

Abstract

The excess of nitrogen and phosphorus in the wastewater has caused crucial distortion in the nature such as eutrophication of water basins, disturbed the ecological balance and spoiled the water quality. Moreover, continuing population growth make that more fertilizers are needed to the agriculture.

To resolve these issues, a large number of researches related to ammonium and phosphate removal and recovery from wastewater have been carried out in the last years. Between the studied techniques, ion-exchange is one of the most competitive due to its simplicity of application and operation, low cost and use of environmental friendly materials.

The goal of this project is to characterize the overall sorption performance of a zeolite synthesized from coal fly ash which was provided in sodium form (Na-Ze), and its modification in potassium form (K-Ze). It was evaluate the sorption performance of these synthesized zeolites in ammonium single system and ammonium-phosphate binary system.

Equilibrium and kinetic studies were performed through the batch experiments. Equilibrium experimental data was well fitted by Langmuir isotherm equation and reported sorption capacities of $109 \text{ mg}\cdot\text{g}^{-1}$ and $21 \text{ mg}\cdot\text{g}^{-1}$ for Na-Ze and $17 \text{ mg}\cdot\text{g}^{-1}$ and $29 \text{ mg}\cdot\text{g}^{-1}$ for K-Ze in single and binary system, respectively. Binary system experiments with both zeolite reported not significant phosphate sorption.

Kinetic studies showed that both sorbents follow a pseudo second order reaction model and demonstrated that the NH_4^+ ions removal rate by K-Ze is initially very high, achieving 90% of total sorption in the first minute whereas Na-Ze achieved only the 60% of total ammonium uptake.

Finally, regeneration and reuse studies evaluated by three continuous sorption-desorption cycles demonstrated that sorption capacities increased in most cases after desorption and regeneration, probably duo to the zeolite surface activation by hydroxides.

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1. Glossary

BET isotherm	Brunauer–Emmett–Teller Isotherm
CEC	Cation exchange capacity
EDS	Energy Dispersive X-Ray Spectrometer
FTIR	Fourier transform infrared spectroscopy
meq	Milliequivalents
MFC	Chamber fuel cell
MSAF	Multifunctional slow-release ammonium fertilizer
SEM	Scanning Electron Microscope
ppm	Parts per million

2. Foreword

2.2. Origin of the project

This Final Degree Project was supported by Zero-discharge project (CTQ2011-26799) and financed by the “Ministerio de Economía y Competividad”, Spanish Government.

2.3. Motivation

Nowadays, the scarcity of water and the high level of nitrogen and phosphorus pollution of water bodies make necessary the removal of these pollutants from wastewater. Moreover, the increasing amount of fertilizer demand due to the population growth has driven society and researchers to define strategies to recover and reuse both nitrogen and phosphate as slow release fertilizer.

With the aim of minimizing the negative impact of nitrogen and phosphorus pollution as well as improving fertilizer use efficiency, it was really interesting performing this study for resolving or enhancing this environmental and health issue.

2.4. Previous work

This study is the continuation of the project carried out by Cheng (2015), where the Na-Ze was characterized by SEM, EDS, BET and FTIR analysis. Furthermore batch equilibrium and kinetic studies of Na-Ze as well as calcium and magnesium (Ca-Ze and Mg-Ze) modified zeolites were conducted with ammonium single solution and ammonium-phosphate binary system.

3. Introduction

3.1. Objectives of the project

The aim of this project is to characterize the overall sorption performance of ammonium and phosphate removal onto the Na-Ze and K-Ze by using synthetic wastewaters.

For achieving this goal, several objectives have been proposed:

- To perform the modification of sodium synthetic zeolite to the potassium form.
- To determine the ammonium and phosphate sorption capacities of Na-Ze and K-Ze.
- To determine the kinetic parameters of ammonium and phosphate sorption mechanism onto both zeolites.
- To evaluate the regenerability and reusability of the both zeolites for several sorption-desorption cycles.

3.2. Scope of the project

As has been exposed before, this project is part of an extensive research about revalorization of the ammonium and phosphate recovered from wastewater treatment plants for slow release fertilizer production.

In this project, all experiments were carried out by using synthetic waters with different concentration of ammonium and phosphate in order to characterize the overall sorption performance of zeolites in sodium and potassium form.

It is important to point out that the entire experimental work was performed in laboratory scale. A possible pilot plant design and implementation is out of the scope of the project.

4. State of the art

Ammonium and phosphate are essential nutrients for life, but the excessive quantities of these nutrients cause eutrophication, which produces deterioration of water quality, damages the balance of organisms present in aquatic ecosystems and increases fish mortality (Wu et al., 2006).

Furthermore, the continuous population growth causes the increasing use of fertilizers (see Figure 1) in order to ensure enough food production. This originates increasingly concerns about the sustainable use of this resource.

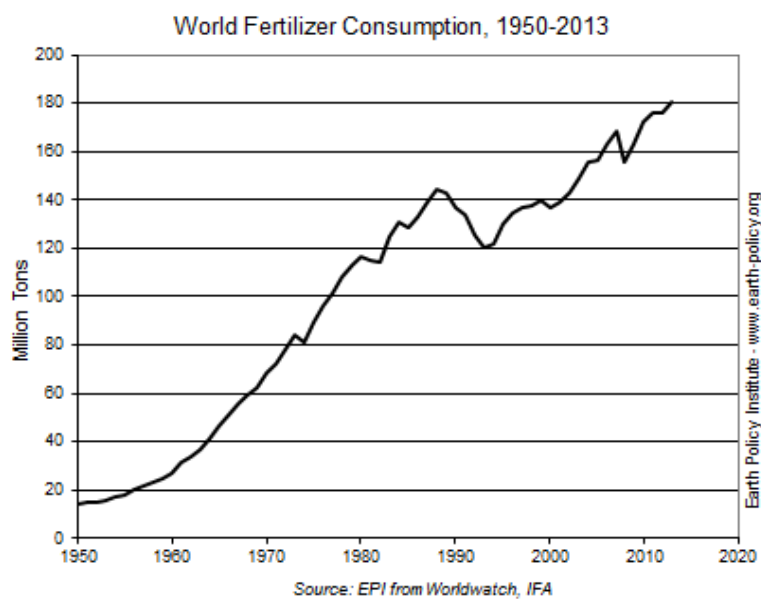


Figure 1: World fertilizer consumption from 1950 to 2013.

Considering these problems, there have been carried out many studies about the sustainable use of the ammonium and phosphate. These studies not only investigate the utilization of efficient materials for the removal of ammonium and phosphate but also its reutilization as slow-release fertilizer to improve the performance of the agriculture.

4.1. Ammonium and phosphate removal from wastewater treatment plant

Nutrient removal from industrial and municipal wastewater has taken an important role in the past decade in order to avoid eutrophication and to minimize water contamination.

Nitrogen can be found in wastewater as ammonia, nitrite, nitrate and organic nitrogen. Organic nitrogen is decomposed to ammonia, which can be assimilated to bacterial cells, leading thus to net growth, or can be oxidized to nitrite and nitrate. This nitrate can be converted to gaseous nitrogen in a second step and is removed from the wastewater.

Phosphorus is present in wastewater as orthophosphate, polyphosphate and organically bound phosphorus, the last two components accounting usually for up to 70 percent of the influent phosphorus (Sotirakou et al., 1999).

Nowadays, the treatment of nitrogen is carried out at the biological nutrient removal processes (BNR). This part of the wastewater treatment plants involves optimal nitrification and denitrification steps. In the aeration basin, ammonium is oxidized to nitrate via nitrite using oxygen and different species of bacteria (nitrifiers). During posterior denitrification, the nitrate is converted to nitrogen gas in the absence of oxygen, creating an anoxic phase and using specialized heterotrophic bacteria. The nitrogen gas formed is harmlessly released into the atmosphere.

By using this treatment, ammonia is almost completely (98%) eliminated within the plant while total phosphorus is removed by 11 to 48% (average 15%).

In a second level of biochemical sewage treatment system, more than 90% phosphorus and parts of nitrogen in influent will be transferred into the sludge, and thus phosphorus and nitrogen usually accounted for up to 4% and 9% of the dry sludge. If the sludge is directly disposed in sea or landfills, the leaching of phosphorus and nitrogen would lead to serious secondary pollution problems (Korboulewsky et al., 2002). Besides, in the sewage treatment system, 20–50% of phosphorus and part of nitrogen in sludge effluent would be returned back to the wastewater treatment system.

Nitrogen and phosphorus recovery is the first step to release nitrogen and phosphorus from sludge. Nowadays, different chemical and physical methods have been used to disintegrate sludge, such as chlorine dioxide (Wang et al., 2011), ultrasonic (Yan et al., 2010), thermal hydrolysis (Appels et al., 2010; Xue and Huang, 2007), ozone (Yan et al., 2009), microwave (MV)-hydrogen peroxide (H_2O_2) method (Eskicioglu et al., 2008), acid and alkaline hydrolysis (Chen et al., 2007; Stark et al., 2006) and microwave (MW) irradiation (Park et al., 2004). In front of all others methods, alkaline hydrolysis has the advantages of single devices, easy operation and high efficiency.

4.2. Ammonium and phosphate removal and recovery technologies

Removing and recovering nitrogen and phosphorus at wastewater became every time more and more important due the excess content of these substances in the wastewater and the scarcity phosphoric rocks due to increasing fertilizer consumption in the world.

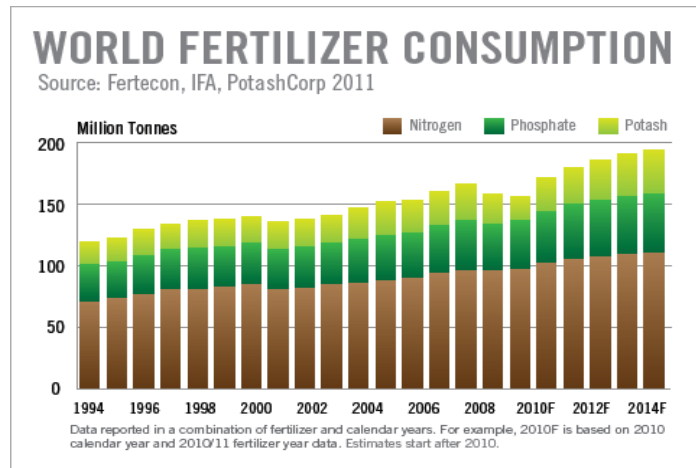


Figure 2: World fertilizer consumption from 1994 to 2014.

In comparison with others nutrients, nitrogen is widely used. More than 50% fertilizer used in the world is nitrogen based (see Figure 2) because of his good efficiency as fertilizer and its easy obtainment. However, phosphate is also taking an importance role in the world fertilizer consumption and phosphorus is a non-renewable resource that may be exhausted in the future.

Therefore, much attention has been paid to the technology for ammonium and phosphate removal and recovery to improve a better life quality and to minimize the impact of the environment that the excess of these substances can cause.

4.2.1. Electrochemical treatment

The electrochemical treatment is a technology based on the separation of the different polarity of the ions. It is very useful for the removal of dissolved ions. This technology is widely applied in metal recovery or heavy metal effluent treatment. This method involves positive charged ions will move to the anode and the negative charged one will move to the cathode obtaining treated water exempt of pollutants. Its low selectivity for phosphate ions in presence of competing ions such as nitrate, sulfate, chloride or hydrogencarbonate is a disadvantage of this method.

This technic has different types such as electrocoagulation, electroflotation and electrooxidation. The first one is the most used electrochemical treatment because of its superior performances in treating effluents containing suspended solid, oil and grease, and even organic or inorganic pollutants that can be flocculated. Furthermore, electrocoagulation has compact treatment facility, relatively low cost, possibility of complete automation and high particulate removal efficiency. Its efficiency depends on current density or charge loading, presence of NaCl, pH effect, temperature, power supply, electrode materials, pollutant concentration, system design and treated effluents. Some effects of these parameters are that removal efficiency increases by increasing current density at the expense of the energy consumption, higher temperature or the addition of NaCl gives higher conductivity hence lower energy consumption and the energy consumption is high at neutral pH due to the variation of conductivity.

Different materials such as iron, aluminium or stainless steel both in mesh and flat plates were tested for performing as electrode concluding that aluminium is usually used for water treatment and iron for wastewater treatment because iron is relatively cheaper. Nevertheless, aluminum plate is also finding application in wastewater treatment either alone or in combination with iron plate due to the high coagulation efficiency of Al^{3+} . Stainless steel is recommended to use when significant amount of Ca^{2+} and Mg^{2+} ions are in the water (Chen, 2004).

With continuous researches, a new high efficient electrochemical treatment was developed for removing phosphate from wastewater. It is a combination of open gradient superconducting magnetic separation and high gradient superconducting magnetic separation using Fe_3O_4 as seeding material. Important parameters that influenced the removal efficiency of phosphate in this treatment are magnetic seeding dosage, coagulant dosage, hydraulic retention time, and magnetic field strength and flow rate. All this parameters have been optimized for obtaining removal efficiency more than 90%. But the main inconvenience is the high energy consumption (Zhao et al., 2012).

4.2.2. Physical precipitation

Salt precipitation is one of the developing wastewater treatments which use a physical support such as fly ash, zeolites, sand or any particulate material with iron, aluminium or calcium ions content to form low solubility salts. Apatite, struvite or calcium phosphate can be the result of this precipitation. The advantage of these salts are that its can be easily separate from the aqueous medium by filtration and be used as sustainable, low cost and low quality fertilizer.

Fly ash, a waste material generated from electric power plants, is differentiating in low-calcium and high-calcium (Zhang, et al., 2011). Due its alkalinity and water sorption capacity,

it has been investigated for phosphate and ammonium removal by precipitation obtaining relatively low removal efficiency fertilizer. Using in combination with other alkaline materials, submitting in acidification with sulfuric acid, hydrochloric acid or heat treatment were useful for improve its effectiveness (Xu et al., 2010; He et al., 2012; Li et al., 2006). Precipitation products can be hydroxyapatite, brushite, calcium phosphate, or aluminium phosphate depending on the solution pH and fly ash composition (You, 2014).

Natural zeolite has been used for phosphorus and ammonium removal from aqueous solutions due to its content in calcium oxide, alumina and ferric oxide (Karapinar, 2009). The advantage of using zeolite is its capability to be used directly as fertilizer once ammonium and/or phosphate salts were precipitated. Many authors synthesized zeolite from fly ash through hydrothermal and fusion method because the chemical composition of fly ash is similar to volcano, the predecessor of zeolite (Ji et al., 2014) and because it is easier to obtain and the cost of this is lower than the natural one. Both zeolites can treated with salts (Wu, D. et al., 2006) (Schick et al., 2011), surfactant (Schick et al., 2011), sulfuric acid (Choi et al., 2012) (Zhang et al., 2007) or chitosan (Xie et al., 2013) (Hamdi & Srasra, 2012) for improve their removal efficiency. The calcium phosphate precipitation mechanism works better in the pH range between 3 and 6. Removal efficiency will decrease at higher pH and the precipitate product becomes hydroxyapatite (You, 2014).

Industrial wastes can be also used for phosphate salts precipitation. Barca et al. (Barca et al., 2012) studied steel slags with two types of pretreatment, one in an electric arc furnace and the other in a basic oxygen furnace for phosphate precipitation in hydroxyapatite. Some parameters such as pH of the solution and initial phosphate and calcium concentrations are influenced its removal capacities. After a series of batch experiments, it demonstrated that the basic oxygen finance steel slags had more capacity than the electric one. Also it was found that the release of calcium ions from slag was not always enough for hydroxyapatite precipitation, but the Ca^{2+} content in wastewater contributes to increase the phosphate removal efficiency (Barca et al., 2012).

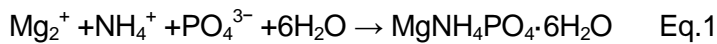
4.2.3. Chemical precipitation

Magnesium ammonium phosphate (MAP) method is an efficiency chemical precipitation technic to recycle the excess of phosphorus and nitrogen in the sludge. It can not only recover the limited phosphorus resource, but also reduce the phosphorus and nitrogen loading of the sewage treatment system (Bi et al., 2014).

The fluoride-containing wastewater from etching and wet cleaning process in semiconductor manufacture is mainly treated by precipitation with addition of calcium salts, such as calcium chloride (CaCl_2) before leave it to the water treatment plant. Because high concentrations of

phosphate and ammonium cannot be effectively removed in biological treatment processes (Warmadewanthi, 2009).

Precipitation using magnesium (Mg) salts could potentially provide simultaneous removal of PO_4^{3-} and NH_4^+ from wastewater. The reaction between Mg_2^+ , PO_4^{3-} and NH_4^+ forms the mineral struvite as can be described in Eq. (1).



Struvite is used as a premium grade fertilizer because of its slow release rate of nutrients, low frequency of application needed, sparingly soluble in water and a lower content of impurities. Several factors, such as pH, concentrations of Mg^{2+} , PO_4^{3-} and NH_4^+ , and presence of other interfering ions, such as calcium (Ca^{2+}) affected the precipitation and the purity of struvite (Zhang et al., 2011; Warmadewanthi, 2009). However, high concentration of Na^+ and SO_4^{2-} alters the induction time of struvite precipitation. The first reduces the induction time and the last increases the induction time (Warmadewanthi, 2009).

The pH not only affects the yield of struvite, but also influences the purity of struvite. (Lee et al., 2003). And the most convenient pH range for struvite precipitation is between 9.5 and 10.5 (Song et al., 2007). Removal efficiency of PO_4^{3-} increased when $\text{pH} > 10$, but bobierrite was the dominant species in this case which was less soluble than struvite, but when pH was higher than 11, magnesium hydroxide would be the dominant species. Based on Eq. (1), the stoichiometry of the molar ratio ($[\text{Mg}_2^+]:[\text{NH}_4^+]:[\text{PO}_4^{3-}]$) to form struvite is 1:1:1. In stoichiometric ratio, 47.4% of PO_4^{3-} was removed at pH 9.

The molar concentration of NH_4^+ was more than two times higher than that of PO_4^{3-} in the supernatant. Therefore, the molar ratio of ($[\text{Mg}_2^+]:[\text{PO}_4^{3-}]\text{P}$) was the critical factor for the recovery of phosphorus and nitrogen from the alkaline hydrolysis supernatant by MAP.

However, Mg_2^+ concentration must be in excess relative to PO_4^{3-} for high removal efficiency of PO_4^{3-} but it altered struvite purity. Removal efficiency of PO_4^{3-} can reached 92% as molar ratio increased to 3:1. Also if the molar ratio of magnesium to phosphate increased from 1:1 to 2:1 the removal efficiency of ammonium increased. When $[\text{Mg}_2^+]:[\text{PO}_4^{3-}]$ was 2.5:1 at pH 9, 84% of PO_4^{3-} and 34% of NH_4^+ was removed, and the dominant species was struvite. But when $[\text{Mg}_2^+]:[\text{PO}_4^{3-}] > 2.5:1$, bobierrite became the dominant species in the solid phase (Warmadewanthi, 2009).

When $[\text{Mg}_2^+]:[\text{NH}_4^+]:[\text{PO}_4^{3-}]$ was 2.5:15:1 at pH 9, the removal efficiency of PO_4^{3-} can increased to 93%. Therefore, the excess of ammonium to the wastewater is beneficial for struvite (MgNH_4PO_4) precipitation (Warmadewanthi, 2009). The optimum removal efficiency reached up to 97% under the conditions of Mg/P molar ratio of 1.4 and pH 9.5 (Song et al., 2007).

4.2.4. Adsorption

Adsorption is an interesting technology which has received increasing attention in the last decade in different industrial fields. It is a reaction where dissolved ions are linked to the functional group of the solid adsorbent.

Sorption processes have many applications such as solutions purification, separation process and extraction of valuable substances such as uranium and plutonium. The most common application is the water deionization in water treatment plants for the elimination of ammonium and phosphate.

Many active researches and studies about sorption revealed that adsorption is more effective when increasing pH due to that anionic species of phosphate –hydrogenphosphate, dihydrogenphosphate and phosphate- are much more reactive for ion exchange than phosphoric acid. Also the presence of metal ions such as iron and aluminum, or weakly metal ions such as calcium, magnesium or ammonium favors the sorption of phosphorus.

One of the most important mechanisms of the adsorption was the ion exchange. It is the reversible interchange of ions between a solid (ion exchange material) and a liquid in which there is no permanent change in the structure of the solid. The following subsections would summarize some important sorbents.

4.2.4.1. Clay mineral

Currently, there is a growing trend to use natural and low cost materials as sorbent materials. So, clay mineral seems to be a very promising material due to his high cation-exchange ability with a high selectivity towards the ammonium ions in the presence of other concurrent cations in the wastewater in addition to the features listed above.

Zeolites are similar in their composition to clay minerals. More specifically, both are hydrated aluminosilicates. They differ in their crystalline structure. Zeolite is also different from clays since it does not swell, and thus will not disperse in water as many types of clay do.

The natural clay mineral can be modified chemically or thermally to improve its sorption capacity. The sorption of ammonium with clay mineral is the result of ion exchange and/or adsorption. Both processes are parallel and usually one of them prevails depending on the solid-to-liquid ratio.

The ammonium removal efficiency is higher for clays in liquid colloidal state than in dry state because the acid modification of the clay decreases the efficiency of ammoniacal nitrogen removal. In the hydrated state, the activities increased since the dispersion of the clay

particles into smaller particles occurs and the specific surface area is thus increased. By increasing the specific surface area the amount of the negative charge is also increased. So, the part of sorption in ammonium retention is higher (Rozic et al., 2000).

The time necessary to achieve sorption equilibrium for NH_4^+ ions from aqueous solution onto the used clay mineral was 20 min. The amounts of NH_4^+ ions sorbed increased, with increasing initial NH_4^+ ion concentration, thereby demonstrating the importance of diffusion in the sorption process. The maximum sorption capacity of bentonite for NH_4^+ ions removal from aqueous solution reached 47,56 meq/100 g of sorbent for an initial NH_4^+ ion concentration of $9 \text{ mg}\cdot\text{dm}^{-3}$. (Eturki et al., 2012)

4.2.4.2. Activated carbon

Coal, charcoal and coal ash have been evaluated for the retention of phosphate ions obtaining good results, especially in the case of virgin coal (Khan et al., 2011). The significant sorption capacity of coal is due to the porosity as well as organic carbon and inorganic elements present in coal. For achieve higher removal efficiency, Yao et al. (Yao et al., 2013) developed a new method for producing biochar directly from plant tissues enriched with magnesium which contains magnesium hydroxide and magnesium oxide nanoparticles which can be used as a high-efficiency sorbent to remove phosphate from aqueous solutions (You, 2014). The maximum sorption capacity observed for ammonia and phosphate were $10 \text{ mg}\cdot\text{g}^{-1}$ and $143 \text{ mg}\cdot\text{g}^{-1}$ respectively. (Wang et al., 2015).

4.2.4.3. Microbial fuel cell

Nitrogen recovery through NH_3 stripping is energy intensive and requires large amounts of chemicals. Therefore, a microbial fuel cell was developed to simultaneously produce energy and recover ammonium. Kuntke et al (2012) investigated ammonium recovery using a two chamber fuel cell (MFC) at high ammonium concentration. It was proved that ammonium can be recovered using a MFC, while energy is produced at the same time. The energy balance showed a surplus of energy $3.46 \text{ kJ}\cdot\text{g}\cdot\text{N}^{-1}$, which means more energy was produced than needed for the ammonium recovery. Hence, ammonium recovery and simultaneous energy production from urine was proven possible by this novel approach. (Kuntke et al., 2012).

The main processes for ammonium transport are migrational flux and diffusional flux. Ammonium was transported against a concentration gradient by migrational flux. Higher transport rates can be achieved by further optimization of the current density (Kuntke et al., 2011).

4.2.4.4. Nanocomposites

Some nanomaterials can be used like a sorbent or for dope some sorbent for improving its efficiency to minimizing the negative impact of nitrogen and improving fertilizer use efficiency. Others examples of nanomaterial sorbents could be charcoal granular activated carbon impregnated with nanosized magnemite (Zach-Maor et al., 2011), the magnetic composite formed by La-EDTA coated with magnetite (Yang et al., 2013), Lewatit FO36 resin covered with Fe³⁺ nanoparticles (Rafati et al., 2012), nanostructured Fe-Al-Mn trimetal sorbent with molar ratio of 3:3:1 (Lu et al., 2013), nanocomposites consisted on polymer doped with aluminium nanoparticles (Oliveira et al., 2012), biochar with bohemite (AlOOH) nanoflakes able to remove both arsenic or methylene blue and phosphate (Zhang & Gao, 2013) chitosan improved with magnetite and zirconium oxide (Jiang et al., 2013) (You, 2014).

4.2.4.5. Sponge iron

Sponge iron is a traditional environmental material, but its application as a sorbent in phosphorus removal is a new research field because of its high phosphorus sorption capacity. Jiang et al (2013) evaluated the physic-chemical characteristics of sponge iron and zeolite to study their phosphorus removal capacities. The results of their static experiments and dynamic experiments indicated that the sorption of phosphorus onto iron sponge was more apt to chemical combination, but zeolite was more apt to electrostatic attraction or ion-exchange (Jiang et al., 2013).

4.2.4.6. Others materials

In addition to the mentioned above, many polymers as fiber ion exchanger and resin, industrial and vegetal wastes can be use as precursor or support for phosphate removal. But most of the vegetal wastes cannot be reused several times due to its decreasing removal capacity after regeneration process.

Iron or zirconium has been used as ligand for selective phosphate removal treatment (Delaney et al., 2011). Both metals work as ligand for ion exchanger; they adsorb phosphate and release functional groups to the solution. For iron, there are a wide variety of sorbents which use it because it is selective to phosphate and capable to be reused. For zirconium or its derivate products, some studies was carried out for phosphate removal due to it highly selectivity and its capability to achieve high removal efficiency at acidic pH. Ren et al (2012) was synthesize an iron-zirconium binary sorbent with a molar ratio of 4:1 to minimize the high price of this material (Ren et al., 2012).

4.2.5. Other ammonium and phosphate removal technologies

There are more different techniques for the removal of phosphorus and ammonium besides techniques commented upon in the previous sections. One of these techniques is filtration. A huge variety of pollutants are removed both in drinking water and in waste water treatment plants using ultrafiltration and nanofiltration. In fact, there is an extensive study about the recovery of phosphate from waste waters using phosphate selective multilayer nanofiltration membranes (Hong et al., 2009). However, this membrane was only tested with chloride as competing anions but more studies are needed for its application with real waters (You, 2014).

There were also developed studies for phosphate and ammonium removal by cultivation of biological species which consume phosphate or ammonium as nutrient. This is the case of using seaweeds (*Ulva lactuca*) as a tertiary treatment (Tsagkamilis et al., 2009) or the cultivation of specific bacteria (Srivastava & Srivastava 2006) for the phosphate removal. For remove ammonium, *Alcaligenes faecalis* no. 4 and *Bacillus* strains were investigated (You, 2014).

Alcaligenes faecalis no. 4 has heterotrophic nitrification and aerobic denitrification abilities. By taking the nitrogen balance under different culture conditions, 40–50% of removed NH_4^+ was denitrified and about one-half of removed NH_4^+ was converted to intracellular nitrogen (Hung-Soo et al., 2005).

In the study of Kim, J.K. et al (2005), it has been found that the *Bacillus* strains were able to performed simultaneously aerobic nitrification/denitrification. The ability to both nitrify and denitrify makes *Bacillus* strains attractive candidates for application in the removal of ammonia nitrogen from wastewater (Kim et al., 2005).

Biological treatments were also studied for ammonium and phosphate uptake from wastewaters. In innovative biological treatments find improvements of conventional active sludge treatment such as two-sludge system for simultaneous removal of all nutrients via nitrite pathway (Marcelino et al., 2011).

5. Materials and methods

5.1. Sorbents and its characterization

For this project were used zeolites synthesized from coal fly ash in sodium form (Na-Ze). The Na-Ze ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$) is a low silica sodium zeolitic material which is known to deteriorate under acid conditions (Zhang et al., 2006). It has high Al (III)/Si (IV) ratio which provide it high cation exchange capacity (CEC) of 2 to 2.7 meq/g (Querol et al., 2007; Moreno, N. et al., 2001).

For the characterizations of the sorbent, Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer (SEM/EDS) was used to obtain the sorbent morphological information.

The scanning electron microscope is used to examine and analyze microstructural features providing solid morphological and topographical information of the surface. It has a very high resolution on the order of tens of Å, and a large depth of focus giving a three dimensional appearance of the image. Its operation is based on sweep with an electron beam on a particular area while on a monitor information is selected depending on the detectors available is displayed.

The fluorescence energy dispersive X-ray (EDS) is used to identify and quantify the elemental composition of specific areas of a sample. This is bombarded with photons from X-ray source expelling electrons home shell. Then the electrons occupy the outermost layers vacant places, emitting fluorescent X-rays or high during the transition. This is because they have to lose energy to occupy the inner orbitals. The radiations emitted during the transition are measured with X-ray spectroscopy.

5.2. Modification of Na-Ze to K-Ze

The modification of Na-Ze to K-Ze was done by alkaline pretreatment before the salt modification. Firstly, 30 g of the Na-Ze were mixed with 250 cm³ of 1M NaOH solution in constant agitation in a magnetic stirrer (Heidolph MR Hei-Tec) during 24 hours. After 24 hours, the solution was filtered with the vacuum filter and the process was repeated.

Then, the filtered zeolite was mixed with 200 cm³ of KCl solution and agitated it in a magnetic stirrer during 2 hours in constant agitation. After 2 hours, the solution was filtered with the vacuum filter and repeats the above procedures for 4 times.

Finally, the zeolite was cleaned with ultrapure water (Milli-Q) filtering the solution with the vacuum filter. After these steps, the zeolite was dried at room temperature during 72 h and it was stored properly for its use.

5.3. Equilibrium adsorption studies

A series of ammonium (NH_4^+) solution of 5-5000 $\text{mg}\cdot\text{dm}^{-3}$ were prepared dissolving NH_4Cl in deionized water. 25 cm^3 of each solution were taken into a series of 30 cm^3 polyethylene tubes (Nalgene Labware, USA) and were mixed with 0.1 g of sorbent.

The samples were mixed with a mechanical shaker (Heidolph Reax 2) at room temperature during 24 hours at constant agitation to achieve the equilibrium ammonium and phosphate uptake.

For equilibrium ammonium and phosphate sorption capacity and removal efficiency (%) were used the Eqs. (2) and (3), respectively:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m_s} \quad \text{Eq.2}$$

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad \text{Eq.3}$$

Where Q_e is the equilibrium sorbent capacity [$\text{mg}\cdot\text{g}^{-1}$], C_0 is the initial phosphate concentration [$\text{mg}\cdot\text{dm}^{-3}$], C_e is the sorbent concentration in equilibrium [$\text{mg}\cdot\text{dm}^{-3}$], V is the treated solution volume [dm^3] and m_s is the mass of sorbent [g].

The Langmuir and Freundlich isotherm models are the most commonly used to describe the sorption process. A simple isotherm equation for a single sorbate is typically applied to ion-exchange reactions despite that several studies were carried out with two component systems (You, 2014).

5.3.1. Langmuir isotherm

The Langmuir isotherm assumes that sorption happens at specific homogeneous monolayer (one molecule in thickness) sites within the sorbent, there is no interaction between the sorbate molecules (Zhang et al., 2011) and the number of energetic sorption sites are homogeneous and can be saturated.

The Langmuir sorption isotherm equation and its saturated monolayer isotherm can be represented respectively as Eq. 4 and Eq. 5.

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad \text{Eq.4}$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad \text{Eq.5}$$

Where Q_e is the equilibrium sorbent capacity [$\text{mg}\cdot\text{g}^{-1}$], Q_m is the maximum monolayer ammonium sorption capacity [$\text{mg}\cdot\text{g}^{-1}$], C_e is the equilibrium concentration of the sorbent [$\text{mg}\cdot\text{dm}^{-3}$] and K_L is Langmuir sorption constant related to the affinity of the binding sites and energy of the sorption [$\text{dm}^3\cdot\text{mg}^{-1}$].

5.3.2. Freundlich isotherm

The Freundlich isotherm is an empirical model describing the non-linear, heterogeneous and reversible sorption equation not restricted to the formation of monolayer. Applying this model, means that each site has different bond energy, with the stronger binding sites first occupied and sorption energy exponentially decreased until sorption process completion. This earliest known relationship also can be applied to multilayer sorption, with non-uniform distribution of sorption heat and affinities over the heterogeneous surface energy systems (Foo and Hameed, 2010).

The Freundlich isotherm equation and its linearization can be obtained from Eq. 6 and Eq. 7.

$$Q_e = K_F C_e^{1/n} \quad \text{Eq.6}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Eq.7}$$

Where Q_e is the equilibrium sorbent capacity [$\text{mg}\cdot\text{g}^{-1}$], C_e is the phosphate concentration in equilibrium [$\text{mg}\cdot\text{dm}^{-3}$], K_F is Freundlich sorption capacity constant [$\text{mg}^{1-1/n}\cdot(\text{dm}^3)^{1/n}\cdot\text{g}^{-1}$] and $1/n$ is the heterogeneity factor, a constant relating to sorption intensity or surface heterogeneity. The isotherm parameters K_F and $1/n$ can be determined from the lineal regression analysis of $\log(Q_e)$ versus of $\log(C_e)$, respectively (Yang et al., 2014).

5.4. Kinetics studies

For kinetic studies, 1 g of zeolite was added into a precipitate glass flask containing 250 cm^3 of ammonium solution with concentration of 20 $\text{mg}\cdot\text{dm}^{-3}$. The system was agitated with magnetic stirrers in order to maintain maximum homogeneity between the sorbent and the solution.

Samples of 8 cm^3 were taken every minute the first 10 minutes, after that the sample were taken every 5 minutes until it reached half hour, thereafter every 20 minutes until it reaches 80 minutes, every 30 minutes until reaching 3 hours and finally one more sample in the equilibrium at 24 hours.

All these samples were filtered using cellulose nitrate membrane filters (Albet 0.45 μm) when it was taken and were stored at a glass test tube.

The kinetics models provide valuable insight into the reaction pathway and describe the solute uptake rate which in turn controls the residence time of solute uptake at the solid-solution interface (Zhang et al., 2011). It gives important information for process designing and modelling (Yousef et al., 2011). In this study, three macroscopic kinetic models: pseudo first order equation, pseudo second order equation and Elovich equation were used for analyzing the experimental data. These models describe the overall relationship between the amount of sorption and sorption time (Tseng et al., 2014).

5.4.1.1. Pseudo first order model

Lagergen's model also named pseudo first order model rate equation was the first one in describing the sorption on liquid-solid systems based on solid capacity and employed to test experimental data (You, 2014). Metal ions and contaminating organic compounds as pollutant and activated carbon as sorbent fitted with this model.

Lagergen's original differential equation is showed in Eq. 8.

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad \text{Eq.8}$$

Integrating Eq. 7 with boundary conditions $t= 0$ to $t= t_e$ and $Q_t= 0$ to $Q_t= Q_e$ can be obtained the linear form of the pseudo first order model equation (Eq. 9).

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \text{Eq.9}$$

Where Q_e is the equilibrium sorbent's capacity [$\text{mg}\cdot\text{g}^{-1}$], Q_t is the sorbent's sorption capacity at time t [$\text{mg}\cdot\text{g}^{-1}$], t is the time [s] and k_1 is the pseudo first order rate constant [s^{-1}]. The kinetic parameters Q_e and k_1 can be obtained from the lineal regression analysis of $\ln(Q_e - Q_t)$ as function of t (You, 2014).

5.4.1.2. Pseudo second order model

Three steps are involved in the pseudo second order kinetic model: the ammonium ions diffuse into the particle pores; the ammonium ions diffuse from liquid phase to liquid-solid interface and the ammonium ions move from liquid-solid interface to solid surfaces (Alshmeri et al., 2014).

The rate expression's differential equation is described in Eq. 10.

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad \text{Eq.10}$$

Integrating Eq. 10 with boundary conditions $t=0$ to $t=t$ and $Q_t=0$ to $Q_t=Q_e$ can be obtained the linear form of the pseudo second order model equation as can be seen in Eq. 11.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad \text{Eq.11}$$

Where Q_e is the amount of sorbate sorbed on the sorbents at equilibrium [$\text{mg}\cdot\text{g}^{-1}$], Q_t is the sorbent's sorption capacity at time t [$\text{mg}\cdot\text{g}^{-1}$], t is the time [s] and K_2 is the rate constant of pseudo second order [$\text{g}\cdot\text{mg}^{-1}\cdot\text{s}^{-1}$]. The kinetic parameters Q_e and K_2 can be obtained from the lineal regression analysis of t/Q_t as function of t .

5.4.1.3. Elovich model

Elovich's or Roginsky–Zeldovich equation has been widely used in kinetics adsorption to describe the chemical sorption of gas onto solid systems and suitable for heterogeneous sorbing surfaces, but recently it has also been applied to describe the sorption process of pollutants from aqueous solutions (Qiu et al., 2009).

The linear form of the Elovich equation is described in the following Eq.

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad \text{Eq.12}$$

Where q_t is the amount of sorbate sorbed at time t , α and β are the Elovich coefficients which represent the initial sorption rate [$\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$] and the desorption coefficient [$\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$], respectively. These coefficients can be calculated from the linear regression of q_t versus $\ln t$ (Abdel, 2012).

5.5. Study of simultaneous removal of ammonium and phosphate

For the equilibrium experiment a series of ammonium (NH_4^+) and phosphate (PO_4^{3-}) solutions of 2-3000 $\text{mg}\cdot\text{dm}^{-3}$ ammonium and 6-9000 $\text{mg}\cdot\text{dm}^{-3}$ phosphate were prepared dissolving NH_4Cl and $\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}$ respectively in ultrapure water. The experimental procedure was the same than explained in section 5.3.

For the kinetic experiment, solution with a concentration of 20 and 60 $\text{mg}\cdot\text{dm}^{-3}$ of ammonium and phosphate, respectively, were prepared and the experimentation was carried out as explain in section 4.4.

Is important to point out that the Na-Ze used in this binary solution was cleaned previously with deionized water due to the presence of phosphorus traces in it composition.

5.6. Regeneration and desorption studies

Regenerations studies were applied in batch isotherm experiments of both zeolites. For the regeneration of zeolites, 10 cm³ of NaOH or KOH 1 mol·dm⁻³ for Na-Ze and K-Ze, respectively, was added to each polyethylene tubes of the series mentioned at the equilibrium sorption section. The samples were mixed with a mechanical shaker (Heidolph Reax 2) at room temperature during 4 hours at constant agitation.

After the zeolite were deposited in the bottom of the polyethylene tube by gravity, the supernatant solutions was extracted with a Pasteur pipette stored in plastic bottles to squirrel away in the refrigerator.

In order to clean up the samples, ultrapure water was put in each sample. Mechanical shaker was used to mix the sample for clean better the zeolite during 4 hours at constant agitation and at room temperature. This process was repeated twice.

5.7. Sample analysis

All sorption samples were analyzed by ionic chromatography (Dionex ICS 1100). The used analytical column (IonPac AS23) was filled with supermacroporous polyvinylbenzyl ammonium polymer, with quaternary ammonium as functional group which provides a capacity of 320 µeq /column. The used anionic eluent was 4.5 mmol·dm⁻³ of sodium carbonate mixed with 0.8 mmol·dm⁻³ of sodium hydrogencarbonate (You, 2014). The used cationic eluent was prepared using 3.9 cm³ of methanesulfonic acid (99.5%) in 2 dm³ ultrapure water. Due to the concentration of hydroxides in desorption sample, they were analyzed by alternative methods.

To analyze ammonium concentration in desorption test, ammonia gas sensing combination electrode was used. The instrument was calibrated using 4 ammonium standard solutions.

For analyzing phosphate concentration, the Vanadomolybdophosphoric Acid Colorimetric Method was used. The samples were filtered using 45µm cellulose nitrate membrane filters before being analyzed in an Ultraviolet/Visible Spectrophotometer (Hewlett Packard) which was calibrated using phosphate standard solutions.

5.8. Material cleaning

All laboratory materials after used were been cleaned with plenty of water and subsequently cleaned with deionized water and in the end clean with ultrapure water. If it enough clean,

can leave it immersed at nitric acid during few hours before clean it with plenty water and finally with deionized water.

6. Results and discussion

The results obtained during the different experiments of this project and its discussions are shown in this section.

Results are structured in sorbent characterizations, equilibrium, sorption kinetics and desorption and reuse studies.

6.1. Sorbents characterization

In this section is presented some comparison of the Na-Ze and K-Ze. The Figure 3 shown the images obtained by SEM of Na-Ze and K-Ze in its virgin state.

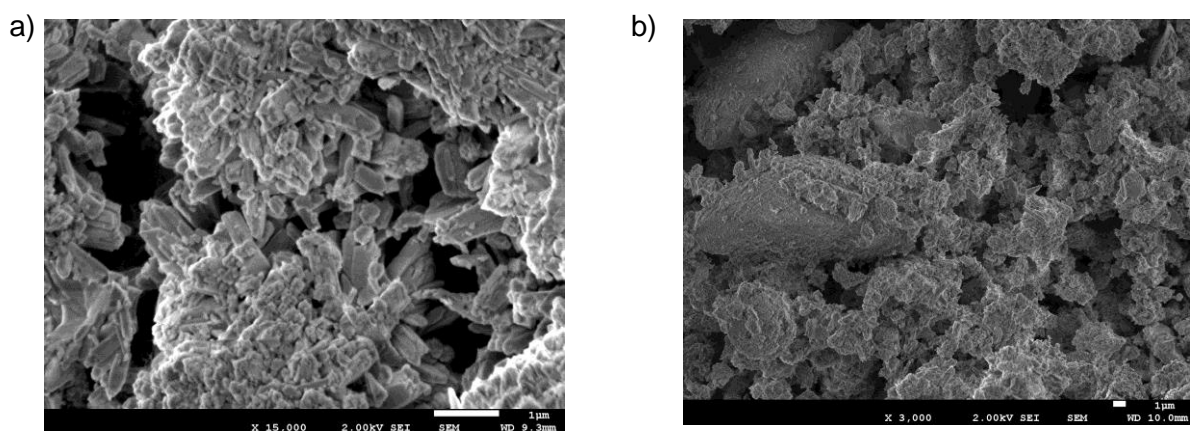


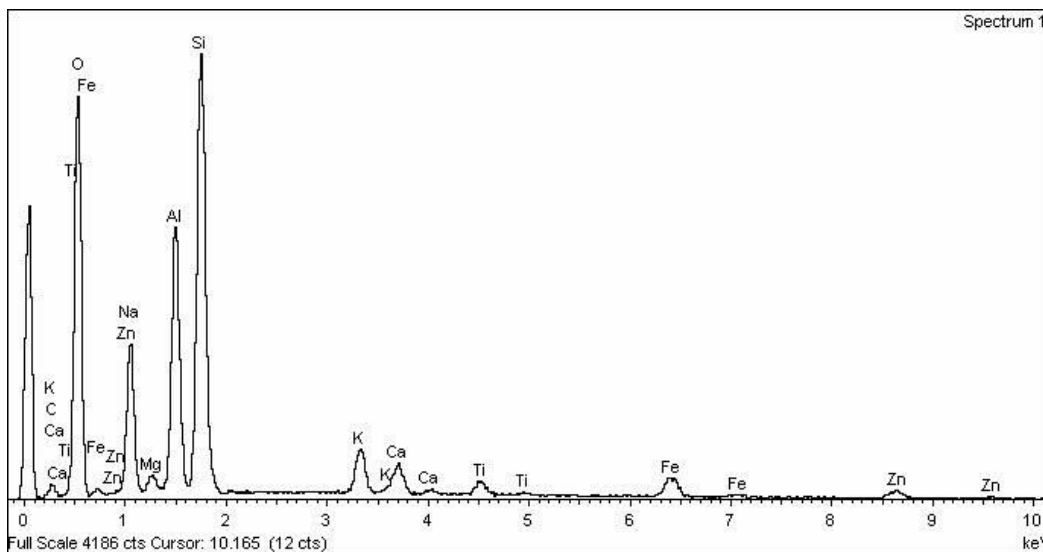
Figure 3: Scanning Electronic Microscopy of a) Na-Ze and b) K-Ze

Through the SEM images can be observed a clear change in the treated zeolite from the original zeolites. After the modification, the zeolite decreased its roughness. In the Figure 3 can be observed that Na-Ze reports more porosity than the K-Ze. This fact could be an indicator of higher sorption capacity of Na-Ze which will be corroborated in following sections.

In the analysis of the sorbent with the Energy Dispersive X-Ray Spectrometer (EDS), the measurements were performed on each sample in order to obtain an average value and to reduce the dispersion due to the heterogeneity of the sample.

The Figure 4 shown the EDS spectrogram for Na-Ze and K-Ze, were can be seen the increment of potassium in the case of K-Ze instead the diminution of sodium.

a)



b)

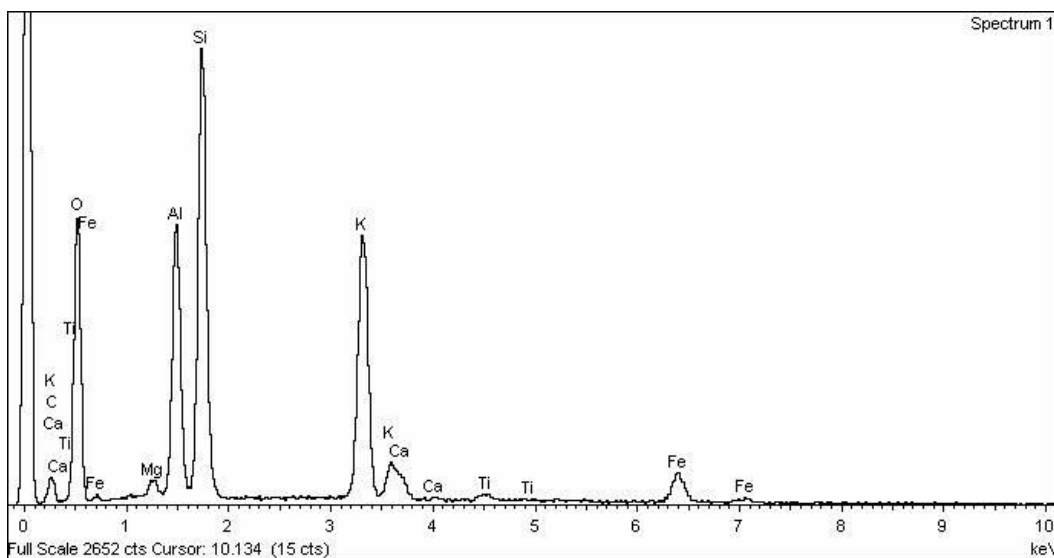


Figure 4: Energy Dispersive X-Ray Spectrometer of a) Na-Ze and b) K-Ze

In Figure 5 are compared the mass composition of both zeolites. It is observed that after the modification, the quantity of the Na decreased from 8.4% to 0% and the potassium composition increased from 2.2% to 11.9%, indicating that the modification procedure was successful in order to substitute all sodium cations by potassium.

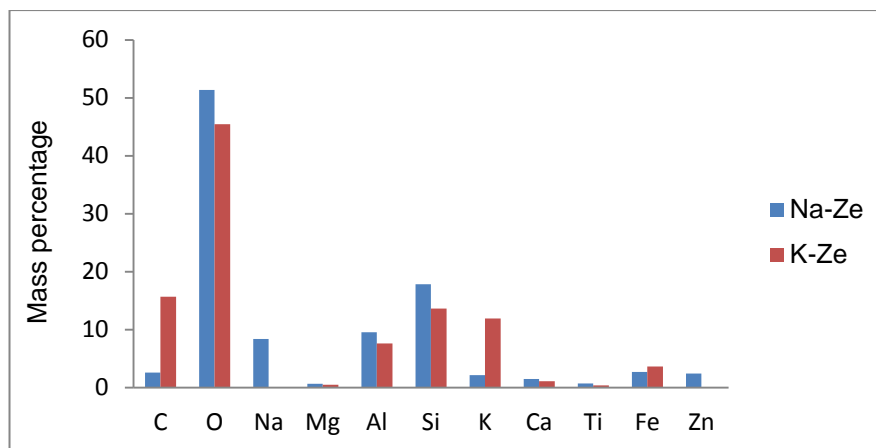


Figure 5: Chemical composition of virgin zeolites in mass percentage

Furthermore, the zeolites presented small quantity of metals that such as titanium or zinc that can be of concern if it is used as low release fertilizer.

6.2. Equilibrium studies

The experimental data from the sorption equilibrium studies demonstrated that both zeolites were no efficient for the phosphate sorption, with no significant sorption performance.

Experimental data were fitted by Langmuir and Freundlich isotherm equations in order to describe the ammonium sorption process. The isotherm parameters are summarized in Table 1.

Table 1: Isotherm parameter for ammonium sorption

Sorbent	Langmuir			Freundlich		
	Q_{max} [$mg \cdot g^{-1}$]	K_L	R^2	n	K_F	R^2
Ammonium						
Na-Ze	109.43	0.002	0.99	1.85	1.65	0.92
K-Ze	21.31	0.011	0.99	1.86	0.63	0.88
Ammonium and phosphate						
Na-Ze	17.22	0.022	0.99	2.57	1.20	0.69
K-Ze	29.05	0.011	0.99	2.02	0.97	0.91

Parameters reported in Table 1 indicated that the correlation coefficient for the Langmuir model is closer to 0.99 for all experiments, which means that all experimental data can be properly described by this isotherm for ammonium removal in both single and binary system. Analyzing the results, it can be highlighted that the sorption capacity of Na-Ze is higher in ammonium single solution than in binary solutions. Na-Ze reported sorption capacities around $109 \text{ mg} \cdot \text{g}^{-3}$ in ammonium single solution and only $17 \text{ mg} \cdot \text{g}^{-3}$ in binary solution.

On the other hand, for K–Ze the difference in sorption capacities are low and in fact the trends is opposite with a slightly increase in the binary solution. Sorption capacities are 21 mg·g⁻³ and 29 mg·g⁻³ in ammonium single solution and binary solution respectively.

These results demonstrated that the Na-Ze was more suitable to remove ammonium and was more efficient than the K-Ze according to the results commented at the sorbent characterization section. According to results reported by Widiastuti et al., (2011); the ion NH₄⁺ is less competitive than Na⁺ but more competitive than K⁺ because the competing ions test demonstrated that the affinity series is K⁺> NH₄⁺> Na⁺> Ca²⁺> Fe³⁺> Al³⁺>Mg²⁺. This means that potassium cations reported more affinity towards zeolite surface, thus the ion exchange process for ammonium removals is not favored.

The experimental data for the equilibrium sorption and the fitting parameters obtained by the Langmuir and Freundlich isotherms are represented in Figure 6, where can be seen clearly the experimental data is well described by Langmuir model.

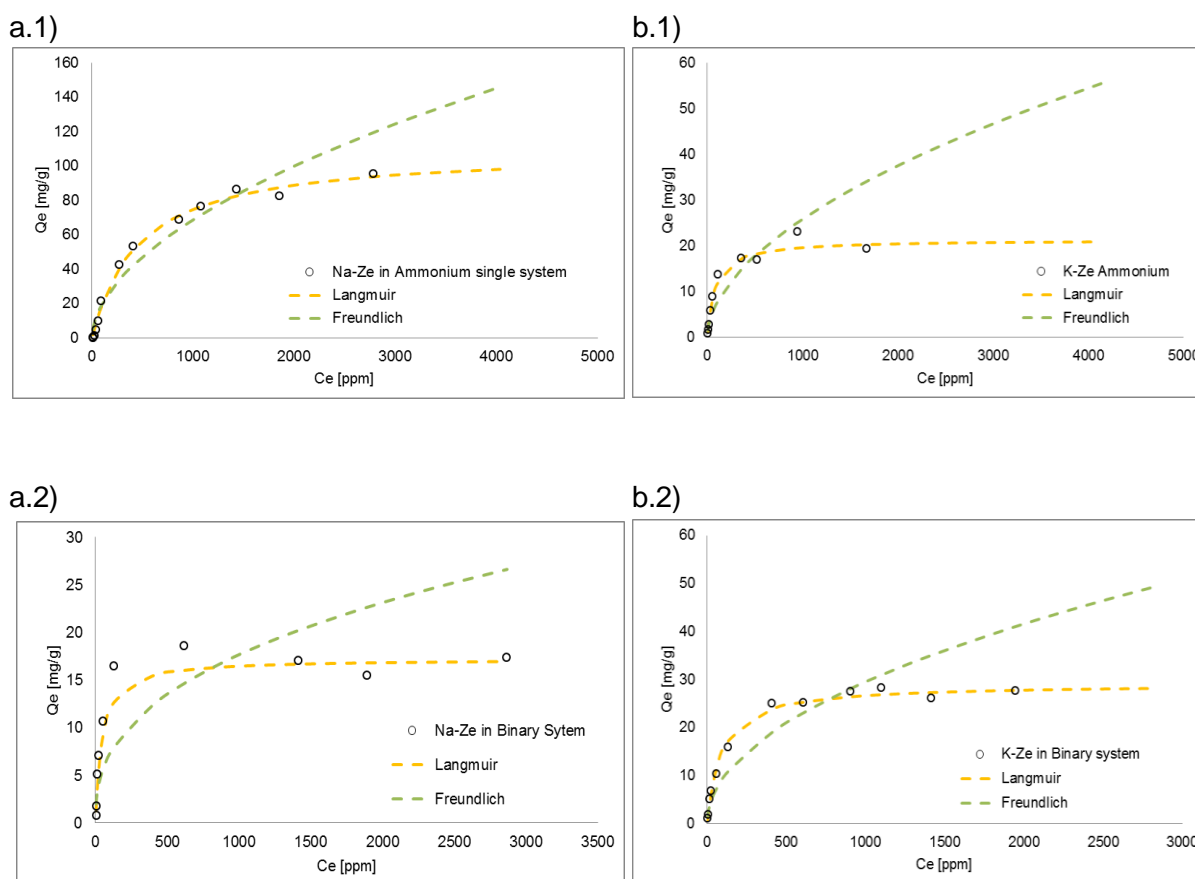


Figure 6: Sorption isotherm modelling for ammonium adsorption of Na-Ze with a.1) ammonium single and a.2) binary system and K-Ze with b.1) ammonium single and b.2) binary system.

The K-Ze reported a relatively low sorption capacity in single system and selectivity towards to ammonium ions for binary test in comparison with no modified Na-Ze and with the others zeolites studied in previous studies (Cheng, 2015).

Finally, to obtain the chemical composition and the surface image of the both sorbent after loaded in a batch sorption process with $3000 \text{ mg}\cdot\text{dm}^{-3}$ and $9000 \text{ mg}\cdot\text{dm}^{-3}$ ammonium and phosphate solution, SEM and EDS analysis were performed.

In Figure 7 can be observed not significant morphological modification compared with virgin zeolites. This fact indicate that the whole sorption mechanism is due to ion exchange and there was not produced the precipitation of any salt which would modified the surface morphology.

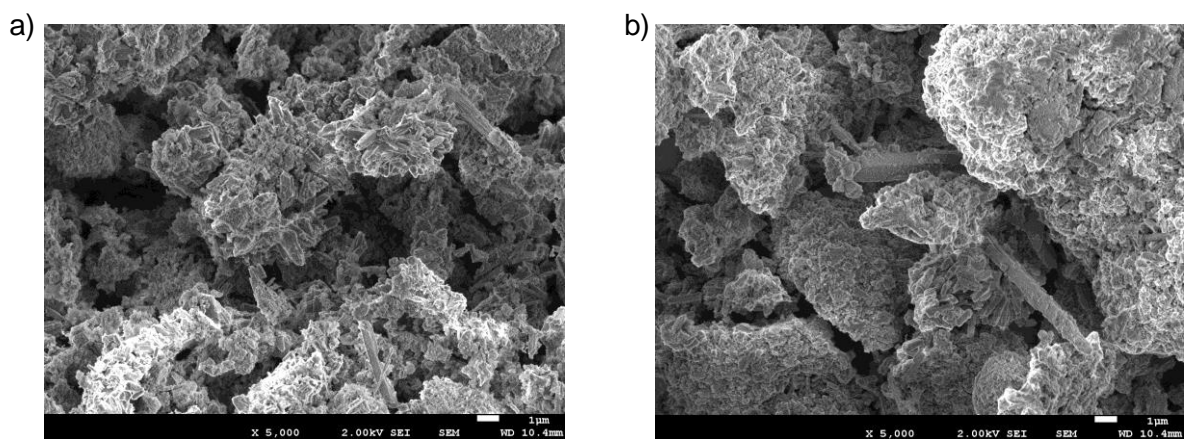


Figure 7: Scanning Electronic Microscopy of loaded a) Na-Ze and b) K-Ze

In Figure 8 is shown the mass composition of loaded zeolites. The loaded K-Ze, as expected, reported a small quantity of Na^+ ions remaining in the sample (less than 1%) because the phosphate solution was prepared with $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ which contained sodium in its composition.

Although these zeolites were not efficient for phosphate uptake, the Energy Dispersive X-Ray Spectrometer detected the presence of phosphate in the sample analyzed. It is because a low amount of the solution can not be removed at all from the sample. So the amount of phosphate at these zeolite were from the solution.

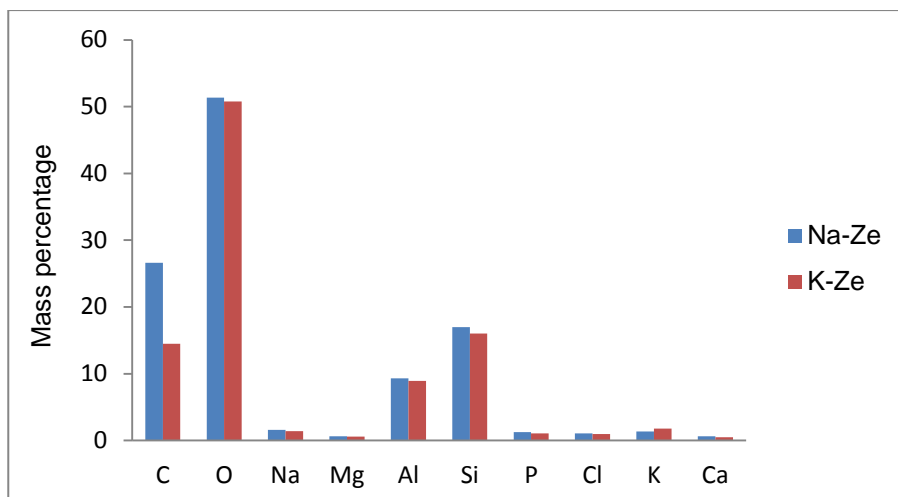


Figure 8: Chemical composition of loaded zeolites in mass percentage

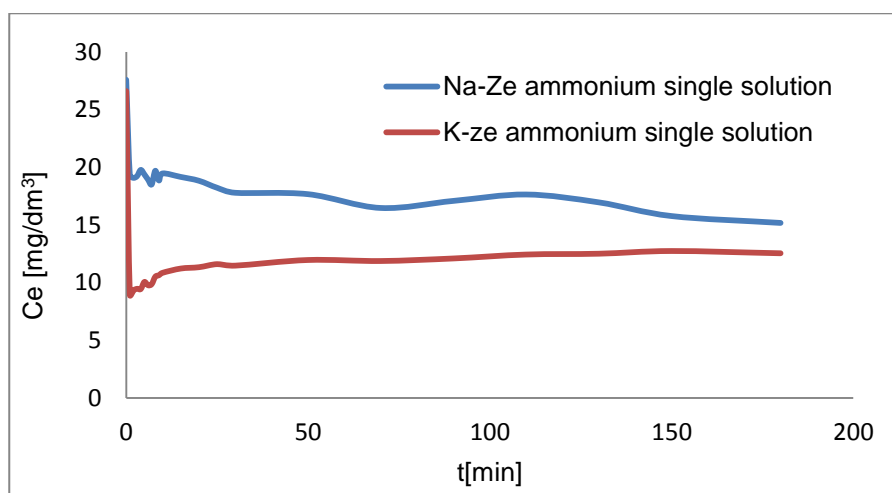
In both loaded zeolites, the nitrogen could not be detected by the Energy Dispersive X-Ray Spectrometer because of a low amount of nitrogen below the quantification limit.

6.3. Adsorption kinetics

The kinetic experiments were monitored for 24 hours despite of important changes can be found during the first three hours of contact for both zeolites, and should be pointing out that a faster decrease in concentration was observed after the first minute of each experiment.

In the Figure 9 is shown the ammonium sorption profile as a function of time for both zeolites.

a)



b)

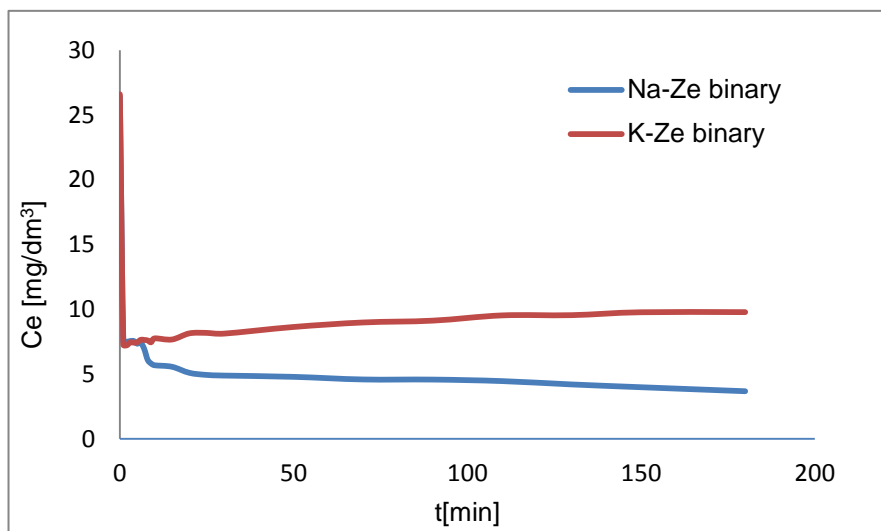


Figure 9: Ammonium adsorption profile as a function of time in Na-Ze and K-Ze in (a) monocomponent solution and (b) binary solution

In the case of Na-Ze in ammonium single solution, after first minute it was removed more than 56% of the total ammonium removed after 24 hours. The kinetics studies demonstrated clearly that the rate of NH_4^+ ions removal by zeolite is initially very high, but thereafter significantly reduces. This change in the sorption rate could be explained by the fact that after zeolite is contact with solution the sorbent sites are available, and the solute concentration gradient is high, but afterwards the decrease in sorption sites lead to decrease of NH_4^+ uptake rate (Zhao et al., 2010).

The Figure 9 also shown that ammonium sorption rate increased in binary solution, especially in the case of Na-Ze. However, this sorbent in the binary system reaches a supersaturation of ammonium allowing to a reversible process and thus, the sorbent desorb progressively ammonium and adsorb sodium in the solution. Even so, experimental data demonstrated that the zeolite was more efficient in removal ammonium in binary solution experiments. In experiment with K-Ze, 73 % of ammonium in solution was sorbed and while in experiment with Na-Ze, 86% of ammonium in solution was sorbed. On the other hand phosphate removal capacity was low for Na-Ze and K-Ze did not report removal.

The experiment with K-Ze in ammonium single solution showed that in the first minute, the sorbent remove 66% of ammonium. However after that, the zeolite release slight amount of ammonium, the same trend was observed for Na-Ze in binary solution.

The pseudo-first, pseudo-second and Elovich equations were used to predicting the ammonium sorption rate as well as ammonium sorption capacity in kinetic experiments. The experimental data was fitted to the linear form of these kinetic models.

The Figure 10 shown the graphic of the Na- Ze in ammonium solution using the three models commented above.

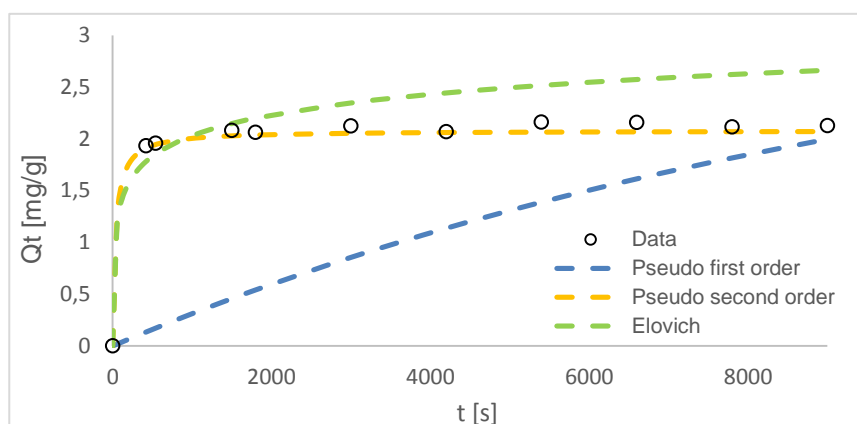


Figure 10: Kinetic models for ammonium sorption onto Na-Ze in ammonium single system

The experimental data was well predicted by the pseudo second order kinetic model as can be seen in Figure 10.

Kinetic experiments were carried out also with K- Ze however, the results (data not shown) was not properly described by any kinetic model because kinetic sorption was too fast to be fitted by this models.

The rate constants, kinetic parameters as well as r^2 values for pseudo-first, pseudo-second and Elovich equation are summarized in Table 2.

Table 2: Kinetic model parameter for ammonium sorption in Na-Ze

Pseudo first order			Pseudo second order			Elovich		
Q_e [mg·g ⁻¹]	K_1 [h ⁻¹]	r^2	Q_e [mg·g ⁻¹]	K_2 [g·mg ⁻¹ ·h ⁻¹]	r^2	α	β	r^2
Ammonium (5 mg·dm ⁻³)								
0.96	4.1E-05	0.22	0.92	0.008	0.99	0.13	0.12	0.86
Ammonium (20 mg·dm ⁻³)								
2.89	4.5E-05	0.26	2.41	0.003	0.99	1.6	0.08	0.34
Ammonium (20 mg·dm ⁻³) and phosphate (60 mg·dm ⁻³)								
6.01	2.5E-05	0.27	5.44	0.004	0.99	0.85	0.68	0.87

After analyzing the different kinetic parameter obtained, the pseudo second order model clearly provide highest correlation coefficient values ($r^2 \approx 1$) compared to other two models for both zeolites, for both experimental systems and at different initial ammonium concentration.

6.4. Desorption experiments

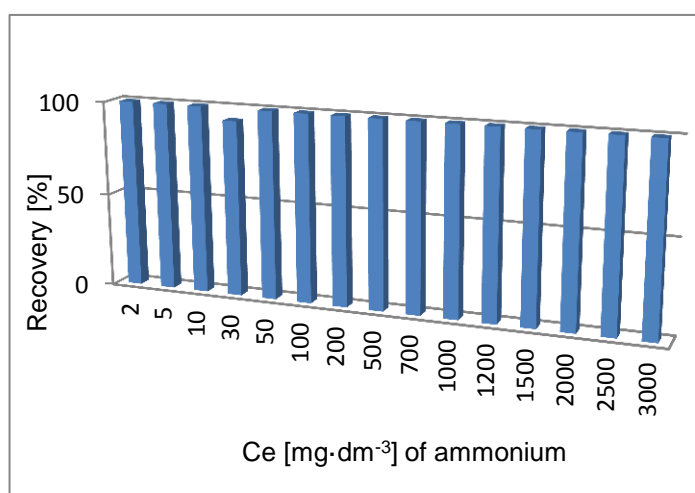
Desorption experiments are essential for the regeneration and reuse studies, ammonium and phosphate desorption from the sorbent loaded were carried out with sodium hydroxide as elution solution. For these studies, sorption and desorption were repeated continually for three continuous sorption-desorption cycle.

The recovery percentage of ammonium was calculated accordingly to equation 13.

$$\text{Recovery}(\%) = \frac{\text{ammonium bounded in the zeolite} - \text{ammonium in solution}}{\text{ammonium bounded in the zeolite}} \cdot 100 \quad \text{Eq. 13}$$

Desorption results for both zeolites with single and binary system are shown in Figures 11 and 12, where can be observed that almost all sorbed ammonium was desorbed by alkaline treatment.

a)



b)

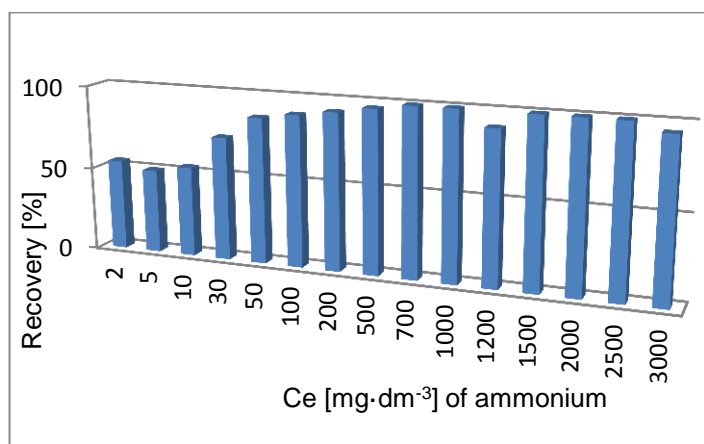
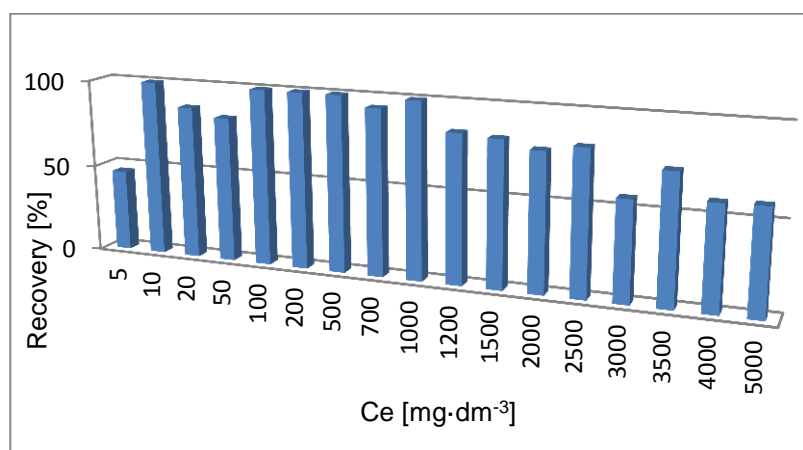


Figure 11: Ammonium recovery percentage for a) Na-Ze and b) K-Ze for different ammonium and phosphate concentration in binary solution

a)



b)

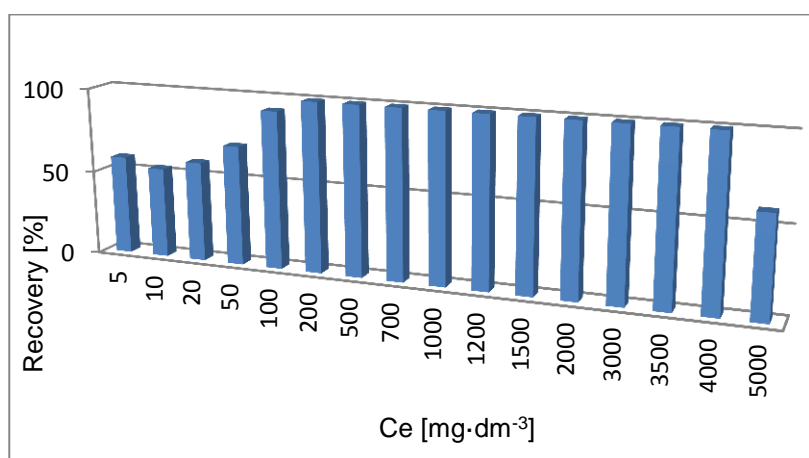


Figure 12: Ammonium recovery percentage for a) Na-Ze and b) K-Ze for different ammonium single solution

The Figure 13 shown the ammonium sorption and desorption recovery of the first sorption – desorption cycle using K-Ze in binary solution. It is observed that desorption of the K-Ze was quite higher, achieving values close to 100% for most of the experiments. So it can be concluded that both zeolites were suitable to recover ammonium and to be reused as sorbent.

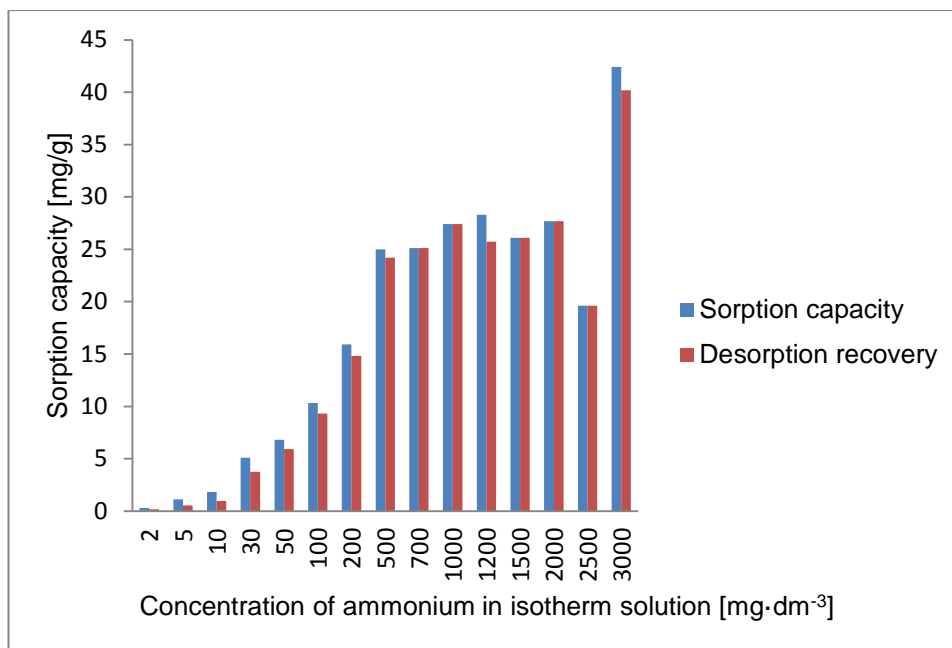


Figure 13: Sorption and desorption capacities of K-Ze in binary solution (first sorption –desorption cycle).

6.5. Regeneration studies

Regeneration study is a really issue in sorbent assessment since it determines the reliability of sorbent reuse and also competitive compared to other sorbents previously reported in literature. Since the potential regeneration of used zeolite can minimize the use of raw material, which lead to less energy consumption and be more sustainable for the environment.

For this project, batch experiments with K-Ze and Na-Ze were carried out in order to evaluate the possibility of the reuse of the sorbent and analyzing their sorbent capacities under different cycles of regeneration. These experiments are essential to shown the availability of the regeneration of the zeolite after used.

After regeneration experiments, phosphate sorption onto zeolites reported poor fit to the isotherm models used in this project. The sorption was insignificant and did not follow any tendency after the first sorption cycle. After the first regeneration, the phosphate sorption onto K-Ze increase and these sorption capacities increase by increasing the phosphate concentration in binary solution. However for Na-Ze, the phosphate sorption did not follow any trend in any regeneration cycle. Then, the sorption capacities for this zeolite were quite low.

Therefore, for the study of these sorbents sorption capacities only was analyzed for the ammonium sorption with Langmuir and Freundlich models.

The following table shows the isotherm parameter for ammonium sorption with different cycles.

Table 3: Isotherm parameter for ammonium sorption with different regeneration cycles

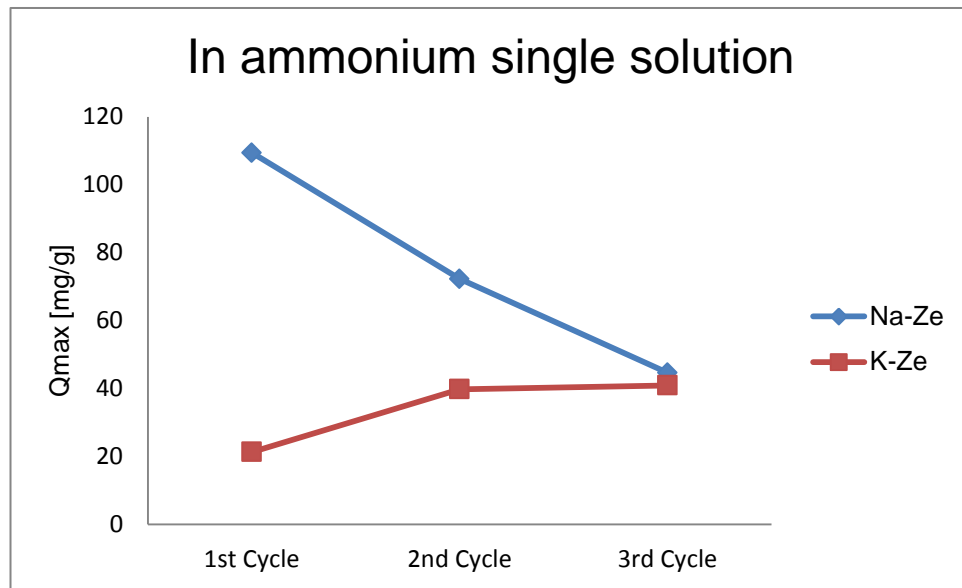
Sorbent	Langmuir			Freundlich		
	Q_{\max} [mg.g ⁻¹]	K_L	R^2	n	K_F	R^2
Ammonium						
Na-Ze 1 st cycle	109.43	0.002	0.99	1.85	1.65	0.92
Na-Ze 2 nd cycle	72.30	0.005	0.99	2.01	1.43	0.95
Na-Ze 3 rd cycle	44.67	0.01	0.99	2.42	2.12	0.96
Ammonium and phosphate						
Na-Ze 1 st cycle	17.22	0.02	0.99	2.57	1.20	0.70
Na-Ze 2 nd cycle	32.60	0.03	1.00	2.30	1.85	0.89
Na-Ze 3 rd cycle	40.88	0.01	0.97	2.79	3.14	0.98
K-Ze 1 st cycle	29.05	0.01	0.99	2.02	0.97	0.91
K-Ze 2 nd cycle	43.25	0.01	0.98	3.150	3.99	0.90
K-Ze 3 rd cycle	36.38	0.03	0.87	2.57	2.36	0.95

This result demonstrated that the Na-Ze in the ammonium single sorption capacity was higher (109 mg.g⁻¹) in its first cycle and then decreased significantly in the second cycle (72 mg.g⁻¹) and the third cycle (45 mg.g⁻¹). Nevertheless, in binary solution the sorption capacities of Na-Ze was quite low at first cycle (17 mg.g⁻¹) but it increased in the subsequent cycles (33 mg.g⁻¹ and 41 mg.g⁻¹).

For the K-Ze, sorption capacities were very low. In the ammonium single solution, the first cycle was 21 mg.g⁻¹, 40 mg.g⁻¹ in the second cycle and 41 mg.g⁻¹ in the third cycle. Instead, in binary solution, sorption capacity was slightly higher than the Na-Ze, 29 mg.g⁻¹ in the first cycle and then increased in the second cycle (43 mg.g⁻¹) and decreased in the third cycle (36 mg.g⁻¹).

The Figure14 represents the results commented above.

a)



b)

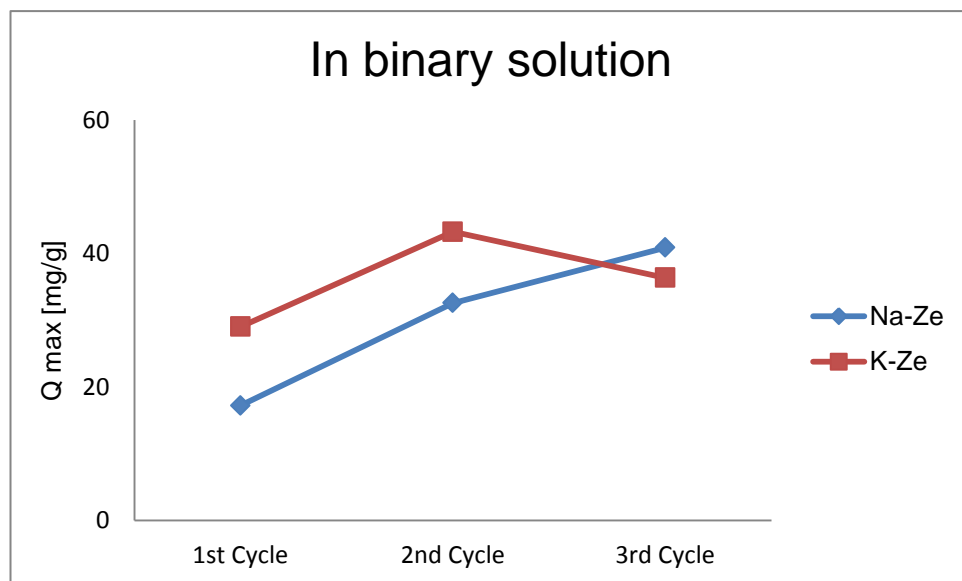


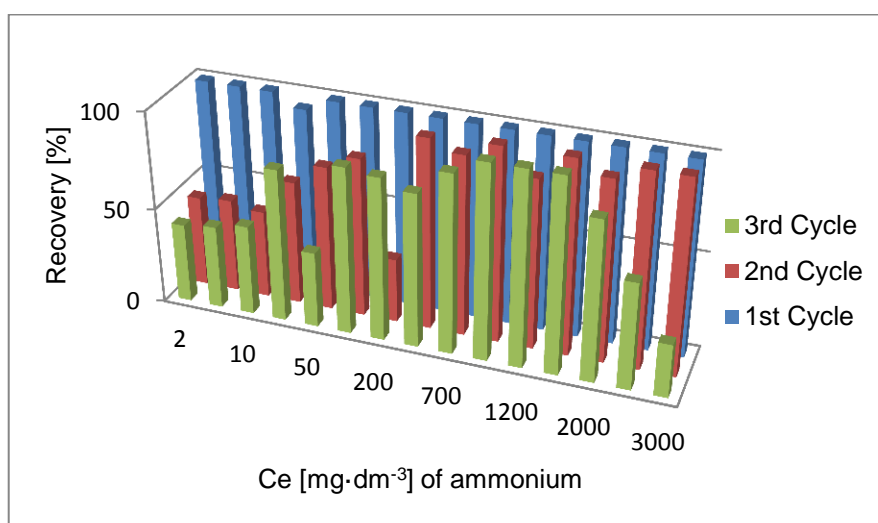
Figure 14: Evolution of the ammonium sorption of Na-Ze and K-Ze in a) ammonium single solution and b) binary solution.

The Na-Ze has a higher ammonium sorption capacity in ammonium single solution than K-Ze. Nevertheless, in its third sorption cycle, the sorption capacity of Na-Ze was decreased and remains similar to the K-Ze. The decrease of sorption capacity is due to that its desorption recovery was relatively low compared to K-Ze, as well as analyzed at the section 6.4.

Otherwise, the sorption capacity of zeolites increased in almost all cases after regenerations, unless in the study of Na-Ze in ammonium single system. This increment could be caused by the NaOH which was used in desorption process because hydroxyl groups likely activated the zeolite.

Moreover, desorption results for both zeolites with single and binary system are shown in Figure 15 and 16, where can be observed that in the first sorption- desorption cycle, almost all adsorbed ammonium was desorbed by alkaline treatment, but in the subsequent cycles, the ammonium is not completely desorbed. This trend is most significant at low concentration samples. This could be a reasonable explanation of sorption capacity decrease after several cycles despite the alkaline activation of sorbent surface commented above.

a)



b)

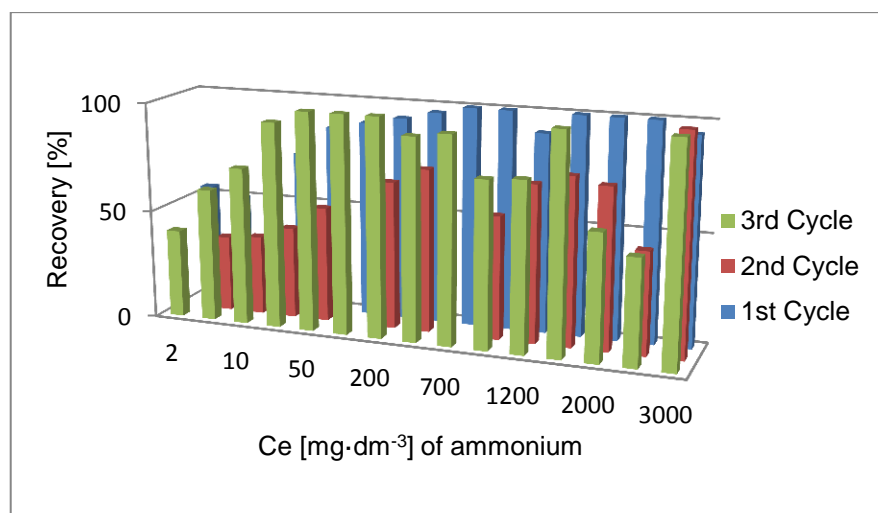


Figure 15: Ammonium recovery percentage for a) Na-Ze and b) K-Ze for different ammonium and phosphate concentration in binary solution for three sorption-desorption cycles

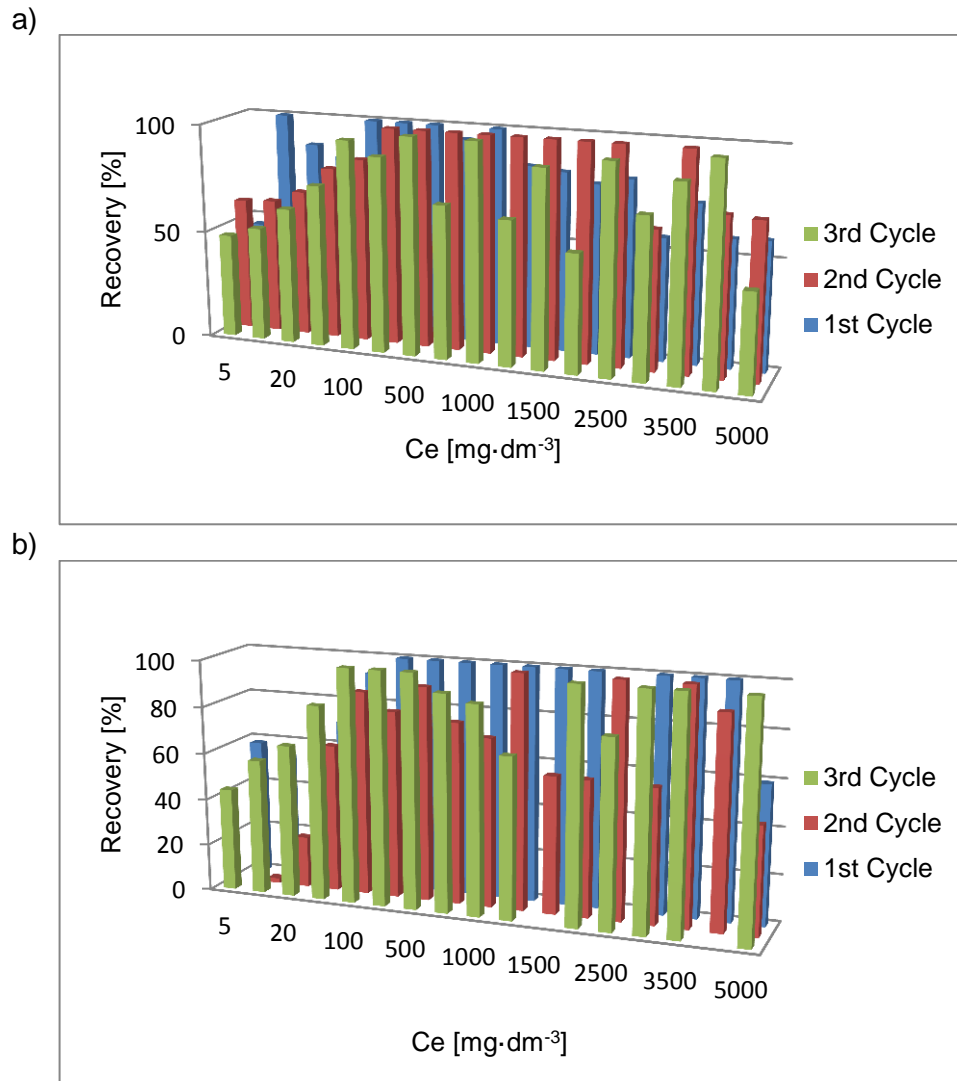


Figure 16: Ammonium recovery percentage for a) Na-Ze and b) K-Ze for different ammonium concentration in single solution for three sorption-desorption cycles

Apparently the ammonium sorption capacity of K-Ze was slightly higher in binary solution but it was not enough evidence to confirm that the use of the K-Ze performs the ammonium sorption capacity at binary solution. To support this fact, more experiments and studies must be performed.

Analyzing these results can be concluded that Na-Ze is not suitable to be reused more than three cycles in the ammonium single experiments because ammonium maximum sorption capacity was decreased by increasing the number of cycles. This sorbent was not efficient for the removal of ammonium in binary solution because its sorption capacity was very low compared to this reported in ammonium single solution and relatively low in comparison with the potassium modified zeolite. Then Na-Ze is very suitable to remove ammonium in ammonium single solution although its ammonium sorption capacities decrease with the increase of the cycles.

Furthermore, the kinetic experiments were also performed for the evaluation of the efficiency of reuse of the Na-Ze to adsorb ammonium in single synthetic water at low concentration of ammonium.

The results of the experiment analysis were represented in the Table 4.

Table 4: Kinetic model parameter for ammonium sorption in different cycle

	Pseudo first order			Pseudo second order			Elovich		
	Q _e [mg·g ⁻¹]	K ₁ [h ⁻¹]	r ²	Q _e [mg·g ⁻¹]	K ₂ [g·mg ⁻¹ ·h ⁻¹]	r ²	α	β	r ²
1 st Cycle	0.96	4.121E-05	0.22	0.92	0.008	0.99	0.13	0.12	0.86
2 nd Cycle	2.26	1.553E-05	0.09	2.09	0.01	0.99	0.52	0.25	0.72
3 rd Cycle	2.18	1.740E-05	0.14	2.09	0.02	0.99	0.46	0.25	0.76
4 th Cycle	2.38	1.370E-05	0.09	2.30	0.05	1.000	0.56	0.28	0.73

As commented in the section 6.3, the ammonium kinetic sorption data of Na-Ze fit better by pseudo second order kinetic model. Table 4 demonstrated clearly that the ammonium sorption capacities of the Na-Ze increased with the number cycles, especially at the second cycle. Ammonium sorption capacities was 1mg·g⁻¹ in first cycle and around 2 mg·g⁻¹ in the following working cycles. The pseudo second order coefficients of all the forth cycles were around 0.99.

It was noteworthy to mention that ammonium sorption increases significantly from the first cycle to the second and then could be considered not significant differences. The Table 5 shown the percentage of ammonium removed by the Na-Ze and can deduce that the ammonium sorption rate increased especially in de second cycle and the ammonium sorption made really important place in the first minute of the experiment. It means that it's really quick to reach to the equilibrium.

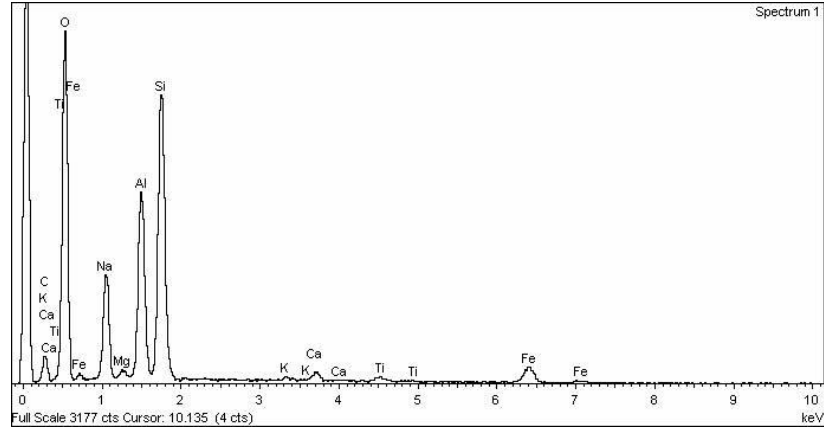
Table 5: Percentage of ammonium eliminated after 1 and 1440 minute.

	% of ammonium eliminated	
	After 1 min	After 1440 min
1 st Cycle	28.57	56.17
2 nd Cycle	88.39	87.50
3 rd Cycle	81.52	84.23
4 th Cycle	87.02	92.05

This kinetic experiment with regenerated zeolite demonstrated that the Na-Ze was suitable to be reused to remove ammonium in low concentration ammonium solution.

Finally, in order to obtain the chemical composition of the both zeolites after the second regeneration cycle, SEM and EDS were carried out and are shown in the Figures 17 and 18.

a)



b)

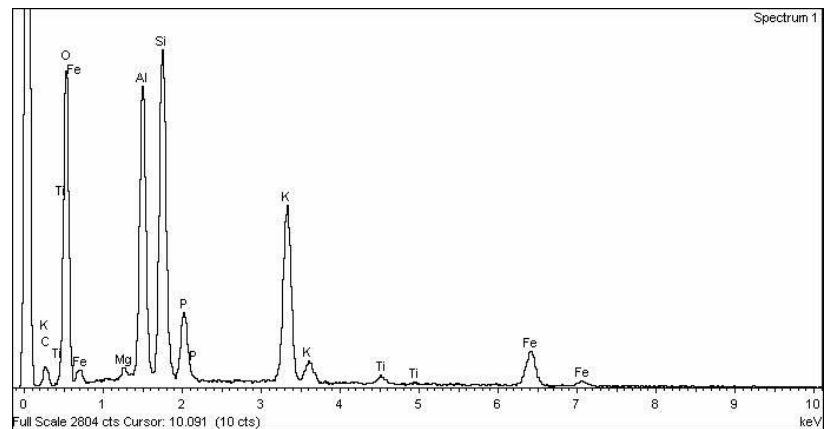


Figure 17: Scanning Electronic Microscopy and Energy Dispersive X-Ray Spectrometer (SEM/EDS) of regenerated a) Na-Ze and b) K-Ze

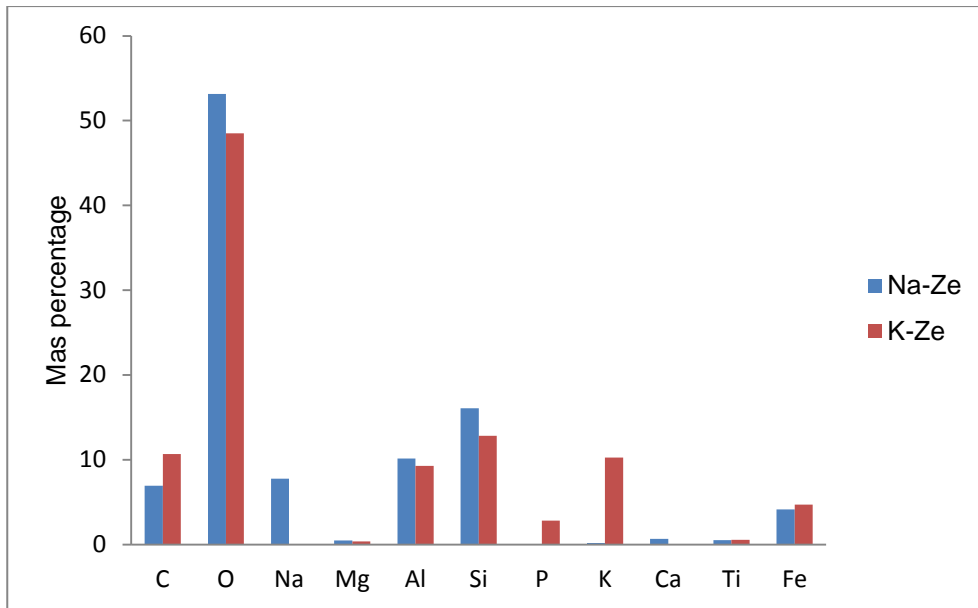
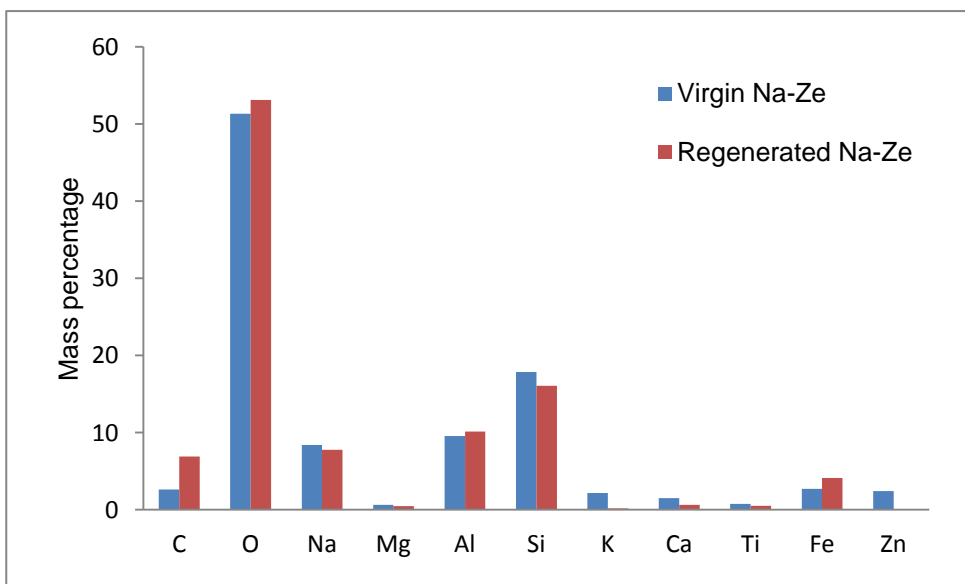


Figure 18: Chemical composition of regenerated zeolites in mass percentage

The Figures 17 and 18 shown that K-Ze, after been regenerated and cleaned, reported a small portion of phosphate. It is because a low amount of the solution can not be cleaned at all from the sample. So the 2% of phosphate in the K-Ze did not reflected the phosphate adsorbed by its.

a)



b)

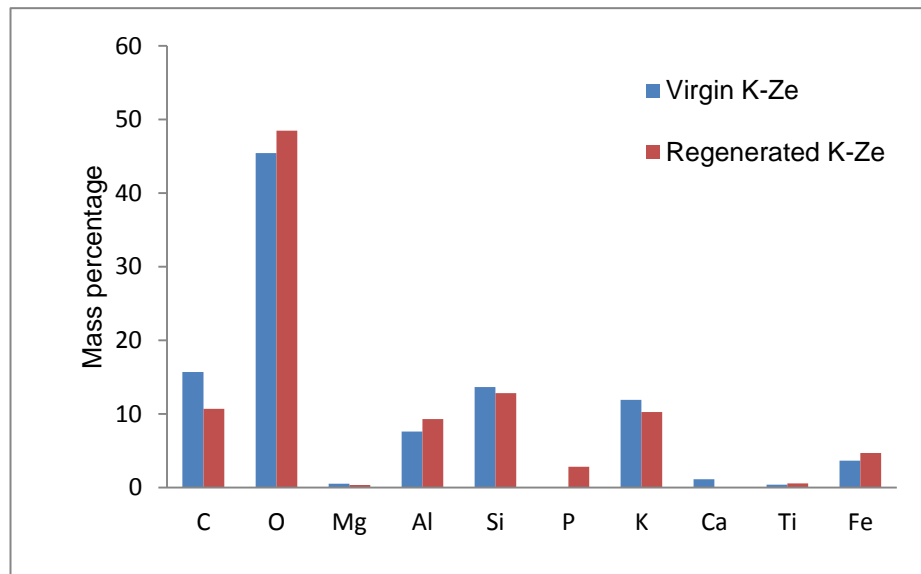
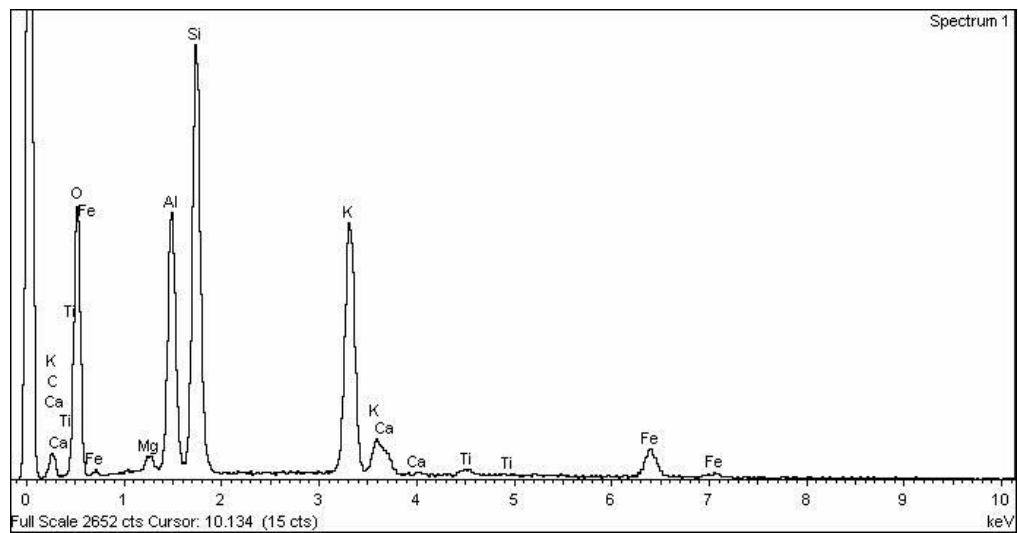


Figure 19: Chemical composition of virgin and regenerated a) Na-Ze and b) K-Ze in mass percentage

The Figure 20 shown the intensity of the potassium in this sorbent was higher than the regenerated and cleaned one because the zeolite become decreasing phosphate and increasing phosphate that did not be recovered 100% from desorption experiments with KCl.

a)



b)

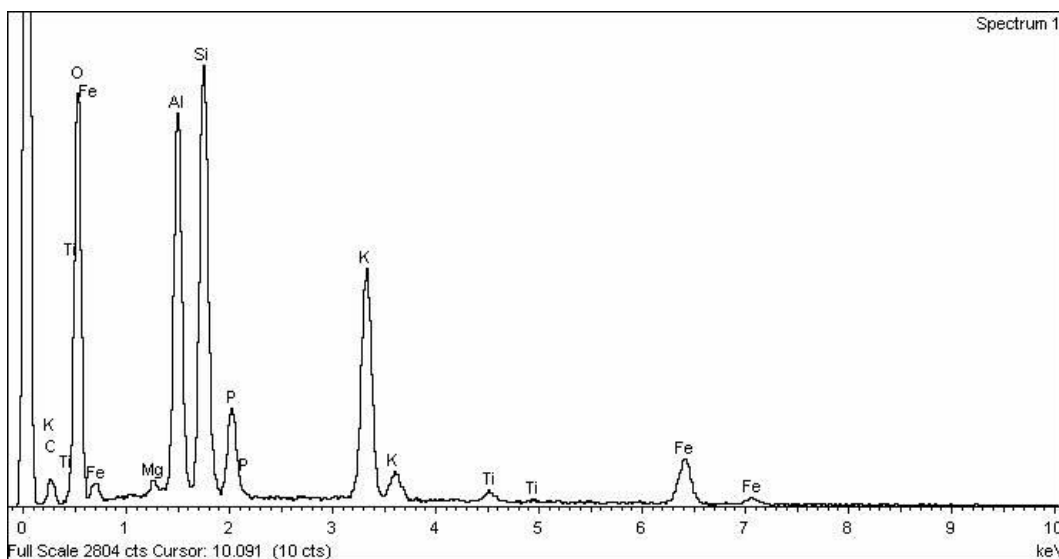


Figure 20: Scanning Electronic Microscopy and Energy Dispersive X-Ray Spectrometer (SEM/EDS) of a) virgin and b) regenerated K-Ze

6.6. Adsorption mechanism

The most probably sorption mechanism of ammonium onto zeolites is due to ion exchange, so in this section is performed a mass balance analysis in order to confirm this hypothesis.

In Figure 21 is shown the evolution of sorbed and released cations in batch experiment of K-Ze in binary solution test. It can be clearly observed that the zeolite release K^+ whereas NH_4^+ is sorbed.

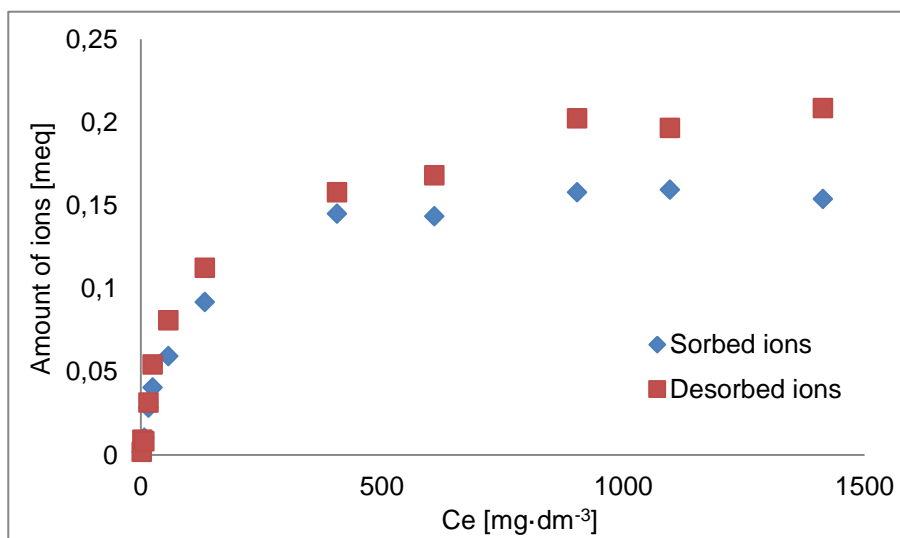


Figure 21: Sorbed and desorbed ions of K-Ze in binary system

The result represented in the Table 6 shown that the difference between sorbed and desorbed ions was low, despite low amount of other ions like calcium and magnesium in the zeolite can exchange ion with NH_4^+ and these cases is not included in the analysis. Therefore it confirms that ion exchange was the mechanism responsible of the ammonium sorption onto zeolites.

Table 6: Geometric mean of the error between adsorbed and desorbed ions

Geometric means of error between adsorbed and desorbed ions [%]	Ammonium single solution		Binary solution	
	Na-Ze	K-Ze	Na-Ze	K-Ze
	2.11	3.93	8.22	11.62

7. Economic study

The total expense during the performance of this project is detailed in this section. It is detailed in terms of equipment, laboratory supply, reagents, human resources and others.

✓ Equipment

The cost related to equipment is calculated as amortization cost in function of its acquisition cost, service time and using time during the project. And not using only the acquisition cost of these equipment because the equipment was in the laboratory before the project beginning and the laboratory equipment service time is longer than project duration.

For estimate the cost of this section can use different considerations. In this study was calculated considering that all the equipment in the laboratory were user only by this project using the following equation:

$$\text{Amortization} = \frac{\text{acquisition cost}}{\text{service time}} \cdot \text{using time} \quad \text{Eq. 13}$$

Equipment	Cost [€]	Service time [month]	Using time [month]	Amortization [€]
Chromatograph	26094	180	7	1014.77
Sampler	2242	180	7	87.19
GLP 22.ISE Electrode	1475	120	7	86.04
Spectrophotometer	1500	120	7	87.5
Vials shaker	2645	120	7	154.29
Magnetic stirrer	1177	60	7	137.32
Bascule	560	120	7	32.67
Micropipette 1-10cm ³	150	24	7	43.75
Micropipette 100-1000nm ³	120	24	7	35.00
Total				1645.86

✓ Laboratory supply

Laboratory supply	Units	Unitary cost [€/u]	Total cost [€]
Pasteur pipette (100u/box)	1	8	8
Tips for micropipette 1-10 cm ³	30	0.03	0.90
Tips for micropipette 100-1000 nm ³	5	0.03	0.15
Parafilm	1	10	10
Latex gloves (200u/box)	1	5	5
Syringe (100u/box)	1	10.60	10.60
Syringe filter 0.2µm (100u/box)	1	68	68
Syringe filter 0.45µm (100u/box)	1	23	23
Beaker 1dm ³	1	5.25	5.25
Beaker 250 cm ³	2	3.25	6.50
Beaker 25 cm ³	2	1.25	2.50
Volumetric flask 250 cm ³	1	4.50	4.50
Volumetric flask 100 cm ³	1	3.10	3.10
Waste bin 25 dm ³	1	3	3
Total			150.5

Some laboratory supply used like plastic bottles of 50 cm³, polyethylene tubes of 30 cm³, glazed spatula, 48 tubes rack, plastic test tube, glass test tube and magnetic stirrer bar were not included in the previous accounting cost because these materials were reused from others projects.

✓ Reagents

Reagent	Units	Unitary cost [€/u]	Total cost [€]
NaH ₂ PO ₄ ·2H ₂ O (500 g)	1	24.49	24.49
NaCl (500 g)	1	14.62	14.62
NH ₄ Cl (500 g)	1	20.83	20.83
NaOH (500 g)	1	16.89	16.89
KCl (500g)	1	27.52	27.52
Mili-Q (dm ³)	70	1	70
Total			174.35

✓ Human resources

Work	Time [h]	Salary[€/h]	Total cost [€]
Experimentation	800	15	12000
Data analysis	100	20	2000
Total			14000

✓ Others

Others	Cost [€]
Water and energy	300
Total	300

✓ Total cost of the project

Finally, the project cost has been calculated adding all of the previous cost: laboratory equipment, laboratory supply, reagents, human resources and others costs.

Concept	Cost [€]
Equipment	1645.86
Laboratory supply	150.5
Reagents	174.35
Human resources	14000
Water and energy	300
Gross total cost	16270.71
V.A.T. (21%)	3416.849
Net total cost	19687.56

8. Environmental Impact assessment

8.1. Experiments at laboratory scale

During all this project experimentation stage there were generated solid and liquid wastes. Also is important to notice that besides these waste generated during the experimentation, the used electricity, water for cleaning tasks were also important factors.

✓ Solid wastes

In this section include the sorbent used in the experiments, the broken material like beakers and volumetric flask where were used to store the solutions and others materials generated like plastic and paper waste which have been separated in the corresponding container for being recycled.

The used zeolite is stored in an exclusive container for its later treatment because it's an exhausted sorbent. Despite they have been desorbed, as have been shown in previous sections, desorption has not 100% efficiency.

✓ Liquid wastes

The main generated liquid waste was huge volume ammonium and ammonium and phosphate concentration effluents from sorption and desorption experiments. Its liquid had different concentrations, from 2 to 9000ppm but all these in a low quantity and deposited in a special container for its later treatment.

✓ Electricity

During the entire project, the electricity was the essential energy both for doing the experiments, analyzing samples and for writing the memory.

✓ Water

Due the large amount of materials were reused at the laboratory, it should take into account in this study the tap water used for cleaning tasks, which has been tried to minimize in order to contribute to sustainability.

✓ Others

Noises were generated when the chromatograph, vials shaker and magnetic stirrer were in operation. These impacts can disturb who worker at the operation area.

8.2. Global environmental Impact

The impact that this study may made is undoubtedly more positive than negative not only to the environment but also to the society and economy. But it is difficult to predict which will be quantitatively the environmental impact of this study in its application at real scale and there are no references which can help to support any supposition.

One of the aims of this project is to enhance ammonium and phosphate removal and recover capacities from waste water. On one hand, it study could reduce the ammonium and phosphate concentration on the discharged waste water and reduce waste water treatment cost and improve its quality. With its technology it may reduce eutrophication cases and obtaining a better ecosystem.

On the other hand, the technologies applying at this study are more sustainable than others exiting technologies because it use less energy and chemical reactants and the sorbent is a recycled modified material from flay ash. So it's easily obtained and it is reusable like a regenerated sorbent or like a low release fertilizer in its end use. This last utility made that less fertilizer for the agriculture has had to produce every year with its raw material. This fact makes that less energy and raw resources will need to use.

In conclusion, the application of zeolite for ammonium and phosphate removal and recovery may results in benefits for environment, society and economy. Although that, it is still need more research to be more sustainable.

9. Schedule

The Gantt diagram for the time distribution in this project's performance is shown in the Figure 22.

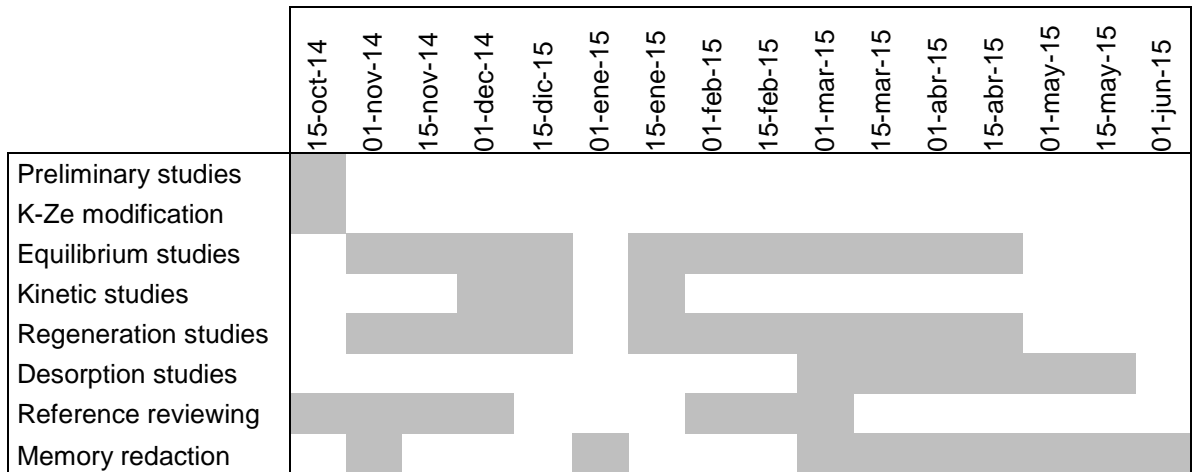


Figure 22: Gantt diagram of the project

Preliminary studies include the reviewing of some final degree project or master projects. For example the master project written by You (2014), who carried out characterization and modelling of phosphate recovery from waste water treatment plant by commercial ion exchangers.

Furthermore, equilibrium studies and regeneration studies were performed in the same time in the sorption-desorption experiments.

Finally, reference reviewing includes the research and reviewing of some research paper about zeolite characterization and modeling and different technologies of ammonium and phosphate remove and recovery.

10. Proposal to continue

As a continuation of this project it would be interesting to study the ammonium and phosphate sorption and desorption with all different zeolites studies in this and in the previous project done by Cheng (2015). And study the influence of the temperature and the pH for the ammonium and phosphate sorption in different zeolites.

It would also be attractive increases the cycles of regenerations to the sorbet studied at this project to draw better conclusion about the increase or decrease of the ammonium and phosphate sorption with the increase of the regeneration cycles.

Finally, it is important to research and evaluate the ecological and economic viability of reusing exhausted zeolites as low cost fertilizer. Due to its content different heavy metal, it would have to assess the heavy metal content of the zeolites and whether to use it in agriculture.

Conclusions

Over the last century, increasing industrialization and population have resulted in the degradation of the ecosystems and make the life quality reduce. One of the important causes is from effluent release of industrials and the fertilizer for the agriculture content a high quantity of nitrogen and phosphate release at lake and river. It fact reduce the quality of the water minimizing the dissolved oxygen caused by algal blooms, asphyxiate fish and bacterial contamination.

Therefore, numerous techniques have been studied and applied to remove or recovery NH_4^+ and PO_4^{3-} from wastewater. Batch experiments performed in this project with Na-Ze and K-Ze in synthetic solution can confirm that these sorbents are good to eliminate and recover ammonium in single solution test, however the simultaneous removal of ammonium and phosphate reported quite low of uptake.

In equilibrium studies, Langmuir isotherm model described properly the experimental data and shown better correlation coefficient than Freundlich model. So it means that zeolites sorption is characterized to be monolayer and homogeneous. Ammonium sorption capacities were $109 \text{ mg}\cdot\text{g}^{-1}$ and $21 \text{ mg}\cdot\text{g}^{-1}$ for Na-Ze and K-Ze respectively in ammonium single solution and $17 \text{ mg}\cdot\text{g}^{-1}$ and $29 \text{ mg}\cdot\text{g}^{-1}$ in binary solution. So the K- Ze has higher affinity for ammonium in binary solution in comparison to Na-Ze.

The pseudo second order model provided the best description for the ammonium removal process by Na-Ze in kinetic studies. Experimental data demonstrated that both zeolites were more efficient in binary solution test to eliminate ammonium. 73% ammonium in the dissolution was sorbet by K-Ze and 86% by Na-Ze. Although, the phosphate removal capacity was really low in Na-Ze and was not reported by K-Ze. It should be mentioned that the ammonium sorption were really fast, almost all the ammonium sorbed was recovered at the first minute.

Desorption experimental data shown the zeolite did not desorb all the ammonium. Despite the ammonium recovery percentage was quite high and almost all sorbed ammonium was desorbed by alkaline treatment for the first cycle time, in the following cycles, desorption is not completely achieved and this trend is most significant at low concentration samples.

The mass balance analysis showed that ion exchange mechanism was responsible for ammonium sorption onto zeolites.

Performed studies with ammonium single and binary solution test shown that both zeolite; K-Ze and Na-Ze could be regenerated and reused several times. The regeneration of Na-Ze in binary solution and K-Ze in single solution test increased their sorption capacities by the increase of the number of regeneration cycles. But in the case of Na-Ze in single solution, its sorption capacity decreased by increasing the sorption-desorption cycles. So the Na-Ze is not suitable to be reused more than three cycles in single experiments. This sorbent was not efficient for the removal of ammonium in binary solution because its sorption capacity was very low compared to values reported by single test.

The kinetic experiment with regenerated zeolite demonstrated that the Na-Ze was suitable to be reused to remove ammonium in low concentration ammonium single solution. In this case sorbent capacity increased by the increase of number of cycles. It is worth to mention that the ammonium sorption was really quick in reaching the equilibrium.

Acknowledgement

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