinity for the molecules of sorbate (Foo and Hameed 2010).

The isotherm model is described by equations EQ ( 6.2 ) and EQ ( 6.3 ):

$$Q_e = \frac{k_L \cdot C_e}{1 + (k_L \cdot C_e)} \quad \text{EQ ( 6.2 )}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot k_L} + \frac{C_e}{Q_0} \quad \text{EQ ( 6.3 )}$$

Where:

- $C_e$ : concentrations of the sorbate at the equilibrium ( $\frac{\text{mg}}{\text{dm}^3}$ )
- $q_e$ : sorption capacity at the equilibrium ( $\frac{\text{mg}}{\text{g}}$ )
- $Q_0$ : maxim capacity of sorption ( $\frac{\text{mg}}{\text{g}}$ )
- $k_L$ : Langmuir's constant, it means the bond strength with the sorbate ( $\frac{\text{dm}^3}{\text{mg}}$ )

The isotherm parameters  $Q_0$  and  $k_L$  can be found through the lineal regression analysis of  $C_e$  versus  $C_e/Q_e$ .

### 6.1.1.3. Freundlich isotherm

The Freundlich model takes a further step to get closer to the reality, as it assumes heterogeneity of sorption sites. Where there is not finite sorption as multiply layers of the sorbent can be formed. Many layer as suitable faces for the sorption could have the solid.

The isotherm model is described by equations EQ ( 6.4 ) and EQ ( 6.5 ):

$$q_e = k_F \cdot C_e^{\left(\frac{1}{n_F}\right)} \quad \text{EQ ( 6.4 )}$$

$$\ln(q_e) = \ln(k_F) + \frac{1}{n} \cdot \ln(C_e) \quad \text{EQ ( 6.5 )}$$

Where:

- C<sub>e</sub>: concentrations of the sorbate at the equilibrium ( $\frac{\text{mg}}{\text{dm}^3}$ )
- q<sub>e</sub>: sorption capacity at the equilibrium ( $\frac{\text{mg}}{\text{g}}$ )
- k<sub>F</sub>: Freundlich's constant, representing the bond strength with the sorbate ( $\text{mg} \cdot \text{g}^{-1} \cdot (\text{g} \cdot \text{dm}^3)^{-1/n_F}$ )
- n<sub>F</sub>: Freundlich's exponent indicates as favoured is the sorption process. Where if n<sub>F</sub> lies between 2 - 10 it is good, 1 – 2 moderately disadvantaged and lower of it would be poor.

The isotherm parameters k<sub>F</sub> and n<sub>F</sub> can be found through linear regression analysis of C<sub>e</sub> versus C<sub>e</sub>/Q<sub>e</sub> and are parameters characteristics of the sorbent-sorbate system.

### 6.1.2. Kinetic studies

The sorption models used are presented below and methodically explained.

#### 6.1.2.1. Pseudo First Order

This model assumes that the main force, responsible of sorption process, is the concentration gradient between sorbate in aqueous solution and the sorbent surface (Plazinski et al. 2009)(Qiu et al. 2009).

The kinetic model is described by equations EQ ( 6.6 ) and EQ ( 6.7 ):

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \quad \text{EQ ( 6.6 )}$$

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 \cdot t \quad \text{EQ ( 6.7 )}$$

Where:

- q<sub>e</sub>: sorption capacity at the equilibrium ( $\frac{\text{mol}}{\text{g}}$ )
- q<sub>t</sub>: sorption capacity at time ( $\frac{\text{mol}}{\text{g}}$ )
- t: time (min)
- k<sub>1</sub>: kinetic constant of Pseudo First Order ( $\frac{1}{\text{min}}$ )

The parameters  $Q_e$  and  $k_1$  can be found through linear regression analysis of  $\ln(Q_e - Q_t)$  versus time.

### 6.1.2.2. Pseudo Second Order

Pseudo second order is based on the same principals as the pseudo first order, but additionally, this model assumes that the chemical sorption or chemisorption is the limiting step of this process (Plazinski et al. 2009)(Qiu et al. 2009).

The kinetic model is described by equations EQ ( 6.8 ) and EQ ( 6.9 ):

$$\frac{dq_t}{dt} = k_2(q_e + q_t)^2 \quad \text{EQ ( 6.8 )}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e} \quad \text{EQ ( 6.9 )}$$

Where:

- $q_e$ : sorption capacity at the equilibrium ( $\frac{\text{mol}}{\text{g}}$ )
- $q_t$ : sorption capacity at time ( $\frac{\text{mol}}{\text{g}}$ )
- $t$ : time (min)
- $k_2$ : kinetic constant of pseudo second order ( $\frac{\text{g}}{\text{mol} \cdot \text{min}}$ )

Then  $Q_e$  and  $k_2$  can be found through linear regression  $t/Q_t$  versus  $t$ , time.

### 6.1.2.3. Elovich

Elovich model was firstly used to describe the sorption in a gas-solid system and can be a good approximation to represent the sorption of solutes in aqueous systems. The base of the mathematical expression describes the behaviour on heterogenic solids.

The kinetic model is described by equations EQ ( 6.10 ) and EQ ( 6.11 ):

$$\frac{dq_t}{dt} = \alpha \cdot e^{-\beta \cdot q_t} \quad \text{EQ ( 6.10 )}$$

$$q_t = \beta \cdot \ln(\alpha \cdot \beta) + \beta \cdot \ln(t) \quad \text{EQ ( 6.11 )}$$

Where:

- $q_t$ : sorption capacity at time ( $\frac{\text{mol}}{\text{g}}$ )
- $t$ : time (min)
- $\alpha$ : initial velocity of sorption ( $\frac{\text{mg}}{\text{g} \cdot \text{min}}$ )

$\beta$ : Relation between covered surface and activation energy of chemisorption ( $\frac{g}{mg}$ )

Then integrating EQ ( 6.10 ) at  $q_t = 0$ , from  $t = 0$  to  $t = t$ , we found EQ ( 6.11 ). Where  $\alpha$  and  $\beta$  are the extrapolation of the linear regression of  $q_t$  versus  $\ln(t)$ .

## 7. Methodology

Methodology and principal characteristics of the sorbents used in this project will be introduced and discussed in this section. Moreover, in the Annexe A and Annexe B it can be found the record of experiments performed and the specifications of some equipment used along this project, respectively.

### 7.1. Sorbent materials studied

For this study 4 sorbents were evaluated. Two fly ash samples and two synthetic zeolites. However, later on all sorbents will be discussed in depth in Chapter 8.1.2, once the properly characterization was done.

#### 7.1.1. Fly ash samples

Two type of fly ash were used in this study, named these as T and B, since the first one came from Teruel (T) and the second one from Los Barrios (B), both two cities of Spain.

Both fly ash samples came from coal thermal plants, where coal burning process to produce electricity is used to supply the surrounding areas.

Fly ash samples were compared with two synthetic zeolites in order to determine the best phosphate sorbent between them. For this purpose, was performed the study of the equilibrium as well as kinetics, XRD and SEM/EDS techniques were used to characterize the products obtained after the sorption, as well as the initial composition of these. Phosphate was determined, before and after the sorption, by using the ionic chromatography technique.

#### 7.1.2. Synthetic zeolites

The other two sorbents used in this project were two synthetic zeolites, one rich in Sodium ions called Na-P1 and the other rich in calcium ions. This last was synthesized from the Na-P1.

Na-P1 synthetic zeolite was synthesized from Nacarea coal fly ash with 3M NaOH solution at 398 K for 8 h by a hydrothermal method as was described by Querol et al. 2007. This process was based on the dissolution of Al–Si-bearing fly ash phases by the alkaline solution and the subsequent precipitation of zeolitic material rich in Na ions (Querol et al. 2002).

The zeolite in calcium form (Ca-Ze) was expected to find a better performance in order to remove phosphate. To that purpose, down below in Chapter 7.1.2.1 will be introduced the procedure to synthesized it.

### 7.1.2.1. Ca-Zeolite (Ca-Ze) synthesis

As part of this project, a rich calcium zeolite was modified from the Na-P1 zeolite, which is rich in sodium cations. This latter was synthesized from fly ash by hydrothermal crystallization process under alkaline (NaOH solution) conditions. The objective of the synthesis was to increase the sorption, of phosphate, on the surfaces and try to obtain a more interesting product, like Hap or calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), more interesting for other industries and uses.

For this study 10000 g of Ca-Ze was prepared from the NA-P1 zeolite. To that purpose, an ion exchange procedure was carried out to exchange of Na in zeolite structure by the calcium ions in solution, as can be seen in Fig. 7.1.

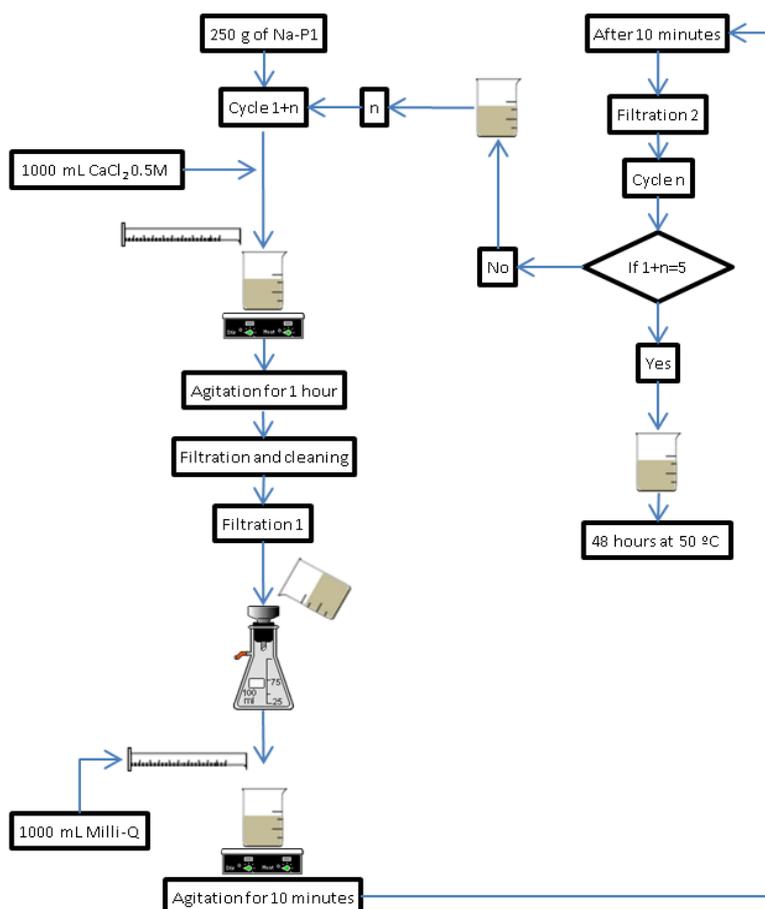


Fig. 7.1. Flowchart for the preparation of Ca-Ze from Na-P1 synthetic zeolite.

The exchange process between  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , in the synthesis of the Ca-Ze from the Na-P1 zeolite, was conducted through a total of 5 cycles. Each one consisting in the alternation of concentrated solutions of calcium chloride ( $\text{CaCl}_2$  : 0.5 M) and rinses of Milli-Q water for each batch of 250 g of Na-P1 to be enhanced. The procedure was carried out as can be seen in Fig. 7.1., taking care to remove as little amount of solid as possible in each filtration between rinses and calcium chloride solution. After the fifth cycle, the amount of zeolite already filtered and cleaned was placed properly in an oven for 48 hours at  $50^\circ\text{C}$ .

## 7.2. Equilibrium studies

Sorption in the equilibrium was evaluated for the four sorbents (T, B, Na-P1 and Ca-Ze). 200 mg of each sorbent, were mixed in  $10\text{ cm}^3$  of solutions of appropriate concentrations of phosphate and from two different sources  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  (100, 300, 500, 1000, 2000, 3000, 5000, 8000, 10000 and 15000 mg  $\text{PO}_4^{3-}/\text{dm}^3$ ). Before starting pH was measured and adjusted to  $8.0 \pm 0.5$  by using 0.1 M NaOH and HCl solutions. After 24 hours of constant stirring, pH was measured and the supernatant filtrated through  $0.20\text{ }\mu\text{m}$  filter. Samples were stored for subsequently analysed by ionic chromatography.

## 7.3. Kinetic studies

The kinetic removal processes, between aqueous phosphate and sorbent, was studied as follows. Experiments with Mili-Q water and the four sorbents were prepared with 200 mg, for each sorbent, poured into a vial with  $10\text{ cm}^3$  of solution of appropriate amount of phosphate concentration (100, 300 and 500 mg  $\text{PO}_4^{3-}/\text{dm}^3$ ). Each vial was left under stirring conditions for different time periods (from 1 minute to 24 hours). The pH was measured previously. For each sample the pH was measured and the supernatant was filtered through  $0.20\text{ }\mu\text{m}$  filter. Samples were stored for subsequently analyse by ionic chromatography. As in the case of the equilibrium test two different sources of phosphate were used.

Experiments with higher amount of sorbent were also performed in a second series of kinetic test, though this time the synthetic zeolite Ca-Ze was evaluated. Conditions were 3000 mg of sorbent and  $1\text{ dm}^3$  of solution, of appropriate amount of phosphate (concentrations of 50, 100 and 300 mg  $\text{PO}_4^{3-}/\text{dm}^3$  and using tap water). The amount of sorbent was mixed with  $1\text{ dm}^3$  of phosphate solution, and then stirred homogenously in a beaker of  $2\text{ dm}^3$  with a magnetic agitator. Upon reaching the different times of removal the pH was measured and the supernatant was filtered through a  $0.20\text{ }\mu\text{m}$  filter. Samples were stored for subsequently analyse by ionic chromatography.

## 7.4. Hybrid sorption and ultrafiltration system for phosphate removal

In view of previous results and the overall sorption performance, calcium zeolite was selected for further studies under more real conditions in a hybrid sorption-ultrafiltration pilot plant system.

The pilot plant consisted of a stirred tank, one tank as reservoir, a level controller, an agitator, an ultrafiltration (UF) membrane module and a pumping system, as can be seen in Fig. 7.2.

The studies performed were addressed to establish the steady state conditions of the pilot plant for continuous sorption process, therefore, parameters like the amount of zeolite, stirring, cycles of sorption and range of concentrations of phosphate were evaluated.

The solutions of phosphate tested were 25 mg  $\text{PO}_4^{3-}/\text{dm}^3$ , 50 mg  $\text{PO}_4^{3-}/\text{dm}^3$  and 100 mg  $\text{PO}_4^{3-}/\text{dm}^3$ , prepared with tap water.

Three types of stirring systems were tested to find the best homogenies in the tank of 40  $\text{dm}^3$ , filed with the phosphate solution and sorbent.

Every sorption cycle was finished once the transmembrane pressure reached 0.9 bar, between permeate and concentrate flows. At this point a cleaning procedure was needed, since the UF membrane porous were blocked by the Ca-Ze zeolite particles. The cleaning procedure consisted in a counter flow of tap water, for removing the obstruction caused by the zeolite. However, this procedure has special considerations. The Ca-Ze particles blocking the UF membrane had to be returned into the tank in order to keep the mass of zeolite constant in each cycle. To accomplish this, all the inflows must be disconnected from the stirring tank.

### 7.4.1. Mass balance

Through a mass balance is possible to quantify each solute in the system at any point of the pilot plant. To that end, it is needed a series of equations which represents the relations between flows, volumes and the concentrations from the data measured during the experiments.

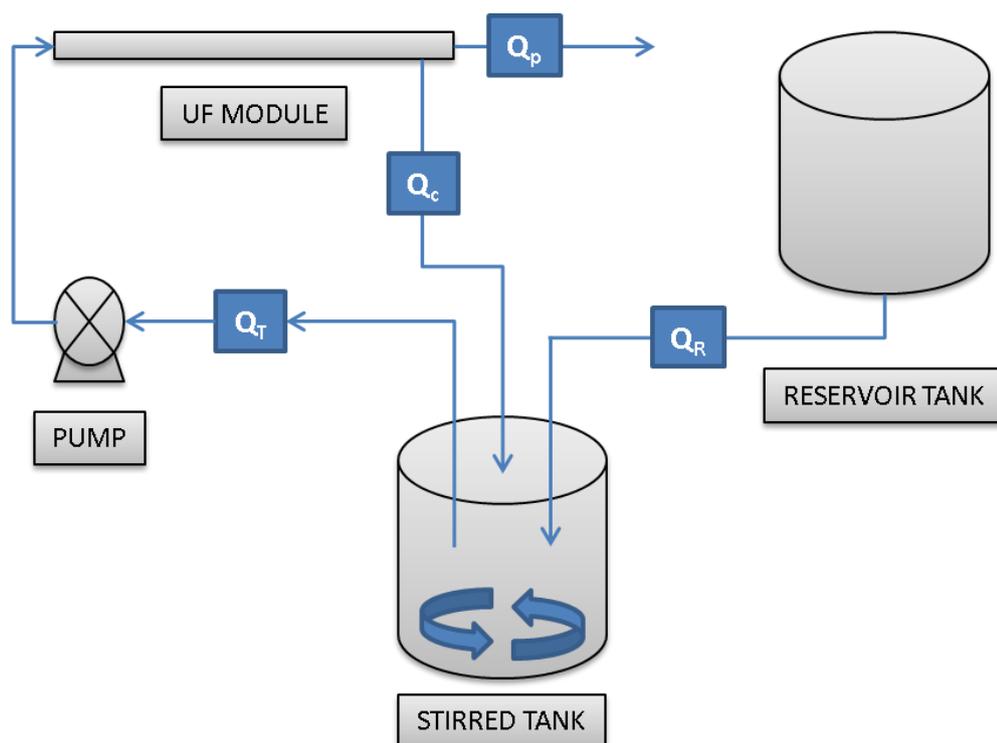


Fig. 7.2. Flowchart and equipment of the pilot plant.

From the equations EQ ( 7.1 ) and EQ ( 7.2 ) it is possible to determine the mass of phosphate at each stream of the system. Since the UF membrane cannot retain phosphate, the concentration of the stream  $Q_T$  has to be the sum of  $Q_P$  and  $Q_C$ , both outlet streams of UF module.

$$Q_T \cdot [C_T] = Q_P \cdot [C_P] + Q_C \cdot [C_C] \quad \text{EQ ( 7.1 )}$$

$$Q_T \cdot [C_T] = Q_R \cdot [C_R] + Q_C \cdot [C_C] \quad \text{EQ ( 7.2 )}$$

Where:

- $[C_i]$ : concentration of the phosphate for each flow ( $\frac{\text{dm}^3}{\text{mg}}$ ).
- $Q_i$ : flow rate for stream of the system ( $\frac{\text{mL}}{\text{s}}$ ).
  - P: permeate
  - C: concentrate
  - T: agitated tank
  - R: reservoir tank

On the other hand, the amount of phosphate recovered by the sorbent Ca-Ze in system can be describe by the equations EQ ( 7.3 ) to EQ ( 7.7 ) as follows below:

$$M_R(\text{PO}_4^{3-}) = M_0 + Q_{R_i} \cdot \Delta t_i \cdot \frac{C_{iR} + C_{i-nR}}{2} \quad \text{EQ (7.3)}$$

$$M_P(\text{PO}_4^{3-}) = M_i + Q_{P_i} \cdot \Delta t_i \cdot \frac{C_{iP} + C_{i-nP}}{2} \quad \text{EQ (7.4)}$$

Where:

- $M_R(\text{PO}_4^{3-})$ : the average amount of phosphate (mg) in the flow R (main input flow) at given time, taking into account the initial amount of phosphate concentration (mg/L) in the stirred tank (40 dm<sup>3</sup>) and the residual time
- $M_P(\text{PO}_4^{3-})$ : the average amount of phosphate (mg) in the flow P (main output flow) taking into account the residual time
- $M_0$ : initial amount of phosphate in the stirred tank (mg)
- $Q_{R_i}$ : flow rate in the stream R at the given time (mL/s)
- $Q_{P_i}$ : flow rate in the stream P at the given time (mL/s)
- $\Delta t_i$ : difference of time between samples in seconds (residual time)
- $C_{ix}$ : phosphate concentration at the given time ( $\frac{\text{mL}}{\text{s}}$ )
- $C_{i-nx}$ : phosphate concentration ( $\frac{\text{mL}}{\text{s}}$ ) in the previous given time (residual phosphate concentration)

Moreover, the system described on Fig. 7.2 can be simplified as a black box, as can be seen in Fig. 7.3.

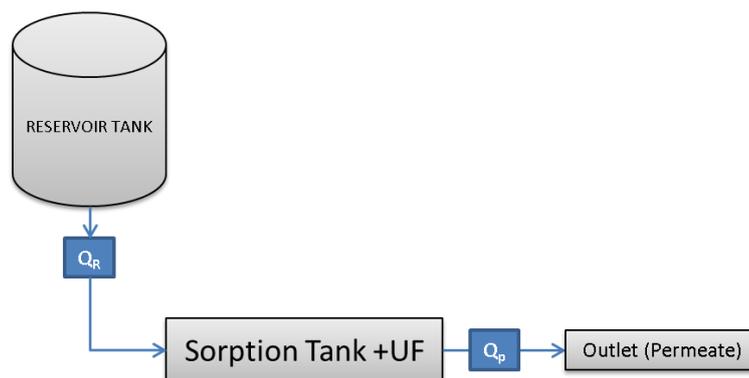


Fig. 7.3. Black box flowchart for the Fig. 7.2.

From Fig. 7.3. can be evaluated the streams R and P to assess the mass of phosphate accumulated in the system as describe the equation EQ (7.5).

$$M_{\text{Accumulated}}(\text{PO}_4^{3-}) = M_{\text{R}}(\text{PO}_4^{3-}) - M_{\text{P}}(\text{PO}_4^{3-}) \quad \text{EQ ( 7.5)}$$

The amount of phosphate in solution, in the stirred tank, can be calculated as follows:

$$M_{\text{Solution}}(\text{PO}_4^{3-}) = V_{\text{T}} \cdot C_{\text{T}} \quad \text{EQ ( 7.6)}$$

Where:

- $M_{\text{Solution}}(\text{PO}_4^{3-})$ : amount of phosphate (mg) in the stirred tank (40 dm<sup>3</sup>)
- $V_{\text{T}}$ : the volume in the stirred tank (mL)
- $C_{\text{T}}$ : phosphate concentration in the stream T ( $\frac{\text{mL}}{\text{s}}$ )

Finally the amount of phosphate removed by the Ca-Ze sorbent from the system can be calculated accordingly to the equation EQ ( 7.7 ) as follows:

$$M_{\text{Ca-Ze}}(\text{PO}_4^{3-}) = M_{\text{Accumulated}}(\text{PO}_4^{3-}) - M_{\text{Solution}}(\text{PO}_4^{3-}) \quad \text{EQ ( 7.7)}$$

In other to evaluate the percentage of phosphate removed by the system can be calculated as described in the equation EQ ( 7.8 ), which takes in consideration the total amount of phosphate introduced in the system for the total time performed in the experiment.

$$\% = \frac{\sum_{i=0}^i M_{\text{Ca-Ze}}(\text{PO}_4^{3-})}{M_0 + \sum_{i=0}^i M_{\text{R}}(\text{PO}_4^{3-})} \cdot 100 \quad \text{EQ ( 7.8)}$$

## 7.5. Analytic quantification

Ionic chromatography was the analytical method used to quantify cations and anions present in samples. However some them were too higher concentration and dilution step was carried out.

This technique is based on the different time of retention for each kind of cation and anion to pass through a fixed exchange ion resin column. The exchange of ions, between resin and solution, makes possible the separation of them at different times. Then they can be quantified in an amperometric detector. The identification is possible as a pick on specific time means just one type of ion.

Quantification was possible as a range of standards were prepared to calibrate the chromatograph. So for each cation and anion a range of concentrations (1, 2, 5, 10, 20 50 and 100 mg/dm<sup>3</sup>) were first evaluated.

## 7.6. Solid analysis

Some techniques were performed to characterise the sorbents before and after some sorption test, a selection of samples from different experiments were studied by different techniques.

X-Ray diffraction (XRD) was used to reveal information about the crystallographic structure and properties of sorbents.

Scanning electron microscopy with X-ray analysis (SEM/EDS) was the technique used for the elemental analysis and chemical characterization.

The Brunauer-Emmett-Teller (BET) technique was performed to determine the total specific surface area expressed in  $\text{m}^2/\text{g}$ .

## 7.7. Preservation of samples and working conditions

Working conditions were standard ambient temperature and pressure conditions (SATP) of the working area ( $25^\circ\text{C} \pm 2$  and  $1.01325 \times 10^5$  Pa).

Samples from experiments were filtered through  $0.20 \mu\text{m}$  filter, stored in test tubes sealed with Parafilm and conserved under refrigeration to avoid degradation of phosphate.

## 7.8. Cleaning procedure

For this project no detergent was used to clean the material used. Since detergents have phosphate in their composition, our target (phosphate) would be contaminated. Thus to avoid future contamination a series of rinses with tap water, and cleanings and immersion, for 24 hours, in solution of distilled water with HCl was first hard cleaning. Then more tap water rinses, followed by distilled and Milli-Q water to remove all the acid. Finally all the equipment was stored in an oven to dry them.

## 8. Results

In this chapter the results obtained from the different experiments carried out are shown.

### 8.1. Sorbent characterization

#### 8.1.1. Ion exchange by the Ca-Ze synthesis

The exchange of  $\text{Na}^+$  ions by  $\text{Ca}^{2+}$  ions in the modification of the Na-P1 to Ca-Ze zeolite was evaluated. Fig. 8.1. shows the average exchanged in each cycle, through the difference between initial and final concentrations of calcium in the solution of  $\text{CaCl}_2$  (see Chapter 7.1.). On the other hand, Table ( 8.1 ) was evaluated the exchange by milliequivalents (meq) of  $\text{Na}^+$  and  $\text{K}^+$  released against the  $\text{Ca}^{2+}$  exchanged.

From Fig. 8.1. was appreciated that after the third cycle the exchange of calcium remains slightly constant around 25%, compared to the 50% and 40% of the exchange observed by the two first cycles.

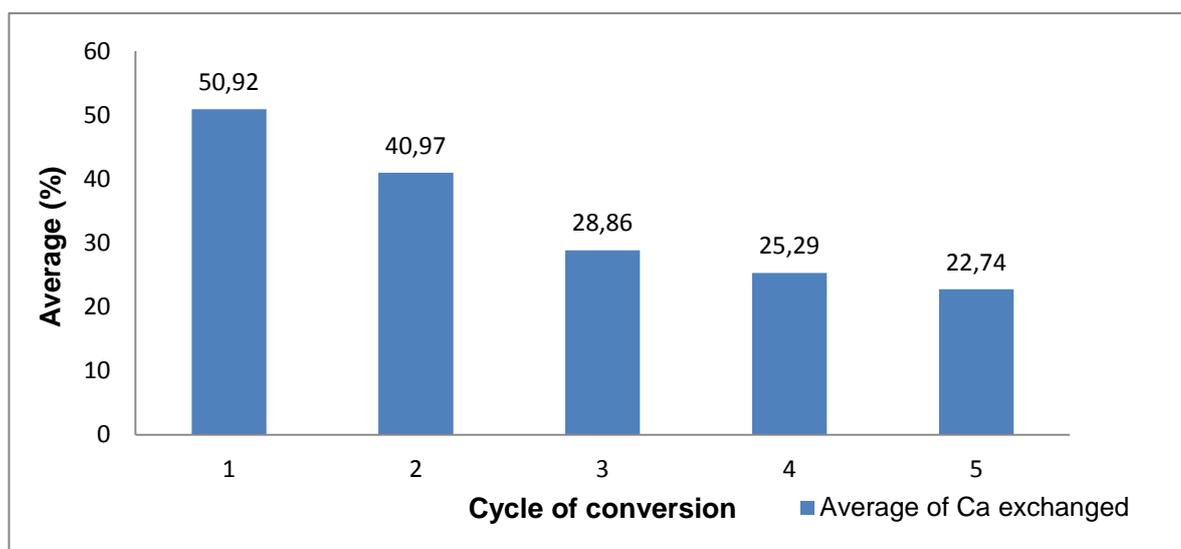


Fig. 8.1. Average of  $\text{Ca}^{2+}$  ion exchanged in each batch test in the modification of Ca-Ze.

Furthermore and according to Table ( 8.1 ). it can be suggested that not only the ion exchange mechanism was carried out to cover the meq of  $\text{Ca}^{2+}$ . Supported this fact by Fig. 8.2. where it can be seen new minerals in the structure of the zeolite, calcite ( $\text{CaCO}_3$ ) and garronite ( $\text{NaCa}_{2,5}(\text{Si}_{10}\text{Al}_6)\text{O}_{32}\cdot 14\text{H}_2\text{O}$ ). Minerals not found originally in the structure of Na-P1. Therefore, the precipitation of calcium should be considered as plausible mechanism by which calcium was incorporated also in the structure of Ca-Ze. Incorporation evaluated from 1.44 % for the Na-P1 to 6.35 % for the Ca-Ze after all cycles performed (Table ( 8.3 )).

Table ( 8.1 ). Conversion rate for the meq/L of calcium versus Na and K ions realised for cycle.

Cycle	meq/L Ca exchanged	meq/L Na and K released	Conversion rate (%)
1	649.9	453.1	69.7
2	524.2	160.3	30.6
3	330.2	68.6	20.8
4	290.1	37.8	13.0
5	260.2	24.4	9.4

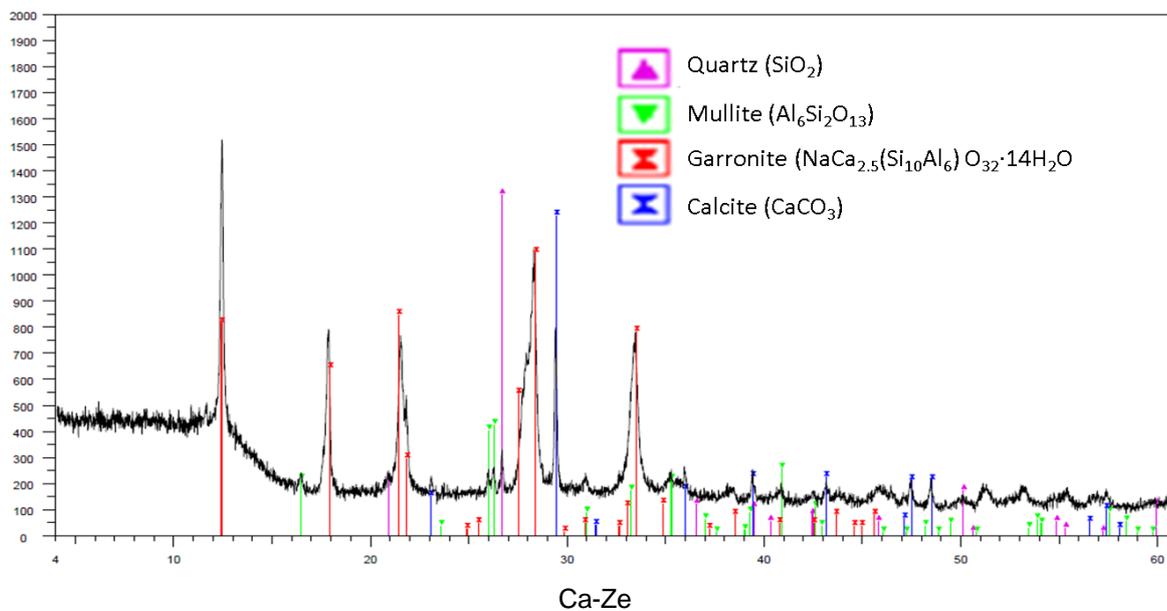
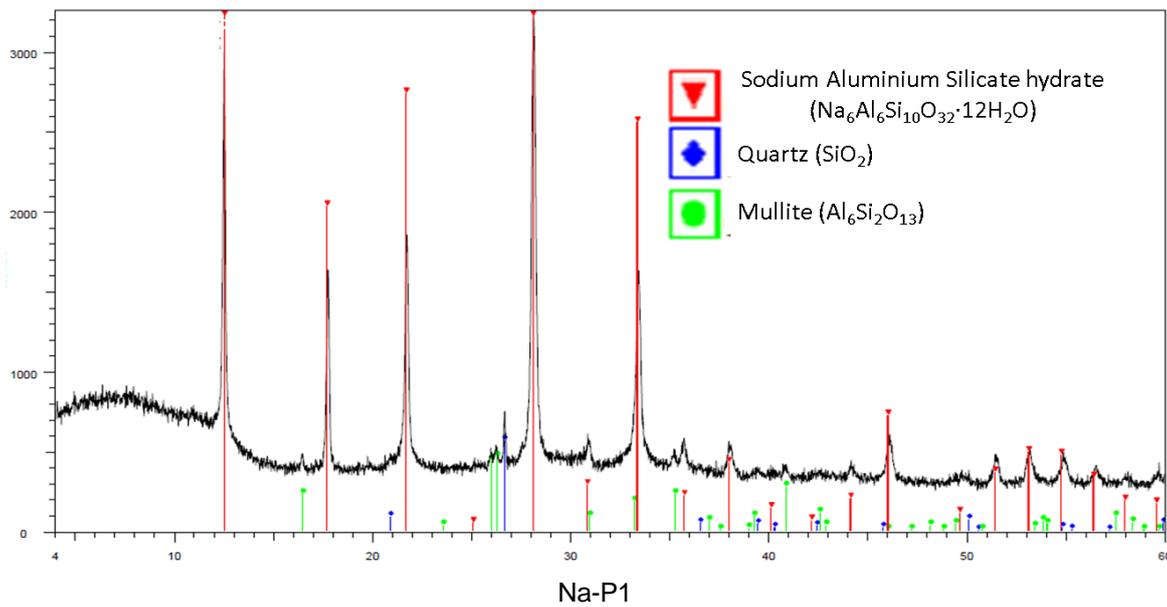


Fig. 8.2. XRD mineralogical composition for Na-P1 and Ca-Ze synthetic zeolite.

On the other hand, as a result of the synthesis process of the Ca-Ze, the specific surface area of Na-P1 was increased remarkably, up to twice its initial value as can be seen in Table ( 8.2 ).

Table ( 8.2 ). Characterisation of specific surface area for all sorbents by Brunauer-Emmett-Teller (BET) technique.

Sorbents	BET (m <sup>2</sup> /g)
T	1.46
B	0.86
Na-P1	6.65
Ca-Ze	12.55

### 8.1.2. Solid samples characterization

The results obtained by XRD and SEM-EDS techniques before and after the sorption process are presented in this section. Samples studied were a selection of samples from isotherm experiments with a concentration of 15000 mg PO<sub>4</sub><sup>3-</sup>/dm<sup>3</sup>.

The micromorphology observations between a typical fly ash and synthetic zeolite are shown Fig. 8.3. The predominantly morphology of fly ash is spherical in shape and consist in cenospheres, irregular-shaped debris and porous unburnt carbon (Yao et al. 2015). A morphology that will remain in the synthesized zeolite, tough a coating of synthetic zeolite will appear over it. This new coating grows as result of the precipitation of zeolitic material (Querol et al. 2002) by the alkali hydrothermal reaction, in the process to enhance the fly ash as zeolite. Furthermore, according to Table ( 8.2 ) due to the synthesizing process from a fly ash, the surface area increases considerably. It makes sense, since due to precipitation of zeolitic material; the channel network grows intricate and large. Therefore, the number of potential sorption sites also increases.

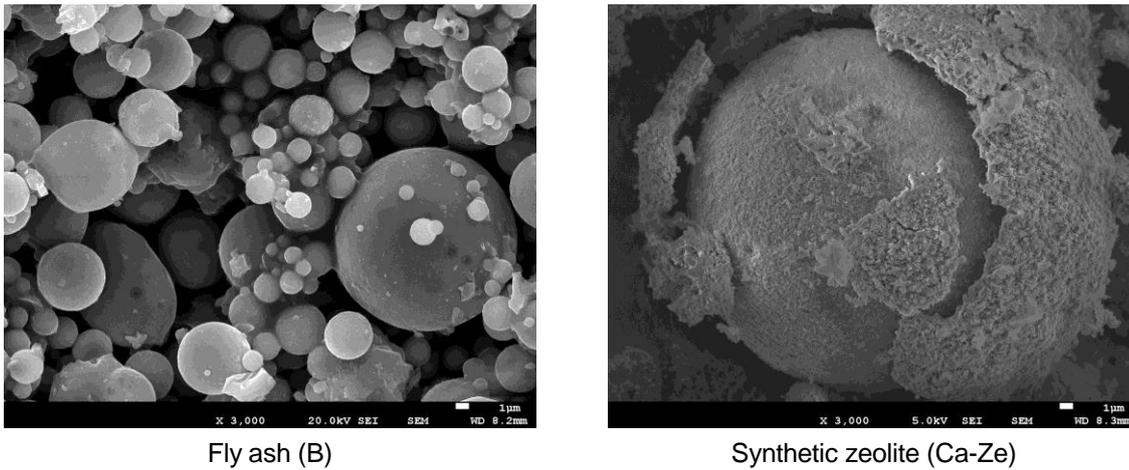


Fig. 8.3. SEM images of fly ash and synthetic zeolite.

Fig. 8.4. shows the original mineralogical composition found for the two fly ash samples. While, the elemental composition of the constitutive minerals found in the original structures of the sorbents, expressed in weight percentage and summarized in Table ( 8.3 ).

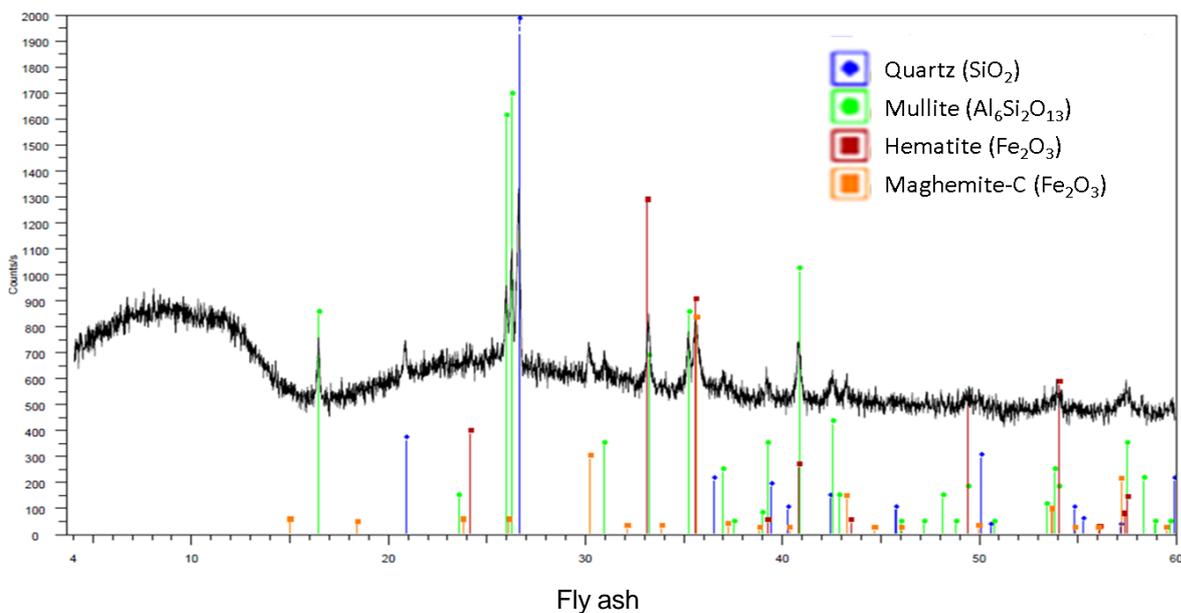


Fig. 8.4. XRD mineralogical composition for fly ash (T and B).

From Fig. 8.2. and Fig. 8.4. can be extracted that all sorbents share the same ore composition in mullite and quartz, rich in Al and Si, respectively. Furthermore, fly ash also showed an iron ore composition, not found in the synthetic zeolites. However, and according to Table ( 8.3 ), all sorbents have a certain amount of iron, which was higher for the T fly ash than for B, Na-P1 and Ca-Ze, with a lower percentage in iron. This may be interpreted, in the case of fly

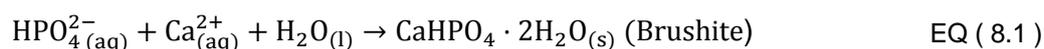
ash, due to its origin, where iron were able to constitute more complex structures because of the high temperatures reached by the coal combustion process. While in the case of synthetic zeolites, iron ore structures were demineralized by the alkaline solution used to obtain them. Thus, the iron detected in zeolites may be a result from precipitation of iron oxides, which were sorbed on the surface.

Table ( 8.3 ). Elemental SEM/EDS characterisation for all sorbents before sorption.

Results in weight %	O	Na	Al	Si	Fe	Ca	P	K
T	44,70		8,28	10,51	6,26	1,81	0,16	0,74
B	45,39	0,56	6,19	14,37	3,49	1,08		1,29
Na-P1	50.59	7.56	8.08	15.11	2.86	1.44	0.38	1.84
Ca-Ze	50.26	0.78	7.29	13.39	2.26	6.35		1.09

From XRD analysis performed was seen that according on the source of phosphate the ions accompanying it can favour the formation of a type of mineral. In the case of  $\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , potassium hydrated aluminium silicate was reported, which was not found it in those samples where the source of phosphate was  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

Different mechanisms such as ion exchange, sorption and precipitation have been proposed to explain the removal of phosphate from aqueous solutions. However, the pH of the solution plays a critical role in the rate and mechanisms of the removal phosphate. Therefore, and since the pH was adjusted between 8-8.5, it may be suggested that the phosphate removal was carried out mainly by precipitation of calcium ions. Depending on the dissolution of  $\text{Ca}^{2+}$  ion from the sorbents, and the dominant species of  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , resulting in co-precipitation of calcium and phosphate found as brushite, as is proposed by the EQ ( 8.1 ).



From EQ ( 8.1 ) it can be argued that while the calcium ions become available in the solution, supplied by the sorbents, the balance is shifted to favour formation of brushite, having in consideration also the amount of hydrogen phosphate available. In the case of Ca-Ze its supplier of calcium was the minerals, present in it, calcite and garronite. Which after the sorption process were not found again, as can be seen in Fig. 8.5. This fact suggests the dissolution of both minerals thus covering availability of calcium ions, and the subsequently precipitation of the brushite. Therefore, it makes sense that it was the Ca-Ze zeolite, which could remove more phosphate in all tests performed. Since it was which had the highest available amount of calcium in its structure that could be released.

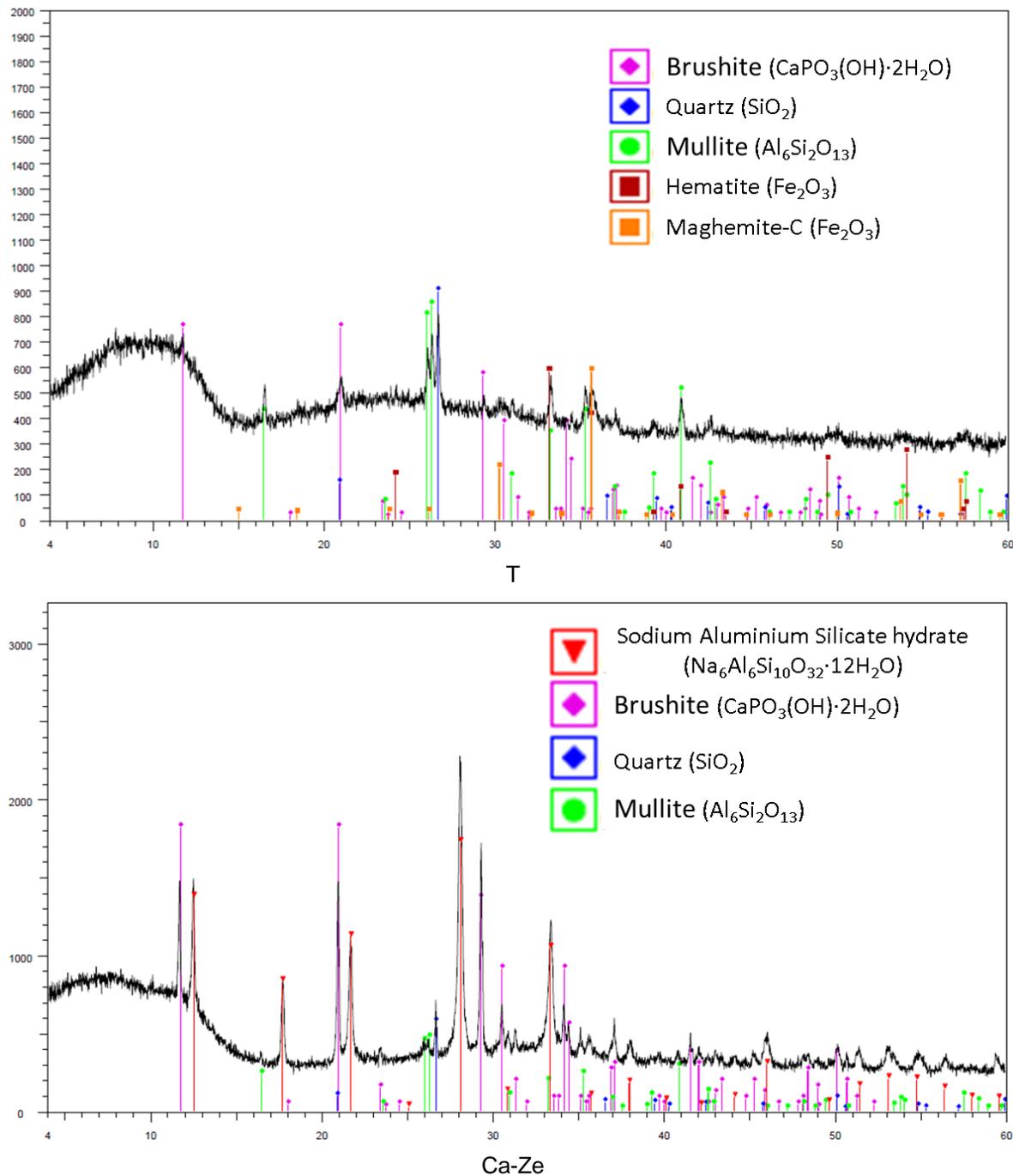


Fig. 8.5. XRD mineralogical composition for T fly ash an Ca-Ze after sorption.

Moreover, most noticeable found it was the presence of brushite for all sorbents after the sorption process as can be seen in Fig. 8.5, except for the Na-P1. Furthermore, all minerals originally found in the sorbents were present again, after the sorption process. Though in the case of the Ca-Ze, the minerals garronite and calcite were not found after the sorption process again. Which supports, that the mainly mechanism to remove the phosphate was by the precipitation of calcium ions supplied from the sorbent.

On the other hand, comparing Table ( 8.3 ) with Table ( 8.4 ) can be noticed that the removal of phosphorus was possible for all sorbents. Although, the large amount of phosphate removed was reported for the Ca-Ze, and for both sources of phosphorus.

Table ( 8.4 ). Elemental SEM/EDS characterisation for all sorbents after sorption of 15000 mg  $\text{PO}_4^{3-}$  /dm<sup>3</sup>.

Results in weight %		O	Na	Al	Si	Fe	Ca	P	K	
Phosphate source	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	T	44.07	0.78	8.06	10.16	5.55	2.22	1.17	0.70
		B	45.04	0.84	5.61	12.67	3.03	1.21	0.79	1.07
		Na-P1	49.10	6.25	6.72	12.23	1.83	1.13	0.87	0.87
	$\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Na-P1	47.39	1.93	6.66	12.38	1.87	1.08	0.91	7.07
		Ca-Ze	45.76	1.62	4.88	8.84	1.38	3.62	2.79	5.08

## 8.2. Equilibrium studies

The data obtained from the equilibrium experiments were fitted to the Langmuir and Freundlich isotherm models, see Chapter 6.1.1.

### 8.2.1. Fly ash (T and B)

Fig. 8.6. and Fig. 8.7. depict the experiments performed with  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ . Furthermore, Table ( 8.5 ) compares the data obtained between the two sources of phosphate studied.

Results showed in Table ( 8.5 ) indicate a better fit the Freundlich equation rather than Langmuir isotherm according to their correlation coefficients. In all cases, correlation coefficients were lower for Langmuir than for Freundlich and for both sources of phosphate. This suggests a heterogenic sorption process, where the sorption was ruled by the conditions of experiments; concentration of sorbent and sorbate, pH and temperature. Moreover, as postulates Freundlich, the heterogeneous sorption implies that once the first sorbate layer has covered the surface of the sorbent, the sorption process was still carried out in a new layer on top of this last and so on, allowing multiple process of sorption at the same time.

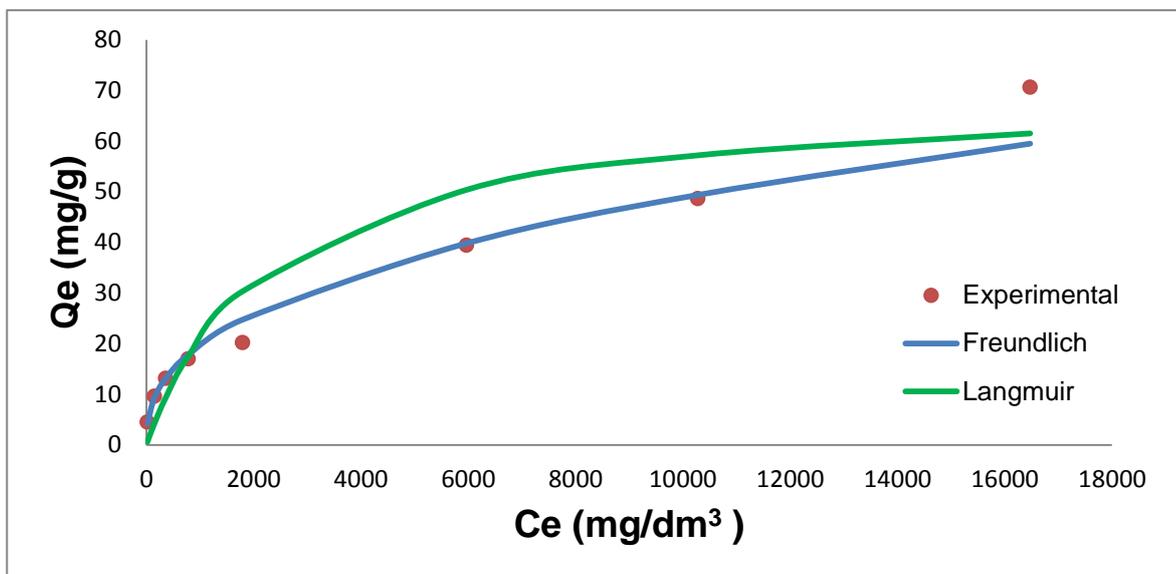


Fig. 8.6. Sorption isotherms for T at pH 8 for a solutions of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

Fig. 8.6. and Fig. 8.7. compare the experimental data and theoretical prediction by Freundlich and Langmuir isotherms. In both cases, it can be seen as the sorption capacity ( $Q_e$ ) increases by increasing phosphate concentration ( $C_e$ ). This suggests a high affinity for the phosphate by the fly ash.

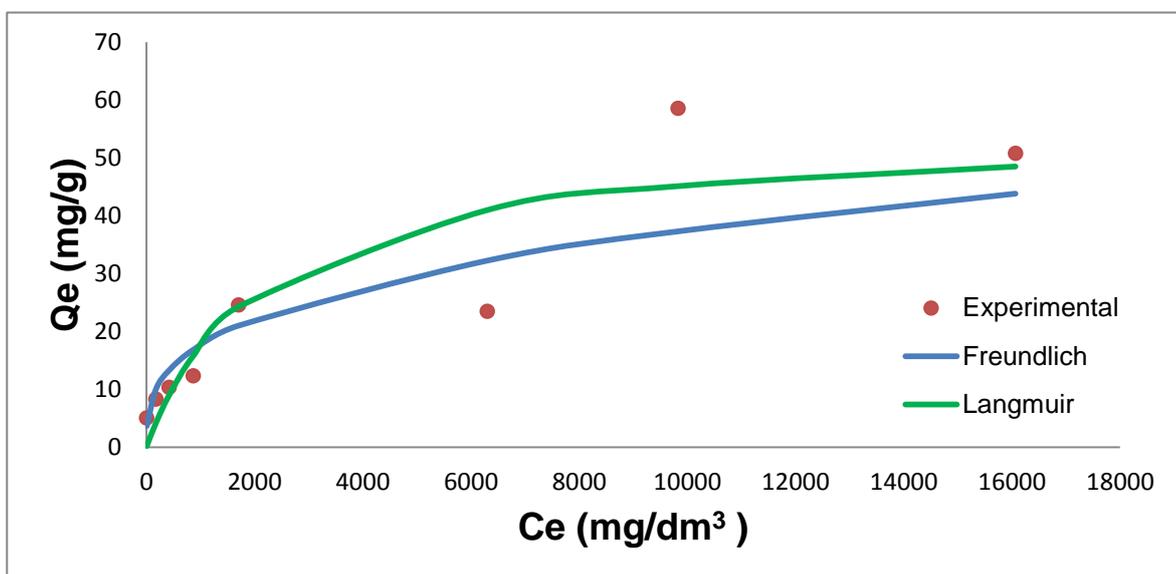


Fig. 8.7. Sorption isotherms for B at pH 8 for a solutions of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

Table ( 8.5 ). Characteristics parameters and correlation coefficients of the experimental data according to Freundlich and Langmuir equations for T and B at pH 8 from two different source of phosphate.

Phosphate source		Langmuir			Freundlich		
		Qe	$K_L$	$R^2$	$K_F$	$n_F$	$R^2$
NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	T	70.3	$4.23 \times 10^{-4}$	0.90	1.3	2.5	0.99
	B	55.0	$4.63 \times 10^{-4}$	0.81	1.8	3.1	0.88
KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	T	33.7	$7.22 \times 10^{-4}$	0.71	3.2	4.3	0.83
	B	38.4	$5.77 \times 10^{-4}$	0.68	2.1	3.5	0.89

### 8.2.2. Synthetic zeolites (Na-P1 and Ca-Ze)

The phosphate sorption isotherms for the synthetic zeolites are shown in Fig. 8.8. and Fig. 8.9. Those figures show similar behaviour than for fly ash sorbents, since the phosphate sorption capacity increases with the phosphate concentrations. It is also observed that sorption capacity reaches a maxim plateau, which is consistent with the values found for the Freundlich and Langmuir constants and the correlation coefficients, given a better fit for Langmuir than Freundlich, showed in Table ( 8.6 ). In all cases, correlation coefficients were lower for Freundlich isotherm than for Langmuir even when the source of phosphorus changes. This suggests that chemisorption was the principal process of sorption onto zeolites to remove the phosphate.

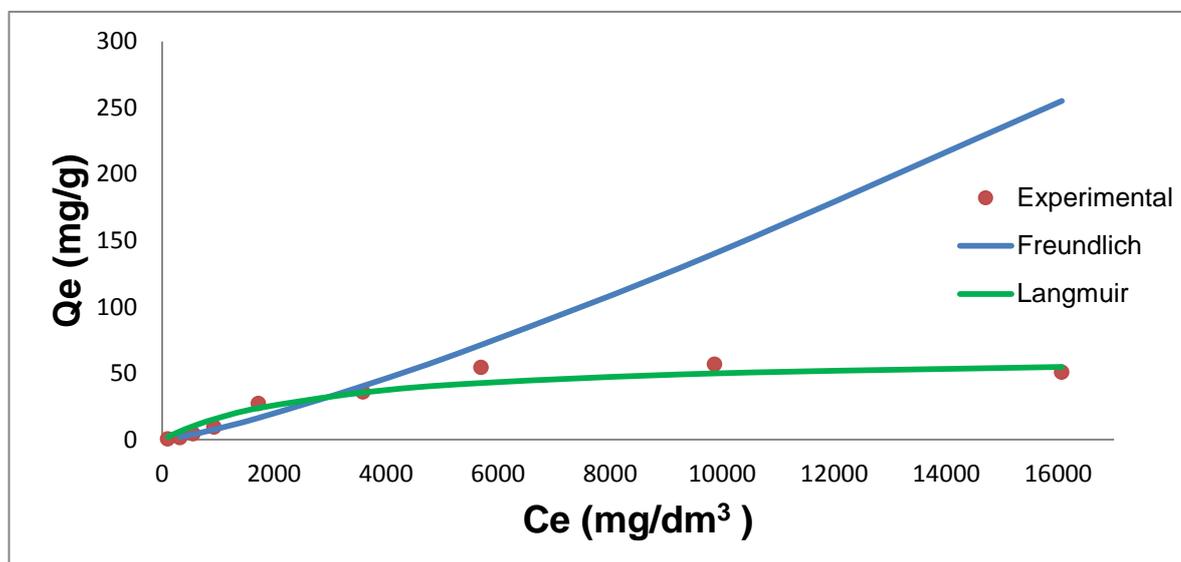


Fig. 8.8. Sorption isotherms for Na-P1 at pH 8 for a solutions of NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O.

Moreover, as can be seen in Fig. 8.9. the  $Q_e$  of the Ca-Ze increases faster until reaching the  $2000 \text{ mg/dm}^3$ . After that point, it seems completely reached the maximum capacity of the sorbent, with a value around  $200 \text{ mg/g}$ , despite further increasing the  $C_e$ . On the other hand, Na-P1 maximum capacity was obtained at  $4000 \text{ mg/dm}^3$ , with a  $Q_e$  of  $65 \text{ mg/g}$ , as can be seen in Fig. 8.8. As mentioned above, appears to be the amount of calcium ions, between the sorbents structures, which made the difference in order to remove the phosphate, in view of the precipitation of brushite found in the Ca-Ze and not in the Na-P1.

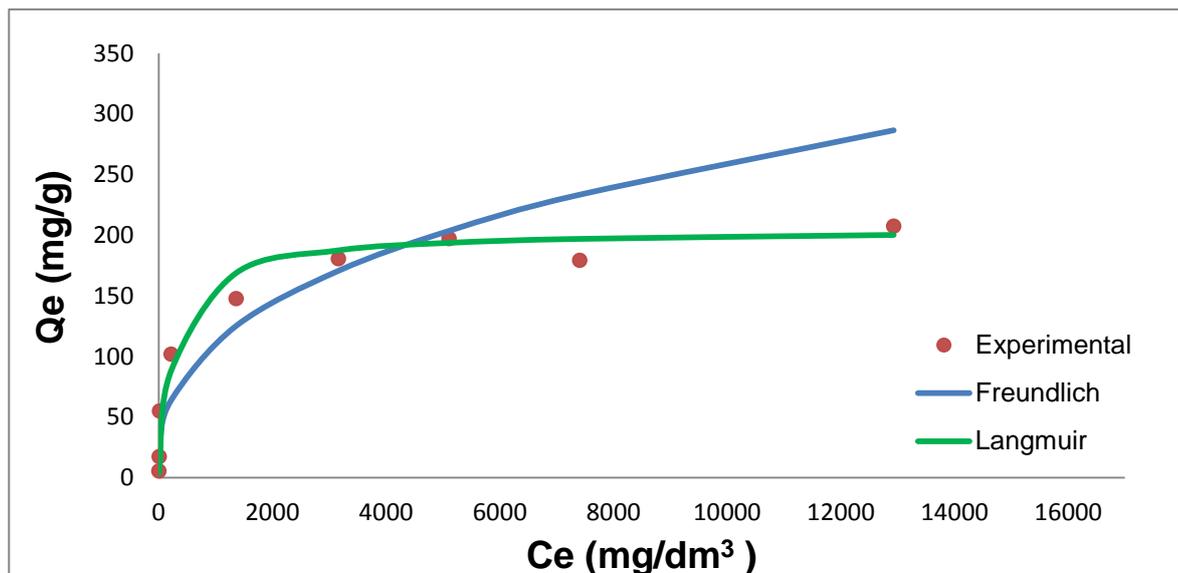
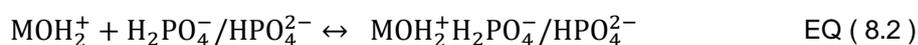


Fig. 8.9. Sorption isotherms for Ca-Ze at pH 8 for a solutions of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

According to this removal patterns, the removal of phosphate ions, mainly  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  forms expected pH range (8.0 to 8.5) by the Ca-Ze and Na-P1 sorbents can be postulated by the following mechanism:

1. Surface complexation with the  $\text{AlOH}$  and  $\text{FeOH}$  functional groups, originally present as Al and Fe oxides or from the zeolitic structure through two main reactions, described by EQ ( 8.2 ) and EQ ( 8.3 ):

- 1.1. Labile complexes with  $\text{MOH}^{2+}$  surface groups



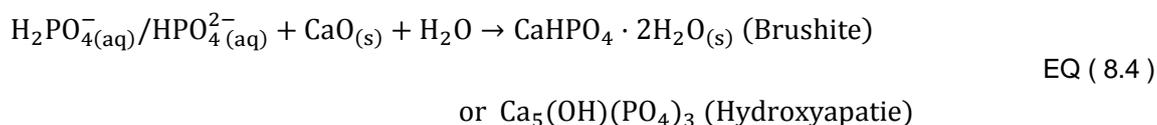
- 1.2. Inner-spheres complexes with  $\text{MOH}$  surface groups



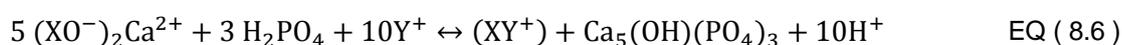
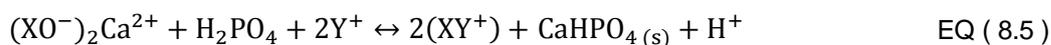
Where M represents Al or Fe.

2. Formation of Ca-phosphate minerals with  $\text{Ca}^{2+}$  ions present on the zeolites through two main reactions, described below:

- 2.1. Ca-phosphate minerals with  $\text{Ca}^{2+}$  ions present on the zeolitic material as  $\text{CaO}_{(s)}$ , described by the EQ ( 8.4 ):



- 2.2. Formation of Ca-phosphate minerals with  $\text{Ca}^{2+}$  ions occupying the ion exchange groups of the zeolitic structure, described by the EQ ( 8.5 ) and EQ ( 8.6 ):



Where:

X: represents the anionic groups of the zeolite structure.

Y: represents the cationic ion exchanged.

Table ( 8.6 ). Characteristics parameters and correlation coefficients of the experimental data according to Freundlich and Langmuir equations for Na-P1 and Ca-Ze at pH 8 from two different source of phosphate.

Phosphate source		Langmuir			Freundlich		
		$Q_e$	$K_L$	$R^2$	$K_F$	$n_F$	$R^2$
$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Na-P1	65.1	$3.33 \times 10^{-4}$	0.91	0.01	1.0	0.91
	Ca-Ze	204.6	$3.45 \times 10^{-3}$	0.99	8.8	2.7	0.88
$\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Na-P1	84.6	$2.19 \times 10^{-4}$	0.96	0.01	1.0	0.89
	Ca-Ze	111.8	$3.87 \times 10^{-2}$	0.99	15.5	4.3	0.70

About the source of phosphate, Ca-Ze shows better results when the mainly ions presents in the solution were sodium rather than potassium, as can be seen in Table ( 8.6 ) for the results of  $Q_e$ . On the other hand, results obtained by Na-P1 shows higher sorption capacity, when the manly ions presents were potassium.

## 8.3. Kinetics studies

### 8.3.1. Kinetic studies with Mili-Q water

Results obtained using Mili-Q water to perform the experiments with all sorbents are shown in this section as part of summarised tables and charts.

#### 8.3.1.1. Kinetics of removal phosphate by fly ash

Fly ash samples were compared under two different concentrations and two sources of phosphate using Mili-Q water as aqueous medium.

The kinetics for the removal of phosphate as a function of contact time, by the fly ash T and B sorbents, are shown in Fig. 8.10. The rates of removal, obtained after 24 hours, were 88.2% for B and 71.9% for T, for the initial concentration of  $100 \text{ mg PO}_4^{3-}/\text{dm}^3$ , against of 31.9% for B and 35.7% of T, for the concentration of  $500 \text{ mg PO}_4^{3-}/\text{dm}^3$ . The efficiency was significantly reduced by increasing the phosphate concentration, since both B and T showed lower removal rates at higher concentration.

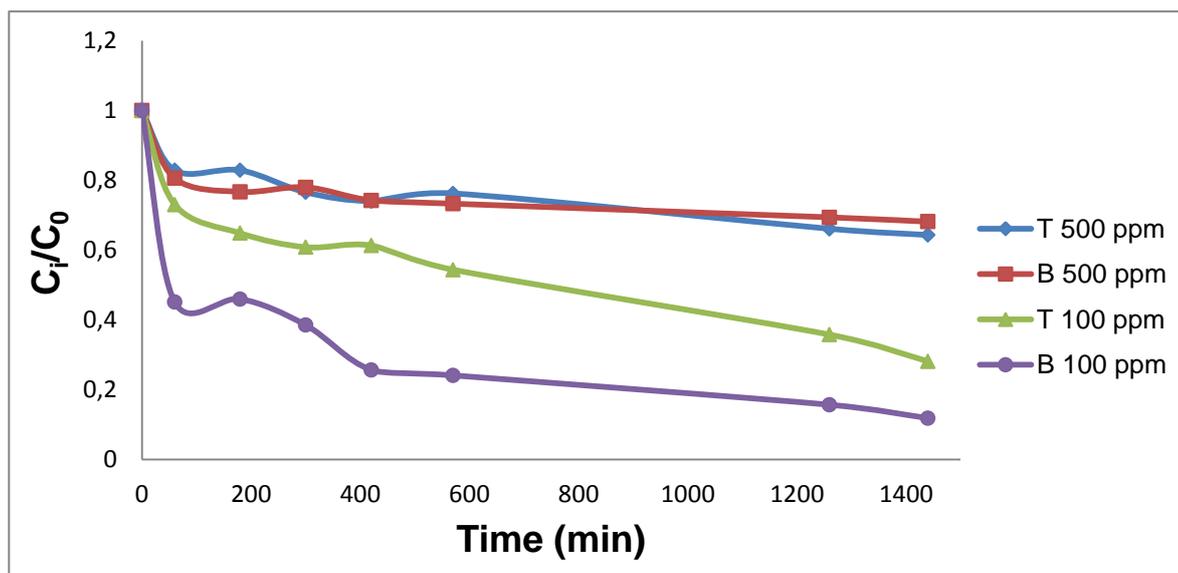


Fig. 8.10. Kinetics at different concentration of phosphate by the fly ash T and B.

In the diffusion process, it is necessary to identify the mechanism or key step in the sorption, such as mass transfer, chemical reaction, etc. There are a variety of kinetic models to check the experimental results of the removal of phosphate on fly ash. In this case, to analyse the kinetic mechanisms, three models were used: pseudo first order, pseudo second order and Elovich, where the model with a higher correlation coefficient indicates the best fit to experimental data. According to the correlation coefficients shown in the Table (8.7), the model of pseudo

second order reported the best fit, suggesting a superficial sorption even changing the source of phosphate and concentration.

Moreover,  $Q_e$  is increasing by increasing the initial concentration for all samples, regardless of the source of the phosphate. However,  $Q_e$  was affected by the source of phosphate, as in the case of equilibrium studies, where higher sorption capacities were for those samples tested with  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , as the source of phosphate.

Table ( 8.7 ). Characteristics parameters and correlation coefficients of the kinetic models used for the sorbents B and T. For the sources phosphate of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

		$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$				$\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$			
		T		B		T		B	
		100	500	100	500	100	500	100	500
Pseudo First Order	$Q_e$	2.9	6.9	2.7	3.9	1.8	5.6	0.8	1.8
	$K_1$	$2.4 \times 10^{-5}$	$2.6 \times 10^{-5}$	$3.7 \times 10^{-5}$	$2.3 \times 10^{-5}$	$5.3 \times 10^{-4}$	$5.8 \times 10^{-4}$	$8.5 \times 10^{-5}$	$7.8 \times 10^{-5}$
	$R^2$	0.97	0.87	0.97	0.83	0.63	0.84	0.39	0.37
Pseudo Second Order	$Q_e$	4.0	11.9	4.9	10.1	2.3	7.2	3.7	7.5
	$K_2$	$2.8 \times 10^{-5}$	$7.2 \times 10^{-6}$	$5.3 \times 10^{-5}$	$1.8 \times 10^{-5}$	$2.5 \times 10^{-4}$	$1.5 \times 10^{-4}$	$7.3 \times 10^{-4}$	$3.2 \times 10^{-4}$
	$R^2$	0.94	0.98	0.99	0.99	0.85	0.99	0.99	0.99
Elovich	$\alpha$	$2.2 \times 10^{-2}$	$1.5 \times 10^{-3}$	$4.3 \times 10^{-2}$	$3.4 \times 10^{-2}$	$4.5 \times 10^{-1}$	$1.8 \times 10^{-1}$	$3.7 \times 10^{-3}$	$1.4 \times 10^{-4}$
	$\beta$	$4.8 \times 10^{-1}$	1.9	$6.0 \times 10^{-1}$	1.15	$1.5 \times 10^{-1}$	$8.4 \times 10^{-1}$	$2.2 \times 10^{-1}$	$3.9 \times 10^{-1}$
	$R^2$	0.83	0.87	0.90	0.91	0.16	0.71	0.64	0.44

### 8.3.1.2. Kinetics of phosphate removal by synthetic zeolites

Synthetic zeolites were studied under three different concentrations of phosphate from the  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  source.

The kinetics performance for both zeolites, Na-P1 and Ca-Ze, was showed in Fig. 8.11. The performance of Na-P1, for all three concentrations, was lower than in the case of Ca-Ze performance. Best removing efficiency was 15.21% for a concentration of  $500 \text{ mg PO}_4^{3-}/\text{dm}^3$  and 14.21% for a concentration of  $300 \text{ mg PO}_4^{3-}/\text{dm}^3$ .

On the other hand, for the concentration of  $100 \text{ mg PO}_4^{3-}/\text{dm}^3$  was observed a release of phosphate by the Na-P1, coming from the phosphorus present (Table ( 8.3 )) in its structure that was dissolved. This fact was proved by an experiment in which 0.2 g of Na-P1 were equilibrated with Mili-Q water at pH 8, and results obtained indicated that this sorbent could

release  $6.1 \text{ mg PO}_4^{3-}/\text{g}$  of sorbent. Furthermore, regardless the concentration studied with the Na-P1, results obtained were not as good as the results shown by the Ca-Ze to remove phosphate. Probably by the low concentration in calcium ions in its structure, as it was suggested already.

Moreover, the kinetics for Ca-Ze showed a capacity, to remove phosphate, from 93% to 99% for the concentrations, tested; reaching the equilibrium at the first 5 hours and after the first 2 hours was reached more than 50%-60% of the total removed.

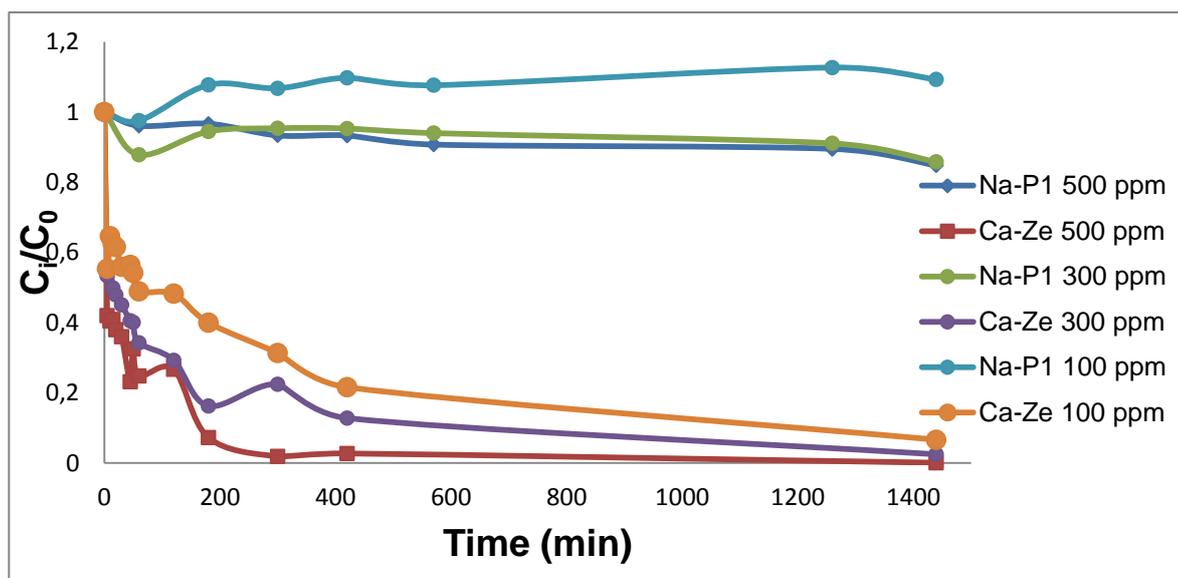


Fig. 8.11. Kinetics at different concentration of phosphate by the Na-P1 and Ca-Ze.

Furthermore, synthetic zeolites were compared under three different concentrations. Results obtained are collected in Table ( 8.8 ). It can be seen that the better fit was for the model of pseudo second order according to their correlation coefficient. Nevertheless, in the case of Na-P1, the correlation coefficients obtained suggest that any of the models studied in this project can describe adequately the kinetic experimental data.

Table ( 8.8 ). Characteristics parameters and correlation coefficients of the kinetic models used for the sorbents Na-P1 and Ca-Ze. For the source phosphate of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

		Na-P1			Ca-Ze		
		100	300	500	100	300	500
Pseudo First Order	Qe	0.433	1.052	2.335	2.957	7.658	12.549
	$K_1$	$3.3 \times 10^{-4}$	$-5.3 \times 10^{-7}$	$1.82 \times 10^{-4}$	$5.0 \times 10^{-5}$	$6.2 \times 10^{-5}$	$1.3 \times 10^{-4}$
	$R^2$	0.68	0.01	0.05	0.99	0.85	0.90
Pseudo Second Order	Qe	1.05	2.04	2.35	5.02	16.34	29.79
	$K_2$	$2.0 \times 10^{-4}$	$2.5 \times 10^{-5}$	$-3.5 \times 10^{-3}$	$6.2 \times 10^{-5}$	$3.4 \times 10^{-5}$	$3.4 \times 10^{-5}$
	$R^2$	0.28	0.72	0.76	0.99	0.99	0.99
Elovich	$\alpha$	$2.9 \times 10^{-2}$	$1.2 \times 10^1$	1.04	$7.8 \times 10^{-2}$	$9.8 \times 10^{-2}$	$3.1 \times 10^{-1}$
	$\beta$	$1.6 \times 10^{-1}$	$1.2 \times 10^{-1}$	$4.4 \times 10^{-1}$	$5.6 \times 10^{-1}$	1.77	2.76
	$R^2$	0.80	0.08	0.10	0.87	0.95	0.88

### 8.3.2. Kinetic studies with tap water

In view of previous results and the overall sorption performance, Ca-Ze was selected for further studies under more real conditions. Three different concentrations of phosphate were prepared with tap water. Concentrations studied were 50 mg  $\text{PO}_4^{3-}/\text{dm}^3$ , 100 mg  $\text{PO}_4^{3-}/\text{dm}^3$  and 300 mg  $\text{PO}_4^{3-}/\text{dm}^3$ . The phosphate source was  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  which has showed the best results in batch and kinetic experiments.

Fig. 8.12. shows the kinetic phosphate sorption onto Ca-Ze for the three difference concentrations. The percentage of phosphate removed, calculated from the initial and final concentration in the solution, gave a performance onto Ca-Ze of 61.92% for 50 mg  $\text{PO}_4^{3-}/\text{dm}^3$ , 77.46% for 100 mg  $\text{PO}_4^{3-}/\text{dm}^3$  and 53.40% for 300 mg  $\text{PO}_4^{3-}/\text{dm}^3$ , although this time to reach such efficiency, the elapsed time needed was about 21 hours.

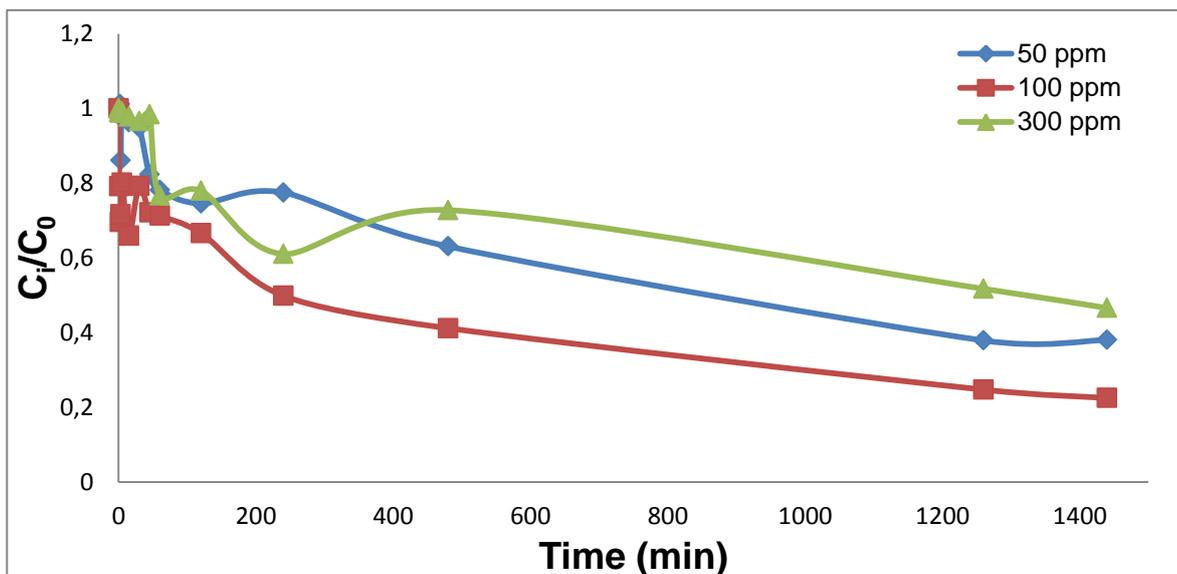


Fig. 8.12. Ca-Ze kinetics at different concentration of phosphate in tap water solution.

On the other hand, this time results obtained shown that best fit was for the pseudo second order model for the concentrations of 50 and 100 mg  $\text{PO}_4^{3-}/\text{dm}^3$ , while for the 300 mg  $\text{PO}_4^{3-}/\text{dm}^3$  results shown that no model was good enough to fit, as can be seen in Table ( 8.9 ).

Table ( 8.9 ). Characteristics parameters and correlation coefficients of the experimental data according to Pseudo first and second order as well as Elovich for Ca-Ze kinetics from the source phosphate of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  at different concentrations.

		$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$			
		50 ppm	100 ppm	300 ppm	
Pseudo	First Order	Qe	0.01	0.02	0.05
		$K_1$	$2.7 \times 10^{-5}$	$4.2 \times 10^{-5}$	$2.9 \times 10^{-5}$
		$R^2$	0.78	0.99	0.83
Pseudo	Second Order	Qe	0.01	0.03	0.09
		$k_2$	$7.0 \times 10^{-3}$	$6.1 \times 10^{-3}$	$2.8 \times 10^{-4}$
		$R^2$	0.94	0.99	0.48
Elovich	$\alpha$	1.55	2.41	$1.3 \times 10^{-1}$	
	$\beta$	$1.1 \times 10^{-3}$	$3.7 \times 10^{-3}$	$1.2 \times 10^{-2}$	
	$R^2$	0.99	0.85	0.86	

## 8.4. Hybrid sorption-ultrafiltration pilot

Finally, ultrafiltration and sorption technologies were integrated in a combined hybrid sorption-ultrafiltration pilot plant. The sorbent selected for these tests was the synthetic zeolite Ca-Ze. The aim was to set up the suitable working conditions of the pilot plant, testing the technical feasibility of remove phosphate from aqueous solution in hybrid system.

Experiments were carried out with tap water as the phosphate matrix solutions. Several concentrations of phosphate and quantity of sorbent were tested as part of different experiments performed.

Three systems of agitation were tested to keep the tank homogenised as can be seen in Fig. 8.13. Between all of them, the one named C reported the better homogenization from bottom to top of the tank. In the case of system B, the flat blade provided a strong resistance against the volume of solution; a total of 40 dm<sup>3</sup> of phosphate solution plus the amount of sorbent. On the other hand, system A had the problem of death spaces on the bottom of the tank, where the shape of the pumps keep the zeolite blocked in the bottom of the stirred tank.

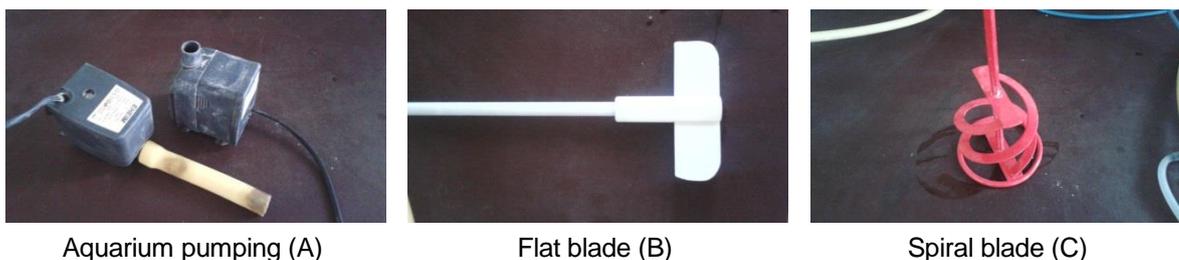


Fig. 8.13. Stirring systems tested.

Along this part of the project other experiments were performed, but they were not included because they do not work out as well as they were designed. Even though they cannot be negligible as they provided valuable technical information, about limitations in the working conditions of the hybrid sorption-ultrafiltration pilot plant system. All the technical information provided for all experiments performed is included in the Table ( 8.10 ), which summarise the operational parameters found.

Table ( 8.10 ). Working conditions for the hybrid sorption-ultrafiltration pilot plant:

	Minimum	Maximum	units
Pumping rate	1	29	%
Agitation rate	250	350	rpm
Amount of sorbent	80	10	g
Phosphate concentration	10	100*	mg/dm <sup>3</sup>
$\Delta P$ transmembrane	0.2	0.9	bar
* Maximum concentration tested between all experiments			
Working conditions for a tank of 40 dm <sup>3</sup> and an agitator classified as C, see Fig. 8.13.			

On the other hand, Kinetic experiments were designed with tap water for the matrix of the phosphate solutions. The two studied parameter that were modified were the initial concentration of phosphate for the main stream  $Q_R$ , see Fig. 7.2, and the amount of sorbent used. The conditions of two experiments, named as UF1 and UF3 are summarized in Table ( 8.11 ). These two experiments will be further explained and commented in the chapter 8.4.1.

Table ( 8.11 ). Experimental conditions carried out in hybrid sorption-ultrafiltration pilot plant.

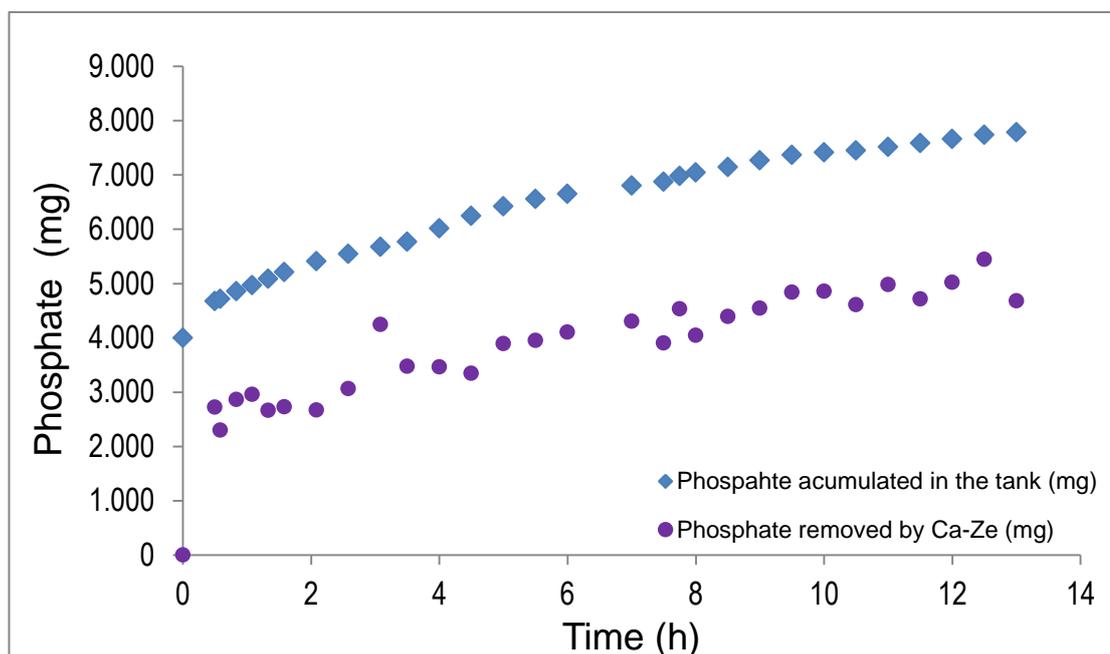
Name of the experiment	Amount Ca-Ze (g)	$Q_{R[Ci]}$ (mg/dm <sup>3</sup> ) of PO <sub>4</sub> <sup>3-</sup>	rpm
UF1	100	100	350
UF3	80	25	350

#### 8.4.1. Mass balance

The phosphate mass balance evolution in the kinetic test for the experiments UF1 and UF3 is plotted in Fig. 8.14. and Fig. 8.15. and working parameters are summarized in Table ( 8.11 ). The mass balance was performed according to the equations EQ ( 7.3 ) to EQ ( 7.7 ).

From figures Fig. 8.14.A and Fig. 8.15.A it was observed that while the amount of the phosphate in the stirred tank was increased, the sorbent capacity followed the same trend until saturation was researched, representing the limit of phosphate sorbed. In the case of the system described by Fig. 8.14.A this saturation limit was not reached after 13 h of operation, and 4681 mg of phosphate were removed at the end of the experiment, while experiment UF3 represented by the Fig. 8.15.A limit was reached after 5-6 hours and 527 mg of phosphate removed after 9 h of operation at the end of the experiment.

A



B

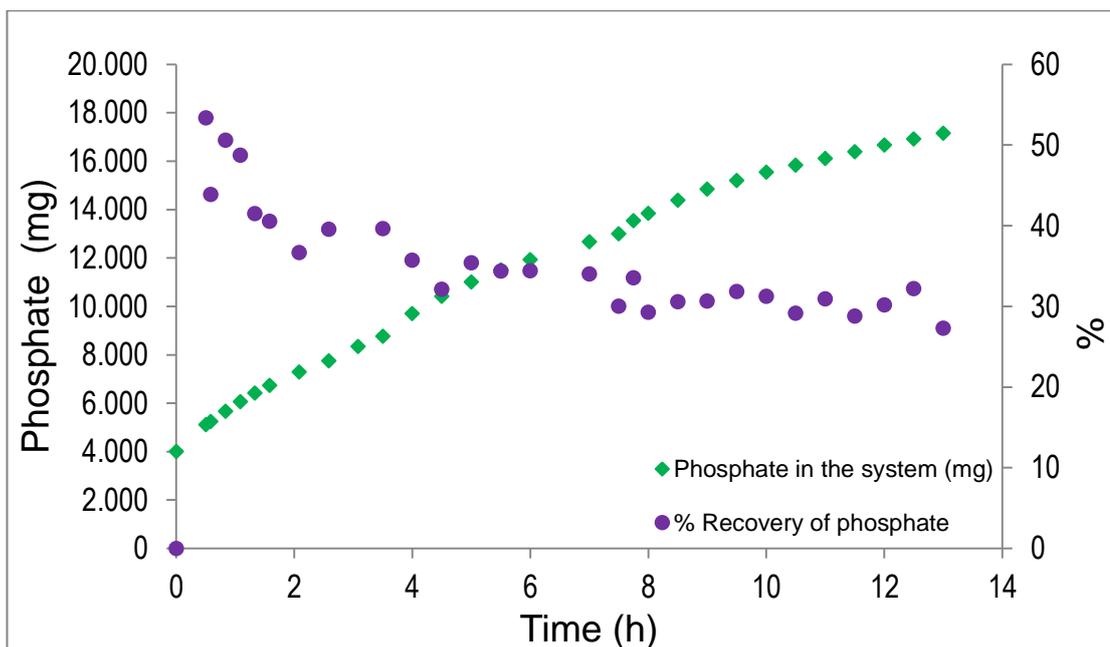
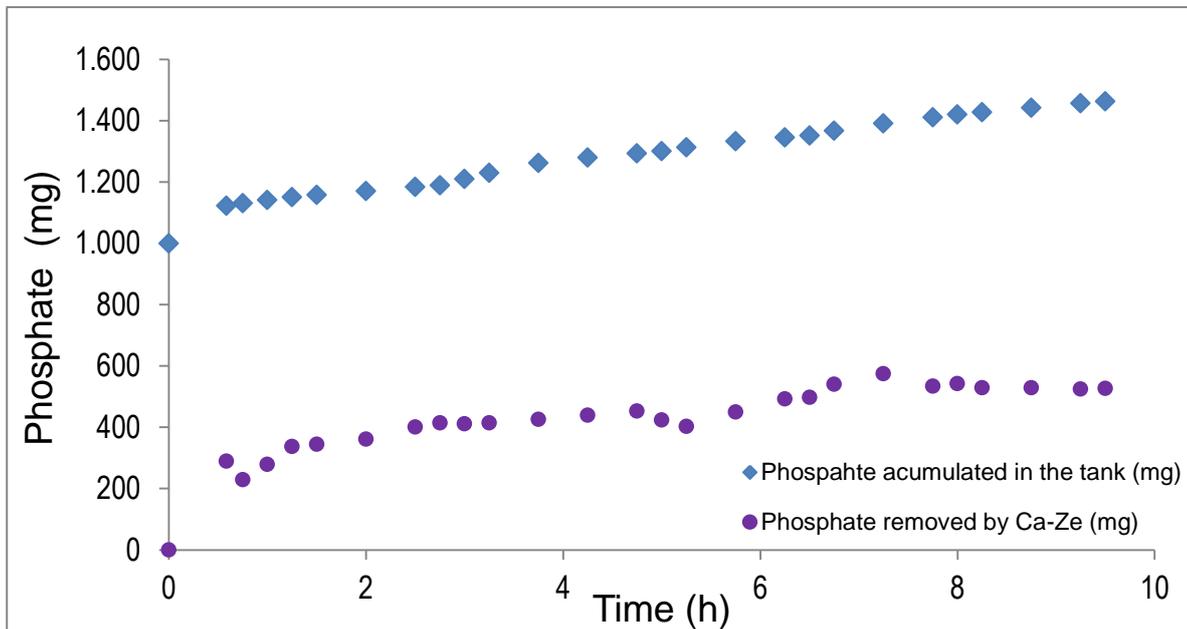


Fig. 8.14. UF1 kinetic experiment. (A) Progression of the phosphate accumulated in the stirred tank and phosphate removed by the Ca-Ze. (B) Progression of the total phosphate introduced in the system and the percentage removed by the Ca-Ze along the operating time.

A



B

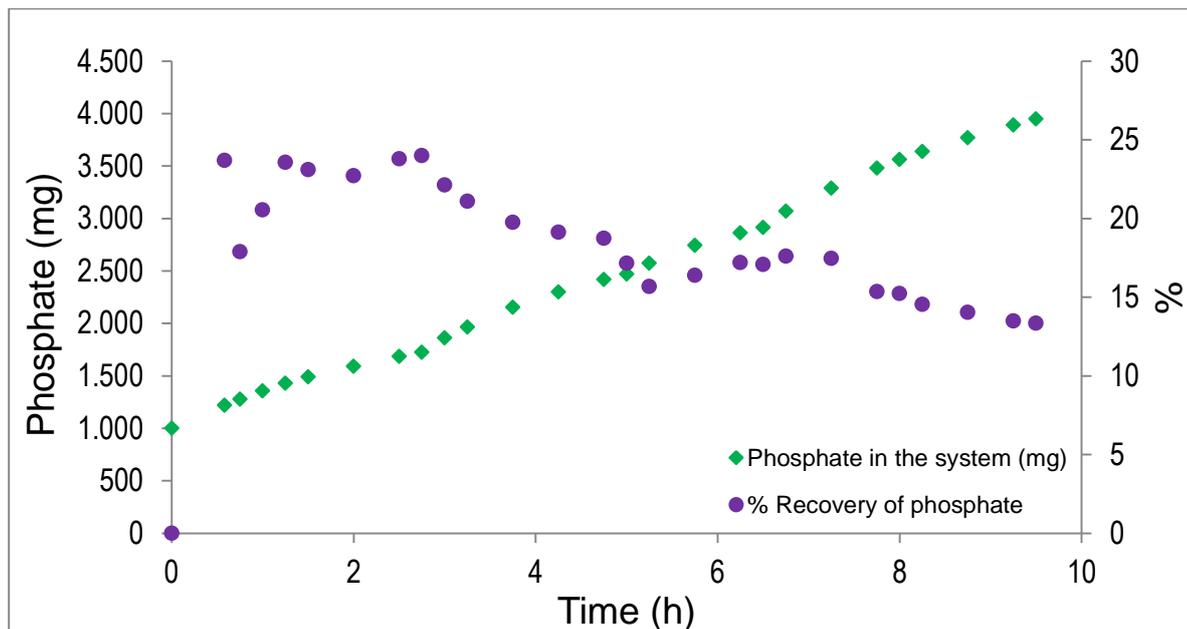


Fig. 8.15. UF3 kinetic experiment. (A) Progression of the phosphate accumulated in the stirred tank and phosphate removed by the Ca-Ze. (B) Progression of the total phosphate introduced in the system and the percentage removed by the Ca-Ze along the operating time.

Considering both experiments and the results from Table ( 8.12 ), it can indicate that the higher amount of phosphate in system the higher uptake by the sorbent. Otherwise the system UF3, with a phosphate concentration four times lower than UF1, showed a larger amount of phosphate removed. Moreover, it seems that the amount of sorbent in the system does not appear significant in recovering phosphate in the hybrid system. But the system UF3 with 1.25 times less amount of sorbent than the UF1 system, could remove 6.59 mg of phosphate sorbed per gram of sorbent, representing a recovery of 13 % of the total phosphate added to the system, as can be seen in Fig. 8.15.B. It can be compared to 46.81 mg of phosphate for each gram of sorbent of the UF1, representing a recovery of 27 % of the total of phosphate introduced in the system, as can be seen in Fig. 8.14.B. Therefore, system UF1 removed 7.1 times more of phosphate per gram of sorbent using just 1.25 more amount of sorbent than system UF3. This fact was consistent with the equilibrium experiments performed; see chapter 8.2.2., where for the same amount of sorbent the higher amount removed was found by the higher amount of phosphate dissolved.

Table ( 8.12 ). Results of phosphate removed by Ca-Ze in hybrid sorption-ultrafiltration pilot plant.

Name of the experiment	% of total phosphate sorbed by the Ca-Ze	mg PO <sub>4</sub> <sup>3-</sup> /g Ca-Ze
UF1	27	46.81
UF3	13	6.59



## 9. Economic study

In this chapter the cost of the project is detailed in concept of reactants, laboratory equipment, personnel and others associated costs. A detailed classification of each group is presented as follows.

### ➤ Equipment costs

These costs would be calculated as the amortization (EQ ( 9.1 )) for each equipment used in this project and not by the cost of them. However, much of these equipment could be already considered amortized.

$$\text{Amortization} = \frac{\text{Equipment Cost}}{\text{Lifespan}} \cdot \text{Time spend} \quad \text{EQ ( 9.1 )}$$

Many auxiliary materials for this equipment could already consider amortized, like the chromatograph's vials and for this reason are not included.

Table ( 9.1 ). Amortised costs for the equipment used.

	Cost (€/Unit)	Lifespan (Years)	Time spend (Years)	Amortised cost (€)
Analytical balance	870	5	1	174.00
Conductivity meter	809.24	5	1	161.85
Chromatograph	20000	15	1	1333.33
Magnetic stirrer	150.96	5	1	30.19
pH meter	652	5	1	130.40
Spectrophotometer	3754	15	0.5	125.13
			Subtotal =	1954.91

### ➤ Material and reactants costs

In this point is shown a complete list of equipment required to begin a study of this nature. However, not all listed and valued elements were necessary to purchase (Table ( 9.2 ) and Table ( 9.3 )), but as the previous point, these were considered as new acquisitions to show the possible associated costs for a project like this one.

Table ( 9.2 ). Reactants costs per unit and total cost.

	Units	Unit cost (€/Unit)	Total cost
CaCl <sub>2</sub> (500 g)	1	24.79	24.79
HCl (1 dm <sup>3</sup> )	1	11.86	11.86
KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O (500 g)	1	31.4	31.4
Milli-Q (dm <sup>3</sup> )	100	1	100
NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O (500 g)	1	24.49	24.49
NaOH (500 g)	1	16.89	16.89
		Subtotal =	209.43

Table ( 9.3 ). Materials costs per unit and total cost.

	Units	Unit cost (€/Unit)	Total cost
Amber flask 1 dm <sup>3</sup>	1	3.21	3.21
Beaker 50 cm <sup>3</sup>	2	2.47	4.94
Beaker 250 cm <sup>3</sup>	4	2.77	11.08
Beaker 2 dm <sup>3</sup>	2	10.64	21.28
Filter 0,2 µm	300	0.68	204
Glass cuvette 1 cm <sup>3</sup>	1	14.72	14.72
Globe Box (200 units)	1	5	5
Hazardous waste container	2	12.79	25.58
Inox turner	1	1.9	1.9
Laboratory clamp	1	1.9	1.9
Magnet stirrer	2	2.28	4.56
Micropipette 0,5-5 cm <sup>3</sup>	1	110	110
Micropipette 1-10 cm <sup>3</sup>	1	150	150
Parafilm (box)	1	25.75	25.75
Pasteur pipette (100 units box)	1	20.69	20.69
Petri dishes (20 units tub)	1	66.16	66.16
Pipet tips PE (200 units box)	1	20	20
Test tub 10 cm <sup>3</sup> (250 units box)	2	34.12	68.24
Timer	1	8.41	8.41
Tube rack 48 test tubs	2	7.99	15.98
Vials 10 cm <sup>3</sup>	40	0.25	10
Volumetric flask 25 cm <sup>3</sup>	4	9.21	36.84
Volumetric flask 50 cm <sup>3</sup>	4	9.72	38.88
Volumetric flask 100 cm <sup>3</sup>	4	12.26	49.04
Volumetric flask 1 dm <sup>3</sup>	2	24.11	48.22
Volumetric flask 2 dm <sup>3</sup>	1	37.33	37.33
		Subtotal =	1003.71

➤ Personnel

Hourly wages are considered for a freelance Engineer, who has to work over the project for a period of time and not as Engineer employed in one company. Remunerations found as reference in the BOE 126 Mayo 2014 and detailed in Table ( 9.4 ).

Table ( 9.4 ). Costs for time and personnel spend.

Technical personnel			
	Time (hour)	Income (€/Unit)	Total cost
Experimental time spend	700	32	22400
Modelling time spend	200	32	6400
Cleaning time spend	100	15	1500
Management personnel			
Direction time spend	50	50	2500
Subtotal =			30880

➤ Others costs

Table ( 9.5 ). Others costs associated to this project.

Others	Cost ( € )
Water and electricity	600
Subtotal =	600

➤ Total project costs

Table ( 9.6 ). Total cost of the project.

	Cost ( € )
Equipment	1954.91
Reactants	209.43
Material	1003.71
Personnel	30800
Others	600
Subtotal =	34648.05
VAT (21%)	7276.09
Net cost	41924



## 10. Environmental impact study

### 10.1. Environmental impact study at lab scale

Next table resumes some of impacts that were taking place as part of the project and the technique to avoid or reduce them.

Table ( 10.1 ). Environmental impacts detected and measures adopted.

Impact	Observed (Yes/Not)	Measure adopted
Vibrations	Yes	Check rubber feet in the equipment
Liquid waste	Yes	Classified by types in hazardous containers
Solid waste	Yes	Dehydrated and placed in the container waste
Hazardous gases	Yes	Work in a fume cupboard

#### ➤ Liquid waste

For this kind of residues was taking the measure to classify these by their composition and stored in special containers, properly marked with the pictograms and labels. Finally these containers are collected, periodically, by a company which was in charge to discard in safety conditions. The company in fact is SITA SPE IBÉRICA, S.L.U, Martorell (Barcelona).

The solutions were classified as:

- Aqueous solutions for acid and basic solutions.
- Phosphate solutions.
- Vanadate solutions.

#### ➤ Solid waste

This kind of residues come basically from the use of zeolite and fly ash, the others like papers and plastics were the most common in this project. For plastic and papers were classification and discarded in the proper container in the la for these. Zeolite and fly ash were placed in the garbage bin, after dehydration, because they were filtered and lived in the oven for further analyses.

#### ➤ Hazardous gases

Basically the gases with potential hazardous effects could affect staff working directly with the products responsible of these emissions. Mainly products like concentrated HCl or vapours in the preparation of the solution of vanadate were the sources of these gases. None serious effects over the environment have been documented about this of products, in

such quantities used on this project. However, to avoid interactions between the personnel and the gases, all manipulations with these kinds of products were carried out in the hood.

## 10.2. Impact on a global scale

The potentially issue documented about utilization of fly ash as by-product is mercury which is contained in the coal and could be mobilized. The production rate of this by-product has almost reached the 5000 million metric tonnes, in the past years and for ratio of 0.3 mg/Kg of Hg in the 2003 was found a total of 1534 t of Hg for the coal processed worldwide (Mukherjee et al. 2008). But since there is not an industry that has begun to produce synthetic zeolites based on fly ash there is not conclude studies in this regard.

However, this project manages two objectives at the same time. On the one hand, from the waste of thermal plant, like flay ash, is possible improve this making a synthetic zeolite, which can be used as sorbent in waste water treatments plants. Moreover, elements like phosphorus, nitrogen and others oligoelements can be sorbed in synthetic zeolites would give a revalorization as a new line of low cost fertilizer (Bansiwal et al. 2006). Although there is no evidence or article of any industrial activity such the one proposed here, it seems an important step forwards to widen the lifespan of phosphorus reserves, though there is no way to know how the activity would impact on global scale.

## 11. Project schedule

In the Fig. 11.1. is shown the project Gantt chart, which provides a graphical representation of the project by mapping individual task on the project calendar.

	01 January 2014	01 February 2014	01 March 2014	01 April 2014	01 May 2014	01 June 2014	01 July 2014	01 August 2014	01 September 2014	01 October 2014	01 November 2014	01 December 2014	01 January 2015	01 February 2015	01 March 2015	01 April 2015	01 May 2015	01 June 2015	01 July 2015
Background documentation																			
Equilibrium isotherms studies																			
Kinetics studies																			
Pilot plant studies																			
Data processing																			
Writing report																			

Fig. 11.1. Project Gantt chart.

By background documentation were the articles, books and websites consulted for the proper planning of the experiments, the correct interpretation of results and consolidation of theoretical concepts.



## 12. Proposal of continuity

This section is intended to highlight the points in which can be worked to complete the study of the used sorbents for the removal and recovery of phosphates.

First, there is need to keep working in the hybrid sorption-ultrafiltration pilot plant, thought under stricter and more reals conditions. Since wastewater have more components which can complicate the sorption process between sorbent and sorbate.

Moreover, it would be interesting to investigate the precipitation modelling for brushite and other by-products that can be obtained by the utilization of synthetic zeolites. Thus, these can be studied as potential low cost fertilizers.

Likewise, it should be identified the principal sorption mechanism and the others for the correct interpretation and modelling of the process.



## 13. Conclusions

After all experiments performed was concluded that all sorbents studies, fly ash and synthetic zeolites, were able to remove phosphate from aqueous systems. Moreover, the amount of calcium ions in its structures seems to play an important role for this purpose. Moreover, under the typical conditions of pH for the treated waste water effluents and concentrations of phosphate the precipitation of brushite was observed.

Moreover, since brushite was found after the sorption process, the by-product obtained could be considered an available source of phosphorus as fertilizer (Bansiwal et al. 2006). To that end the synthesis of zeolites from fly ash enhanced by adding calcium ions appears an interesting field of research to keep working.

From equilibrium studies was found that best capacity of sorption was for the Ca-Ze, with a maxim  $Q_e$  found of 204.6 mg/g. Moreover, fly ash shown not significant difference between them with a  $Q_e$  maxim found of 70.0 mg/g for T and 55.0 mg/g for B. On the other hand, Na-P1 shown the best  $Q_e$  was 84.6 mg/g when the source of phosphate was a  $\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ .

The phosphate sorption process is complex and it is compromised in the presence of competing ions present in solution. As it was demonstrated by the kinetic studies performed, by using two different matrixes of water, Mili-Q water and tap water. Results obtained for the capacity to remove phosphate were larger for those where the Mili-Q water was the matrix, since its lower amount of ions present allow a lower interference between sorbent and phosphate. On the other hand, tap water has a higher concentrations of ions, between all them predominate Mg, Ca and K, among others, which can easily interact with sorbent or /and phosphate.

On the other hand, sorbents as the synthetic zeolites can be used in hybrid ultrafiltration and sorption systems. The results derived from the experiments performed at the pilot plant scale suggested that an industrial design could be interesting in order to remove phosphates from wastewater effluents. In addition if a synthetic zeolite, rich in calcium, is the sorbent the potential product it can be brushite, which can be used as slow release fertilizer.



## Acknowledgements

Nunca somos lo que quisiéramos ser, pero la lucha y la confianza  
nos devuelve a la realidad y nos acerca a nuestra perfección.

Ernesto Sabato

As part of a long journey, through my degree on Chemical Engineering, is this project the sum up of my work and efforts, but none of this could have been possible without all those people that complemented me on my weakness and making me better and better with all their knowledge and lessons.

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## Annexes

### Annexe A

In Annexe A was attached the total of experiments performed along this project, resumed them in the Table ( A.1 ) with their specification. All experiments were performed under standard ambient temperature and pressure conditions (SATP).

Table ( A.1 ). Record of experiments.

Name	Experiment	Sample	Weight	Source	[Ci] ppm	Time	rpm	Volume (mL)
<a href="#">EXP1</a>	Equilibrium	Na-P1	0,3 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP2</a>	Equilibrium	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP2</a>	Equilibrium	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP3</a>	Kinetic	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	6 h	500	100
<a href="#">EXP3</a>	Kinetic	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	6 h	500	100
<a href="#">EXP4</a>	Kinetic	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	6 h	500	100
<a href="#">EXP4</a>	Kinetic	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	6 h	500	100
<a href="#">EXP6</a>	Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP7</a>	Equilibrium	Ca-Ze	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP8</a>	Equilibrium	Na-P1	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP9</a>	Equilibrium	Na-P1	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP10</a>	Kinetic	T	0,4 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	11 h	500	100
<a href="#">EXP10</a>	Kinetic	B	0,4 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	11 h	500	100
<a href="#">EXP11</a>	Equilibrium	T	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP11</a>	Equilibrium	B	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 >15000	24h	250	10
<a href="#">EXP12</a>	Kinetic	Na-P1	0,3g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	30	6h	500	100
<a href="#">EXP13</a>	Kinetic	Na-P1	0,3g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	6h	500	100
<a href="#">EXP14</a>	Kinetic	T	0,4 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	24h+ 16h	500	100
<a href="#">EXP14</a>	Kinetic	B	0,4 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	24h+ 16h	500	100
<a href="#">EXP15</a>	Kinetic	T	0,4 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	1000	24h	500	100
<a href="#">EXP15</a>	Kinetic	B	0,4 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	1000	24h	500	100
<a href="#">EXP16</a>	Kinetic	T	1 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	24h + 6 h	500	100
<a href="#">EXP16</a>	Kinetic	B	1 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	24h + 6 h	500	100
<a href="#">EXP17</a>	Equilibrium	Na-P1	0,2 g	H <sub>2</sub> O	H <sub>2</sub> O at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP19</a>	Kinetic-Equilibrium	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	1>24 h	250	100
<a href="#">EXP19</a>	Kinetic-Equilibrium	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	1>24 h	250	100
<a href="#">EXP20</a>	Kinetic-Equilibrium	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	1>24 h	250	100
<a href="#">EXP20</a>	Kinetic-Equilibrium	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	1>24 h	250	100
<a href="#">EXP21</a>	Repetitions	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10000/15000	48	250	10

<a href="#">EXP21</a>	Repetitions	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10000/15000	48	250	10
<a href="#">EXP21</a>	Repetitions	Na-P1	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10000/15000	48	250	10
<a href="#">EXP22</a>	Kinetic-Equilibrium	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5'>24	250	10
<a href="#">EXP22</a>	Kinetic-Equilibrium	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5'>24	250	10
<a href="#">EXP23</a>	Equilibrium	T	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 ppm at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP23</a>	Equilibrium	B	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 ppm at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP23</a>	Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 ppm at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP23</a>	Equilibrium	Na-P1	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100 ppm at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP24</a>	Equilibrium	T	0,2 g	H <sub>2</sub> O	H <sub>2</sub> O at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP24</a>	Equilibrium	B	0,2 g	H <sub>2</sub> O	H <sub>2</sub> O at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP24</a>	Equilibrium	Ca-Ze	0,2 g	H <sub>2</sub> O	H <sub>2</sub> O at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP25</a>	Repetitions	T	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10000/15000	24h	250	10
<a href="#">EXP25</a>	Repetitions	B	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10000/15000	24h	250	10
<a href="#">EXP25</a>	Repetitions	Na-P1	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10000/15000	24h	250	10
<a href="#">EXP26</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	30'>24h	250	10
<a href="#">EXP26</a>	Kinetic-Equilibrium	Na-P1	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100-500	1'>24h	250	10
<a href="#">EXP27</a>	Equilibrium (Procedure blank)	Na-P1	0,2 g	H <sub>2</sub> O	H <sub>2</sub> O at pH: 6, 7, 8 i 9	24h	250	10
<a href="#">EXP28</a>	Kinetic-Equilibrium	Na-P1	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	5'>1 h	250	10
<a href="#">EXP28</a>	Kinetic-Equilibrium	Na-P1	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	300	0,5'>24h	250	10
<a href="#">EXP29</a>	How to make Ca-Ze	Na-P1	20 g	CaCl <sub>2</sub>				
<a href="#">EXP30</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5'>3h	250	10
<a href="#">EXP30</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	5'>3h	250	10
<a href="#">EXP31</a>	Kinetic-Equilibrium	T	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5'>3h	250	10
<a href="#">EXP31</a>	Kinetic-Equilibrium	B	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5'>3h	250	10
<a href="#">EXP32</a>	Kinetic-Equilibrium	T	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	5'>3h	250	10
<a href="#">EXP32</a>	Kinetic-Equilibrium	B	0,2 g	KH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	5'>3h	250	10
<a href="#">EXP33</a>	How to make Ca-Ze		250 g	CaCl <sub>2</sub>				
<a href="#">EXP34</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5'>1 h	250	10
<a href="#">EXP35</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	5'>1 h	250	10
<a href="#">EXP36</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	300	5'>1 h	250	10
<a href="#">EXP38_UF0</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	1,5	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10	5'>24h	360	1500
<a href="#">REP_UF0</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	1,3	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10	5'>24h	360	1300
<a href="#">EXP39_UF1</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	5g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	10	2'>4 h	????	4x10 <sup>4</sup>
<a href="#">EXP40</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	1h > 7h	250	10
<a href="#">EXP40</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	300	1h > 7h	250	10
<a href="#">EXP40</a>	Kinetic-Equilibrium	Ca-Ze	0,2 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	500	1h > 7h	250	10
<a href="#">EXP41</a>	Kinetic_Reactor_	Ca-Ze	3 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5' >	500	1000

	UF_TAPW					24 h		
<a href="#">REP_EXP4_1</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	3 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5' > 24 h	500	1000
<a href="#">UF1_1</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	100 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	100	5' > 24 h	1000	4x10 <sup>4</sup>
<a href="#">EXP42</a>	How to make Ca-Ze		250 g	CaCl <sub>2</sub>				
<a href="#">EXP43</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	3 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	300	5' > 24 h	500	1000
<a href="#">EXP44</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	3 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	50	5' > 24 h	500	1000
<a href="#">EXP45</a>	How to make Ca-Ze		250 g	CaCl <sub>2</sub>				
<a href="#">UF3</a>	Kinetic_Reactor_UF_TAPW	Ca-Ze	80 g	NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	25	5' > 24 h	320	4x10 <sup>4</sup>



## Annexe B

In Annexe B was attached the principal equipment used along this project.

➤ Analytical equipment



Fig. B.1. Ionic chromatographer. Model DIONEX ICS-1000-1100.



Fig. B.2. Scanning electron microscopy with X-ray analysis (SEM/EDS). Model Bruker D8 A25 Advance X-Ray Diffractometer  $\theta$ - $\theta$ , with  $\text{CuK}\alpha 1$  radiation, Bragg-Brentano geometry, and a lineal LynxEyeXE detector.



Fig. B.3. pH Meter. Model Crison GLP22.



Fig. B.4. Brunauer-Emmett-Teller (BET). Model Micromeritics Flow Sorb II 2300.

➤ Equipment



Fig. B.5. Agitator for vials (Equilibrium studies). Model REAX 2.



Fig. B.6. Hybrid sorption-ultrafiltration pilot plant.