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Simultaneous ammonium and phosphate removal by metal inorganic salt modification of natural zeolite

Author: Blanca Ventosa i Capell

Director: José Luis Cortina Pallas

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Escola Tècnica Superior
d'Enginyeria Industrial de Barcelona



ABSTRACT

Nutrients discharge into receiving waters can cause an environmental problem capable of deathly altering ecosystems. Natural zeolites are low cost resources with ion exchange capacity that have been widely studied. This study deals with simultaneous adsorption of nutrients; viz. ammonium and phosphate, onto different modifications of natural zeolite, clinoptilolite. Research has been focused on the optimization of surface modification procedures to raise clinoptilolite efficiency and to enhance the capability of regeneration.

Four columns were filled with approximate 12 grams of zeolitic material; namely, natural non-treated (Z-N), manganese-modified (Z-Mn), iron-modified (Z-Fe) and aluminium-modified (Z-Al) clinoptilolite. During three cycles, both adsorption and removal rate were investigated to evaluate clinoptilolite capacity loss.

- For adsorption studies influent was synthetic wastewater (4 L of loading solution containing 100 and 10 ppm of NH_4^+ and PO_4^{3-} , respectively).
- For desorption studies influent was basic solution (1 L of 0,05 M of NaOH).

On one hand, ammonium analyses reported similar results for each tested zeolite. Inorganic salt modification seemed not to increase clinoptilolite ammonium adsorption capacity. Generally, it was high during the first run. However, better ammonium removal from the influent was observed after column regeneration. Basic treatment probably activated the zeolite; thus enhancing first run results. Capacity results were in range of 9,0-16,0 mg $\text{NH}_4\text{-N/g}$ of zeolite. Highest ammonium removal was reported of 0,2 g.

On the other hand, phosphate analyses reported different results for each tested zeolite. Inorganic salt modification increased clinoptilolite phosphate adsorption capacity since natural clinoptilolite possess barely any selectivity towards phosphate ion. In general, phosphate adsorption was low, achieving a maximum removal of 10,1 mg adsorbed by Al-modified clinoptilolite. Two different mechanisms might rule over phosphate removal. Adsorption onto the zeolite framework was observed before basic treatment; and after, partial precipitation. This theory is buttressed with low percentage of phosphate recovery during the regeneration, especially in Z-Al experiments. In 3rd cycle regeneration analyses, phosphate recovery percentage was 55%, 79% and 33% for the Mn-modified, Fe-modified, and Al-modified clinoptilolite.

Global tendency is to guarantee water resources for supply and quality of water within aquatic systems. The proposed cost-effective technique promotes the recovery of nutrients, thus obtaining a potential fertilizer application very attractive to investors and stakeholders.



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1. GLOSSARY

<1>GREEN HOUSE EFFECT: process by which thermal radiation from a planetary surface is absorbed by some atmospheric gases (CO_2 ...), and is re-radiated in all directions.

<2>DEFORESTATION: removal of a forest or stand of trees where the land is thereafter converted to a non-forest use.

<3>OCEAN ACIDIFICATION: ongoing decrease in the pH of the Earth's oceans, caused by the uptake of carbon dioxide (CO_2) from the atmosphere.

<4>HUMAN POPULATION GROWTH: global human population growth amounts to around 75 million annually, or 1,1% per year. The global population has grown from 1 billion in 1800 to 7 billion in 2012. It is expected to keep growing, where estimates have put the total population at 8.4 billion by mid-2030, and 9,6 billion by mid-2050.

<5>TOXINS DISPOSAL: waste material that can cause death, injury or birth defects to living creatures. It spreads easily and can contaminate lakes, rivers, and the atmosphere. The term is often used interchangeably with "hazardous waste", or discarded material that can pose a long-term risk to health or environment.

<6>REACTIVE NITROGEN: variety of nitrogen compounds that support growth directly or indirectly. Representative species include the gases nitrogen oxides (NO_x), ammonia (NH_3), nitrous oxide (N_2O), as well as the anion nitrate (NO_3^-).

<7>ARTIFICIAL OIL-BASED FERTILIZERS: methane (CH_4) is used to fix the nitrogen (N_2) from the air to make ammonia (NH_3) which is then the precursor for the various fertilizers like ammonium nitrate (NH_4NO_3).

<8>APATITE: is a group of phosphate minerals with high concentrations of OH^- , F^- and Cl^- ions, respectively, in the crystal. the crystal unit cell formulae of the individual minerals are written as fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$, chlorapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{Cl})_2$ and hydroxiapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

<9>ACTIVATED SLUDGE: process for treating sewage and industrial wastewaters using air and a biological floc composed of bacteria and protozoa.

<10>HYDROLYTIC BACTERIA: constitute a domain of prokaryotic microorganisms which cleavages chemical bonds by the addition of water.

<11>FERMENTATIVE BACTERIA: constitute a domain of prokaryotic microorganisms that together with hydrolytic bacteria form a variety of reduced end-products from a substrate.

<¹²>ACETOGENIC BACTERIA: constitute a domain of prokaryotic microorganisms that are capable of producing acetate

<¹³>METHANOGENIC BACTERIA: constitute a domain of prokaryotic microorganisms that are capable of producing methane.

<¹⁴>COD: chemical oxygen demand. It measures the amount of organic compounds in water, which are the carbon source in the traditional nitrification/denitrification methods.

<¹⁵>PAO: bacterial cultures capable of accumulating greater quantities of phosphorus are known as polyphosphate-accumulating organisms.

Available from:

<¹>"Annex II Glossary". Intergovernmental Panel on Climate Change. Retrieved 15 October 2010

<²>SAFnet Dictionary Definition for [deforestation]. Dictionary of forestry.org (2008-07-29). Retrieved on 2011-05-15.

<³>Caldeira, K.; Wickett, M. E. (2003). "Anthropogenic carbon and ocean pH". *Nature* 425: 365–365.

<⁴>Population Reference Bureau. "2013 World Population Factsheet". www.pbr.org. Population Reference Bureau. Retrieved 5 December 2014.

<⁵>Sutton, Mark A.; Bleeker, Albert "Environmental science: The shape of nitrogen to come" *Nature* 2013, vol. 494, pp. 435-437.

<⁶>David Briggs et al. "Health Impact Assessment of Waste Management Facilities in three European countries" *Environmental Health: A Global Access Science Source*. Web 15 Feb. 2012.

<⁷>Worstal, Tim "We're not going to run out of oil-based fertilisers" *Forbes* contributor. Opinions expressed by Forbes Contributors are their own.

<⁸> <http://www.mindat.org/min-1572.html>

<⁹>Beychok, Milton R. (1967). *Aqueous Wastes from Petroleum and Petrochemical Plants* (1st ed.). John Wiley & Sons Ltd.

<¹⁰⁻¹⁴>Cairó, J.J. and París, J.M. (1988). *Microbiología de la digestión anaerobia, metanogénesis*. 4o Seminario de Depuración Anaerobia de Aguas Residuales. Valladolid. F.F. Polanco, P.A. García y S. Hernando. (Eds.) pp. 41–51.

<¹⁵>D. Mara, N. Horan, C. H. Wong, G. W. Barton, and J. P. Barfor, *Handbook of Water and Wastewater Microbiology*. 2003, pp. 427–439.

2. PROJECT AIMS

2.1. MOTIVATION

Sustainability is an increasingly concern reflected in governmental policy. Commitments such as the Rio Summit Agenda 21 or Kyoto Protocol reflect the international agreements industrialized nations must comply in the behalf of environment. Nowadays, there are many environmental problems mankind must face in order to ensure the specific conditions that support life on planet Earth. Top 5 environmental concerns in my opinion could be: green house effect^{<1>}, deforestation^{<2>}, ocean acidification^{<3>}, human population growth^{<4>} and toxins disposal^{<5>}.

If no action was to be taken against these global tendencies, dreadful consequences may occur, including: depletion of biodiversity, climate change, contamination of surface and groundwater resources, thickening of the Artic ice cover, desertification or degradation of the ozone layer.

This project plunges into the need of every living being of accessing to fresh clean water. Rapid economic development in many nations have resulted in an increasingly production of sewage which has been for many decades released into the oceans regardless of the pollutants contained. There have been some environmental catastrophes in water treatment plants: *Chrysochromulina polylepis* algae boom that killed about 100 tones of farm cultivated fish in Sweden, as well as 500 tones in Norway [1]; and biogas storage tanks explosions in Turkey (1992), Italy (1996), Germany (2009), India (2009), etc [2].

2.2. OBJECTIVES

The main objective of this project is the use of selective ion exchange process at a lab scale for the simultaneous removal of ammonium (NH₄-N) and phosphate (PO₄-P) ions. To accomplish the task, three different modifications of natural clinoptilolite were tested; together with natural non-treated clinoptilolite. Ion exchange capacity and recovery rate of each experiment are also studied.

The conditions of the four experiments remained constant in order to properly compare their behavior, as well as their performance.

2.2.1. Primary objectives

- i. To study the simultaneous removal of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ using natural clinoptilolite as an ion exchanger.
- ii. To corroborate the improvement in the adsorption capacity that natural clinoptilolite presents with the modification with inorganic salts. Besides, to determine which modification performs better in the simultaneous removal of nutrients.
- iii. To learn about the mechanisms of phosphate uptake onto different zeolitic materials.
- iv. To study future trends in water and wastewater treatment that may be fully developed in a few decades. This way the results presented in this report may contribute to a database of knowledge about water treatment technologies.

2.2.2. Secondary objectives

- i. To study parameters that influence the ion exchange; basically flow rate and pH.
- ii. To observe the effect of the regeneration in the adsorption capacity of each ion exchanger.
- iii. To observe the effect of regeneration in the exhaustion of the ion exchanger.
- iv. To give an approach to the economical and environmental feasibility of a plant-scale project.

2.3. SCOPE

The scope of this thesis is to design a set of experiments to test the removal of ammonium and phosphate by ion exchange from synthetic wastewater.

Four columns were filled with approximate 12 grams of zeolite; namely, natural non-treated, manganese-modified, iron-modified and aluminium-modified clinoptilolite. For each column, both adsorption and regeneration capacities were studied during three cycles.

The experimentation took five months, from July to December. July was dedicated to assist a PHD who has been working with natural clinoptilolite for two years, while from September to December the experiments presented in this report were conducted. During these months, an exchange student very much assisted with the analyses and laboratory work.

3. LITERATURE REVIEW

3.1. NUTRIENT CYCLE, EFFECTS IN ACUATIC ECOSYSTEMS

3.1.1. Nitrogen

Nitrogen is mostly found in the atmosphere as the unreactive form, namely N_2 gas. This form is unusable for the majority of living organisms which need other forms, collectively known as reactive nitrogen^{<6>}. Unreactive nitrogen can be fixed whether by natural processes, such as lightning, or by anthropological processes, like fossil fuel burning [3].

The major processes that transform molecular nitrogen into reactive nitrogen are shown in *Figure 3.1*, which explains in detail nitrogen cycle and its interaction with biological carbon and phosphorus cycles.

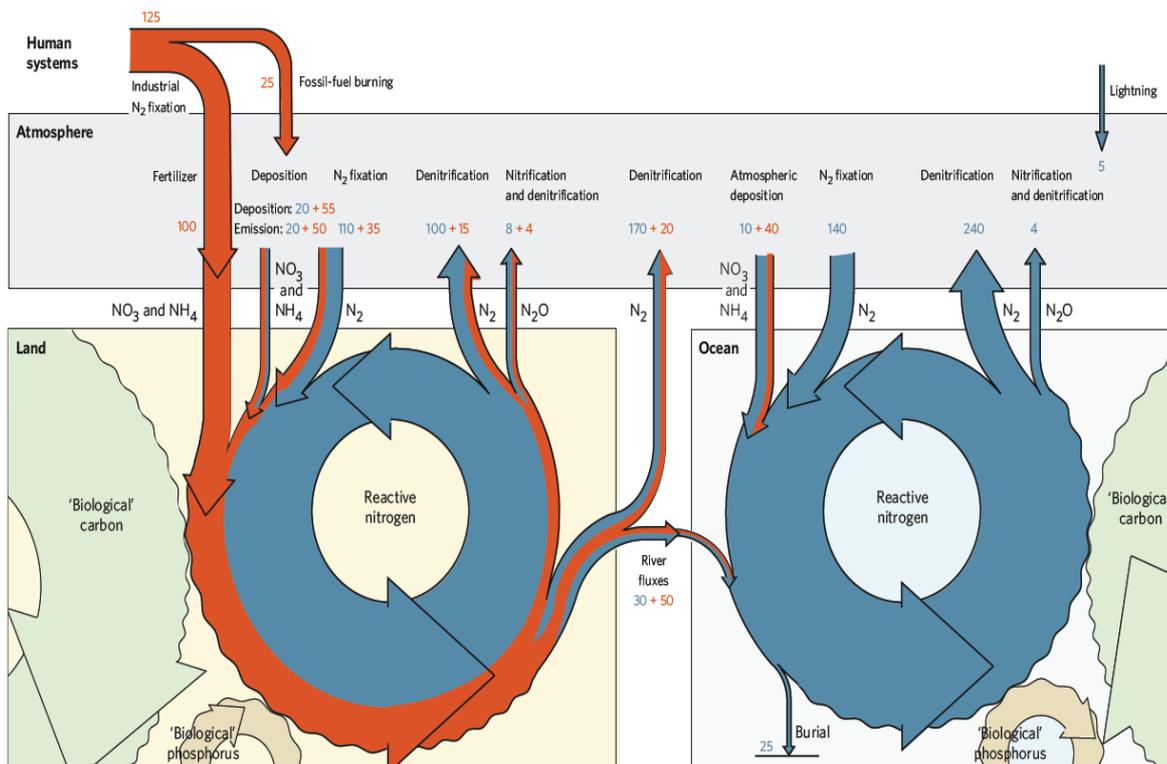


Figure 3.1. Depiction of the global nitrogen cycle [4]

There is a significant portion of reactive nitrogen coming from human systems. The use of artificial oil-based fertilizers^{<7>} worldwide has enabled humankind to increase food production, but it has also led to environmental problems [4].

In the last century, reactive nitrogen created by natural processes has decreased about a 10%; whereas, reactive nitrogen created by anthropological processes has increased about 15% [4]. Therefore, the concentration of reactive nitrogen in soil, water and atmosphere is disturbingly increasing. Although there are many problems derived from accumulation of reactive nitrogen in the environment including: greenhouse effect, smog, haze and acid rain; this project delves into the accumulation of reactive nitrogen in water that enhances a process called eutrophication [5].

Nitrogen compounds in municipal wastewater principally originate from urine and feces. These two residues hold large amounts of organic reactive nitrogen that is decomposed to ammonium on their way to treatment plants. Wastewater not only contains cationic pollutants like ammonium, but also contains many others including: anionic ions, oil and organic pollutants [6]. Hence, cost effective technologies must be developed to ensure Earth's drinking water resources.

3.1.1.1. Ammonium / ammonia equilibrium

Nitrogen compounds in aquatic systems are found as ammonium (NH_4^+) or ammonia (NH_3). The portion of ammonium ion and unionized ammonia in water is mainly affected by pH. Ammonium ion is relatively non toxic and it predominates in acid aqueous solutions, whereas, ammonia is much more toxic and it predominates in basic aqueous solutions [6], [7].

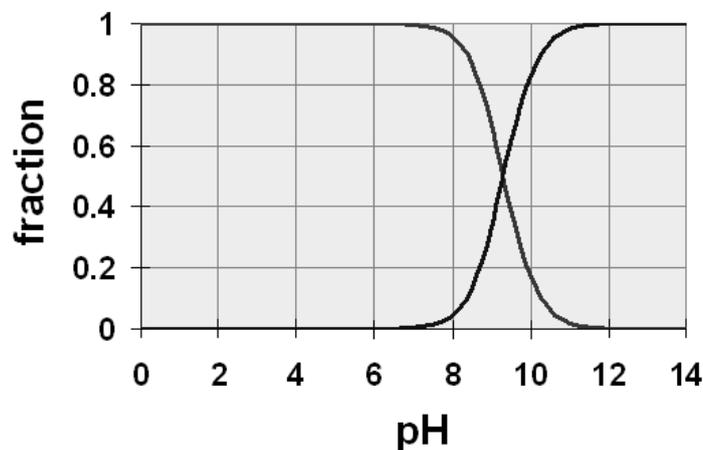


Figure 3.2. $\text{NH}_4^+ / \text{NH}_3$ distribution curve

3.1.2. Phosphorus

As other biological nutrients, phosphorus is also an important element to sustain life. In nature, it can be in the organic form or the inorganic one.

Organic phosphorus is normally found in soil and water as humic acid, phospholipids or nucleic acids. It proceeds either from animal excrements and living-beings residues or from artificial oil-based fertilizers^{<7>}, after suffering a microbial decomposition process on their way to treatment plants [8].

Inorganic phosphorus can be found as phosphate rock, viz. apatite^{<8>}. Different compositions exist including, fluorapatite, chlorapatite and hydroxiapatite. Phosphorus in soil has been immobilized in this form thanks to long-term processes of mineralization. Also, in aquatic systems phosphoric acid can precipitate in presence of heavy metal ions or alkaline ions; usually in the form of phosphate salts of manganese, iron, aluminium, calcium or magnesium [9].

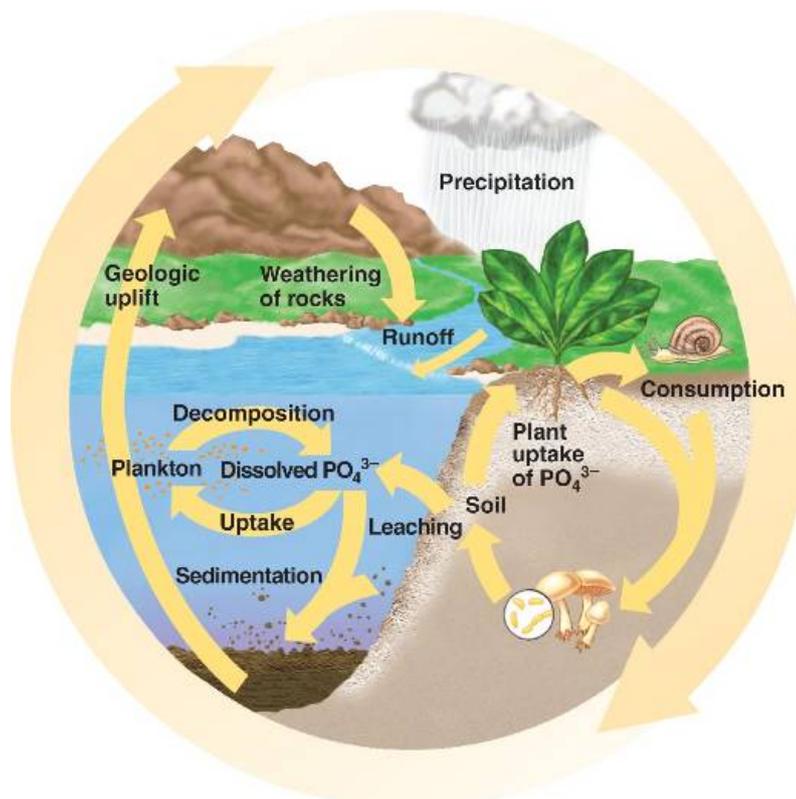


Figure 3.3. Depiction of the global phosphorus cycle [9]

As Figure 3.3 illustrates, phosphorus enters in aquatic systems by natural processes such as surface run off, leaching or wind erosion. However, there are also anthropogenic processes that increase its concentration in Earth water system.

There is no environmental or technical reason for not recycling phosphorus in aquatic systems. Indeed, there are beneficial aspects from reducing reliance on phosphate rock as phosphorus source [10]. This project delves into the accumulation of organic phosphorus in water that enhances a process called eutrophication.

3.1.2.1. Phosphoric acid equilibrium

Phosphorus compounds in aquatic systems are found as phosphoric acid (H_3PO_4) and its ionized forms; namely, H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} . The most relevant factor that regulates the portion of each ion in aqueous solution is pH [8].

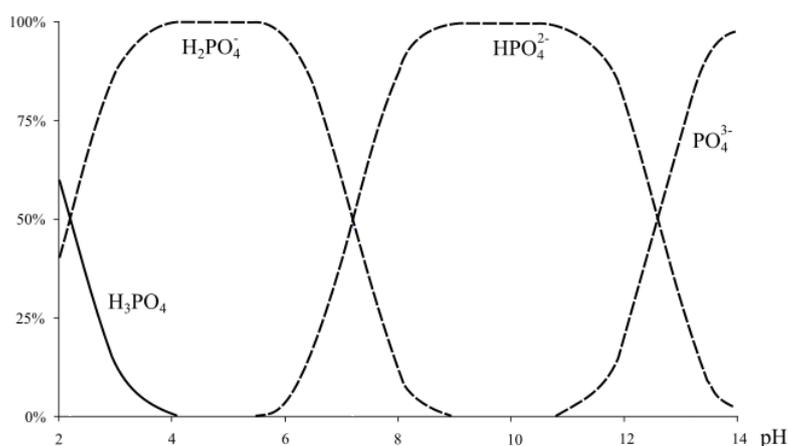


Figure 3.4. $\text{H}_3\text{PO}_4 / \text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-} / \text{PO}_4^{3-}$. distribution curve [10]

3.1.3. Eutrophication^a

Enormous amounts of nitrogen and phosphorus in the forms of ammonium and phosphate ions are present in swine wastewater. When these compounds are present in substantial quantities in rivers, lakes and coastal ocean zones; plant growth increases stimulating algae and other microorganisms to breed wildly. As a consequence, the quantity of oxygen dissolved in the water decreases in order to decompose the excessive organic matter.

Eventually, the nutrients effect on the oxygen content of receiving waters aggravates so much that converts water into a hostile toxic environment for aquatic invertebrate and vertebrate species.

^a Information in this section was extracted from *Industrial Chemistry* class notes.

3.2. WATER TREATMENT METHODS

Development of technologies for nutrients removal appeared in the 1950s, in response to the growing problem of eutrophication. The use of artificial nitrogen and phosphorus fertilizers increased to face the food demand of a postwar society. Alarming levels of nutrients entering the surface waters were to be reduced. That is the reason why water treatments plants and a number of technologies have been developed during the last century.

The main function of a water treatment plant is to collect either industrial wastewater or sewage and apply several treatments in order to return safe, contaminant-free water into the environment. First there is a pretreatment; then, there are three main stages: primary, secondary and tertiary treatment [11].



Figure 3.5. Satellite view from Granollers water treatment plant, Barcelona^b

In the earliest stage, wastewater passes through filters, some made of layers of sand or gravel, that help remove dirt and other particles suspended in water.

In the next stages, different technologies that remove organic matter and nutrients from wastewater can be used including: chemical precipitation, biological treatments and crystallization. In addition, other relevant technologies such as ion exchange are at different stages of development [10],[12].

^b Web image, available from: <<http://www.besos.cat/sisgranollers.htm>>

3.2.1. Chemical precipitation and crystallization

Nowadays, some water treatment plants use chemical precipitation technique during the primary treatment. Others use a process called coagulation-flocculation to remove particles suspended in water.

Removal of phosphorus was initially achieved by chemical precipitation and it remains the leading technology nowadays [10]. This physico-chemical process consists on the addition of a divalent or trivalent metal salt to wastewater, causing precipitation of an insoluble salt. Added as chlorides or sulphates, iron and aluminium proved to be suitable metals. The solid separation is achieved by sedimentation.

Although chemical precipitation is a flexible approach to phosphorus removal, it produces metal salts within the wasted sludge which are not feasible to recycle. Moreover, the cost and hazard associated to the disposal of these chemicals is high enough to be relevant [13].

The development of crystallization technology started in the 1970s and its major advantage is the removal of phosphorus without creating an additional sludge, only a quantity of water-free pellets [10]. DHV Consulting Engineers is the leader in this field of expertise and its process is based on the crystallization of calcium phosphate within a fluidized bed. Pellets, which are periodically replaced by smaller diameter seed grains, may be re-used as fertilizers [14].

3.2.2. Biological nutrient removal

The traditional method for ammonium, phosphorus and organic removal from wastewater is based on biological treatments due to lower operational cost and energy saving. Beer industries, dairy industries, paper industries and many more use this technique.

In the secondary treatment, bacterial cultures are isolated from activated sludge^{<9>} which is suspended above the sewage. The initial load of bacteria usually originates from the wastewater itself. This process can be made with or without oxygen but the result is always the same, the degradation of organic matter [15].

On one hand, aerobic procedure converts organic matter into carbon dioxide and water, which are the final products. That is to say that bacterial cultures use oxygen to consume the organic matter in order to reproduce and to increase their population. Part of activated sludge is purged to avoid the accumulation of microorganisms [7].

On the other hand, the procedure without oxygen, viz. anaerobic digestion, involves a series of specific microorganisms capable of converting organic matter into a mixture of gases commonly known as biogas. Its main components are methane (CH₄ 40-70%), hydrogen (H₂, 2-3%) and hydrogen sulfide (H₂S, 0,5-2%); also, it can contain other gases such as carbon dioxide or carbon monoxide [11].

There are four different groups of bacteria which intervene in different stages of the organic matter degradation; including: hydrolytic^{<10>}, fermentative^{<11>}, acetogenic^{<12>} and methanogenic^{<13>} bacteria [15].

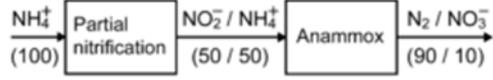
Biological nitrogen removal techniques transform nitrogen from ammonium to nitrite, nitrate and, finally, to nitrogen gas. Much research is being undertaken in biological nitrification/denitrification processes [16], [17]. A general overview of the different nitrogen pathways and biochemical conversions for traditional processes is presented by simplified equations in *Table 3-A*.

Table 3-A. Simplified equations for traditional nitrification/denitrification process [15]

Process	Biochemical conversion
Nitritification	$NH_4^+ + 1,5 O_2 + 2 HCO_3^- \rightarrow NO_2^- + 2 CO_2 + 3 H_2O$
Nitratation	$NO_2^- + 0,5 O_2 \rightarrow NO_3^-$
Nitrification	$NH_4^+ + 2 O_2 + 2 HCO_3^- \rightarrow NO_3^- + 2 CO_2 + 3 H_2O$
Denitratation	$2 NO_3^- + C \rightarrow 2 NO_2^- + CO_2$
Denitrification (via nitrite)	$4 NO_2^- + 3 C + 2 H_2O + CO_2 \rightarrow 2 N_2 + 4 HCO_3^-$
Denitrification	$4 NO_3^- + 5 C + 2 H_2O \rightarrow 2 N_2 + 4 HCO_3^- + CO_2$

Over the past few years, many different processes and new techniques have been developed for ammonium removal based on partial nitrification, including: oxygen-limited autotrophic nitrification/denitrification (OLAND), complete autotrophic nitrogen removal overnight (CANON), anaerobic ammonium oxidation (ANAMMOX), and wetland based systems [7], [18].

Table 3-B. General overview of the different nitrogen pathways and biochemical conversions for new processes. Presented by simplified equations for complex nitrogen transformation processes and flux diagrams for each process, traditional and new.

Process	Biochemical conversion	Flux diagram	Reference
ONLAND	$NH_4^+ + 0.75 O_2 \rightarrow 0.5 N_2 + H^+ + 1.5 H_2O$		[19]
CANNON	$NH_3 + 0.88 O_2 \rightarrow 0.11 NO_2^- + 0.44 N_2 + 0.14 H^+ + 1.43 H_2O$		[19]
ANNAMOX	$NH_4^+ + NO_2^- \rightarrow N_2 + 2 H_2O$		[20]
Traditional	Table 3-A		[15]

Generally, traditional nitrification/denitrification methods consume a considerable amount of resources: 4.57 kg O₂ and 2–4 kg COD^{¹⁴} are required per kg ammonium nitrogen [7]. Besides, this technology is based on total microbial nitrification, thus facing technical problems when carrying denitrification.

Although new technologies which are based on partial nitrification seem to be less problematic, different operational factors such as pH, dissolved oxygen concentration, temperature and ammonium load must be controlled during the nitrification stage [7], [21].

Biological phosphorus removal is achieved in two steps together with the nitrification/denitrification processes. First, the activated sludge is introduced in an anaerobic zone where bacteria take up the volatile fatty acids present in the organic matter and release phosphorus into solution. Then, in the aerobic stage a phenomenon known as “luxury uptake” occurs thanks to polyphosphate-accumulating organisms^{¹⁵} (PAO) [13].

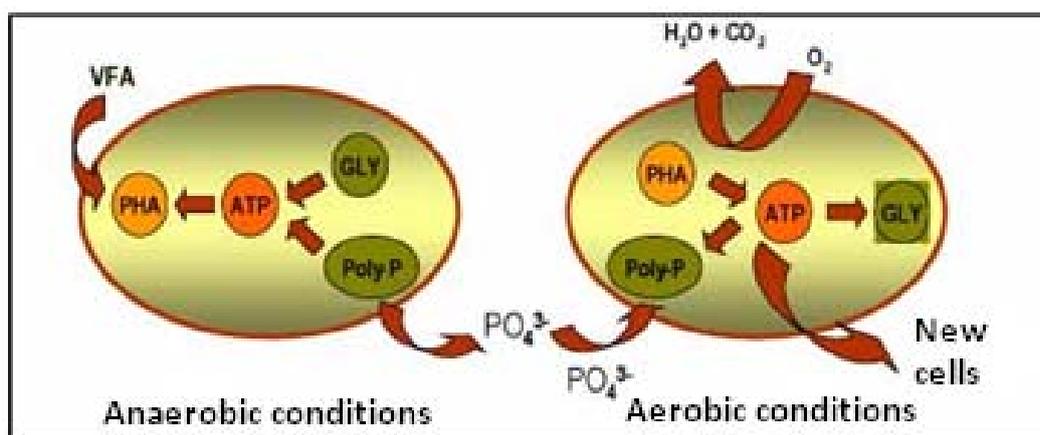


Figure 3.6. Model of biological phosphorus removal; anaerobic and aerobic mechanisms [22]

In anaerobic conditions, PAOs transport volatile fatty acids (VFA), generated in the organic matter degradation process, inside the cell. They are stored as polyhydroxyalkanoates (PHA) using adenosine triphosphate (ATP) as an energy source. During this process glycogen (GLY) is hydrolyzed; whereas phosphate (Poly P) is released into the water outside the cell [15].

In aerobic conditions, PHA is oxidized creating GLY as well as storing energy in the form of ATP. To do so, PAOs need to uptake phosphate from wastewater. On balance, phosphate ion is removed from sewage with the periodical purge of activated sludge [23].

Even though biological wastewater treatment is widely used in water treatment plants

all around the world; and although it has proven to remove nitrogen and phosphorus compounds, there are some limitations that should be overcome.

First, the organic matter degradation process is rather slow and big extensions are needed to install the necessary reactors^c. Second, during the nitrification process not only growth and activity of nitrifying bacteria must be carefully controlled, but also both carbon and oxygen sources are needed. Meanwhile, the PAOs need also specific aerobic/anaerobic conditions that have to be controlled in order to optimally remove phosphate. Last but not least, there is no valuable byproduct to reuse, apart from biogas. As for nitrogen, N₂ gas is released to the atmosphere engraving the anthropogenic release of nitrogen; and, regarding phosphorus, phosphate is continuously used as an energy source in the form of ATP. Therefore, it is useful to investigate non-microbial treatment techniques for the removal of nitrogen and phosphorus pollutants.

^c See *Figure 2.3 Satellite view from Granollers water treatment plant, Barcelona.*

3.3. ION EXCHANGE & ADSORPTION IN WATER TREATMENT

In this section other methods are described to explore cost-effective technologies for nutrients removal from sewage. For the last decades, many authors have been studying the use of natural occurring minerals such as zeolite, clay, etc... and their modified forms as ion exchangers for water and wastewater treatment. A brief review of some studies conducted is shown in *Table 3-E*.

The process of exchanging ions between a solid and a liquid phase is known as **ion exchange**. Given that the solid phase is charged, ions of the opposite charge are needed not to disturb electroneutrality. In contact with a solution, ions from the liquid phase (B) diffuse into the solid structure while ions from the solid phase (A) are released into the solution. Helfferich et al. (1965) named these ions, A and B, counterions [24].

In this situation, there is a considerable concentration difference between the phases, thus forcing ions to level out the existing concentration differences. Eventually, the equilibrium is established [24], [25].

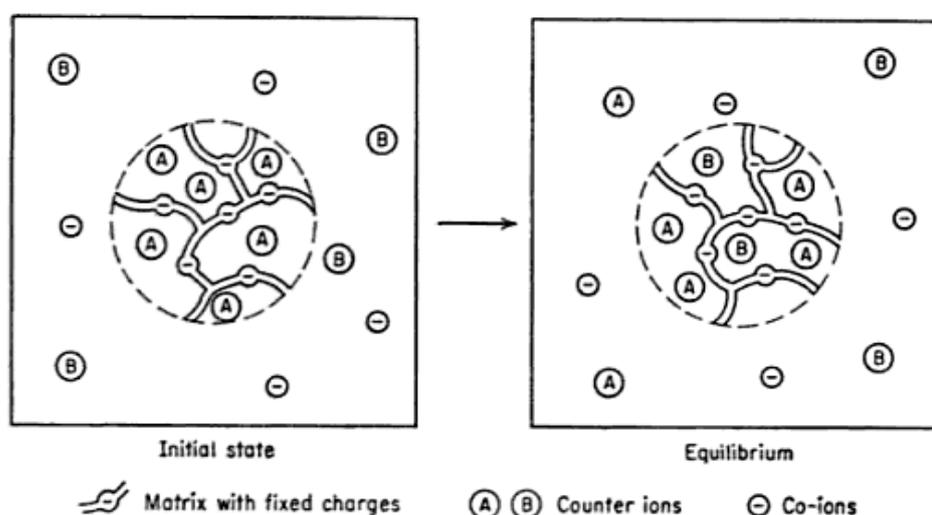


Figure 3.7. Example of ion exchange with a solution [26]

IUPAC definition for **adsorption** is as follows. Increase in the concentration of a substance at the interface of a condensed and a liquid or gaseous layer owing to the operation of surface forces [27]. Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of concentration at constant temperature.

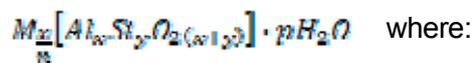
These two physical phenomena resemble in that dissolved species are taken up by a solid, yet the difference resides on the way this solid adsorbs these species. In adsorption, the solid phase does not exchange any specie with the aqueous phase; whether in ion exchange the solid phase is continuously replacing ions from the solid's structure for ions dissolved in the solution. In practice, this distinction is difficult to detect because most ion exchange processes are accompanied by a sorption or desorption process. [24]

Ammonium exchange with zeolites is explained in *Figure 3.7*, where Na^+ would be the counterion A and NH_4^+ would be the counterion B.

Phosphate mechanism of removal is believed to be an adsorption process together with a precipitation of a phosphate salt or hydroxiapatite. This process would bind alkaline or heavy metal ion (counterion A) with phosphate [10].

3.3.1. Properties of natural zeolites

Natural zeolites are hydrated aluminosilicate minerals with valuable ion exchange and sorption properties. In the general chemical formula of zeolite three relatively different compounds can be found; the aluminosilicate framework, the exchangeable counterions or cations and zeolitic water [28].



- *M is an exchangeable cation*
(Na, K, Rb, Cs, Ca, Mg, Ba, Sr)
- *n is cation charge; $y/x=1\sim6$; $p/x=1\sim4$*

First, the aluminosilicate framework is negatively charged. Zeolite's matrix does not contain ionic groups with fixed charges, yet negative charge is more or less uniformly distributed in the framework. As a result, the aluminosilicate framework charge is constant. Second, the exchangeable cations which participate in ion exchange do not occupy fixed positions, but are free to move in the channels of the lattice framework [25]. Last, zeolitic water usually forms aqueous bridges with the exchangeable cations, though it can be present in some voids of the aluminosilicate framework.

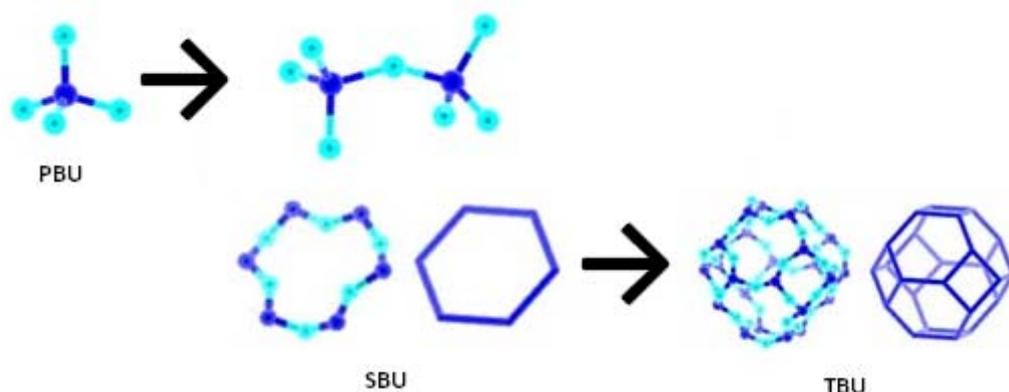


Figure 3.8. Binding of building blocks in three-dimensional zeolite (CHAbazite structure)^d

Zeolites present three building blocks; primary building blocks, secondary building blocks and tertiary building blocks. A building scheme of PBU, SBU and TBU is shown on *Figure 2.7* [29].

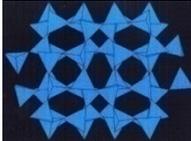
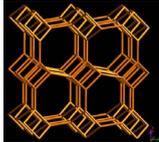
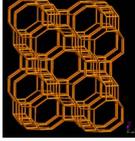
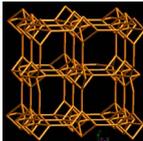
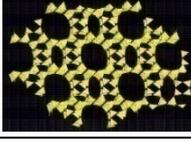
Primary building units (PBU) are SiO_4 and AlO_4 that present a tetrahedral structure; hence, every tetrahedron found in zeolites is composed by a silicon or aluminium atom at the center with four oxygen atoms at the vertices. Substitution of Si^{4+} by Al^{3+} defines the negative charge of the zeolite framework, which is compensated by alkaline and earth alkaline metal cations.

Secondary building units (SBU) are the result of connecting PBU via oxygen ions. Not every type of zeolite presents the same SBU, different framework types in zeolitic materials are presented in *Table 3-C*.

Finally, tertiary building unit (TBU) is the succession of SBU linked into a three-dimensional crystalline structure of zeolite.

^d Web pictures (<http://www.port.ac.uk/research/cmd/research/zeolitemodelling>)

Table 3-C. Building scheme of PBU, SBU and TBU. Structural properties of some natural zeolite [30]

Zeolite	Primary cell formula	Crystal system Framework type ^e	FD (PBU/10 ³ Å ³) Channel dimensions (nm)	Exchangeable ions
Analcime (ANA)	$Na_{12}Al_4Si_{12}O_{38} \cdot 16H_2O$	Cubic 	18,5 0,16 x 0,42	Na, K, Ca, Rb, Cs
Laumontite (LAU)	$Ca_4Al_8Si_{16}O_{48} \cdot 16H_2O$	Monoclinic 	17,8 0,40 x 0,53	Na, K, Ca
Phillipsite (PHI)	$K_2(Ca, Na_2)_2Al_8Si_{10}O_{32} \cdot 12H_2O$	Monoclinic 	15,8 0,38 x 0,38	Na, K, Ca
Chabazite (CHA)	$(Ca, Na_2, K_2)_2Al_4Si_8O_{24} \cdot 12H_2O$	Hexagonal 	14,5 0,38 x 0,38	Na, K, Ca
Scolecite (NAT)	$Ca_4Al_8Si_{12}O_{40} \cdot 12H_2O$	Ortho-rhombic 	17,8 0,25 x 0,41	Na, K, Ca
Mordenite (MOR)	$(Na_2Ca)_4Al_8Si_{40}O_{70} \cdot 28H_2O$	Ortho-rhombic 	17,2 0,65 x 0,70	Na, K, Ca
Heulandite Clinoptilolite (HEU)	$(Ca, Na_2, K_2)_3Al_6Si_{30}O_{72} \cdot 21H_2O$	Monoclinic 	17,1 0,44 x 0,72	Na, K, Ca, Sr, Ba

Many natural occurring zeolites can be found around the world. Although their categorization

^e Web pictures (<http://www.iza-structure.org/databases>)

and classification is difficult owe to their variety; one criterion to distinguish zeolites is framework density (FD). It is obviously related to the pore volume but it does not reflect the size of the pore openings. FD is the number of PBU per 1000 Å³ and it distinguishes between porous and dense frameworks.

Since new zeolites are being synthesized, the number of different framework structures is increasing. Every time a new one is reported, the Structure Commission of the International Zeolite Association (IZA-SC) assigns a three-letter code if the framework structure is found unique. This code is part of the official IUPAC nomenclature for crystalline minerals [29]. At the moment, there are 218 framework type codes cataloged by IZA. The structural properties of some natural zeolites are presented in *Table 3-C*.

In the present work clinoptilolite is used as the ion exchanger owe to its proven selectivity towards ammonium ions, high cation exchange capacity and its ion sieving properties. Clinoptilolite, which is one of the most investigated zeolitic materials, is the most abundant natural occurring zeolite. It is widely used in the world due to its unique structural units which provide it with an exceptional macroporosity [30], [31].

Three types of channels are found in clinoptilolite's structure; first, two parallel channels defined by ten and eight-membered rings and second, a vertical channel defined by eight-membered rings. In these channels, hydrated cations can occupy several places [32].

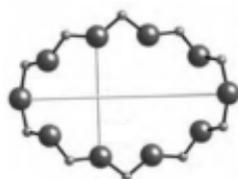


Figure 3.9. 10-ring
viewed along [001]

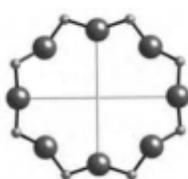


Figure 3.10. 8-ring
viewed along [001]

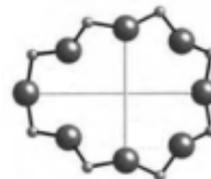


Figure 3.11. 8-ring
viewed along [100]

3.3.2. Concept of capacity in zeolite ion exchange systems

IUPAC recommendations for ion exchange nomenclature define the following capacity types:

- Theoretical specific capacity
- Apparent capacity or effective capacity
- Practical specific capacity
- Useful capacity
- Breakthrough capacity

Considering the fact that ion exchange capacity is a rather simple concept determined by a mass balance, this vast differentiation between capacity terms is surprising. Proper

experimentation to obtain reliable and comparable results is vital; especially in fixed-bed experiments since columns suffer of non idealities strongly related to flow rate. Also, inorganic ion exchangers like zeolites present a non constant number of active ion exchange and adsorption sites depending on the zeolitic material [25].

The capacity term this project will deal with is breakthrough capacity, which is further explained in *Chapter 5: Results and discussion*.

3.3.3. Modification of the natural clinoptilolite

Many authors have discussed several pretreatments in order to increase zeolite's exchange capacity. Mainly, inorganic salts/surfactant modification, acid/basic treatment, and hydrothermal treatment have been studied.

3.3.3.1. Modification with solution of inorganic salts

Chemical modification with inorganic salts increases zeolite efficiency in water treatment. Some researchers have studied the improvement onto the zeolite properties of different inorganic salts including: sodium chloride (NaCl), calcium chloride (CaCl₂), barium chloride (BaCl₂), ammonium chloride (NH₄Cl) and iron chloride (FeCl₃) [33][34][35][36].

Studies of chemical modification with FeCl₃ report that many parameters have to be controlled such as pH solution, ionic strength of the solution, iron concentration, oxidation-reduction parameters (Fe²⁺/Fe³⁺ ratio), etc [37].

Figure 3.12-A shows zeolitic structure under normal conditions; large cavities inside the zeolite framework are filled with zeolitic water that forms spheres around the exchangeable cations. *Figure 3.12-B* shows zeolitic structure after the contact with NaCl. The zeolite has been converted into its homoionic form, which is the conversion of all exchangeable ions into one species. It can be seen that ion exchange between the counterions from the zeolite framework (Mg²⁺, Ca²⁺, Na⁺, K⁺, etc.) and the ions from the solution (Na⁺) occurs. *Figure 3.12-C* shows the zeolitic structure from *Figure 3.12-B* after the contact with FeCl₃, this modification results in the formation of oxi-hydroxides which react with anions from the solution forming stable complexes [30].

To put it in a nutshell, the modification with inorganic salts results into an increase of specific surface area (BET) of natural clinoptilolite improving the total sorption into the zeolitic framework [38].

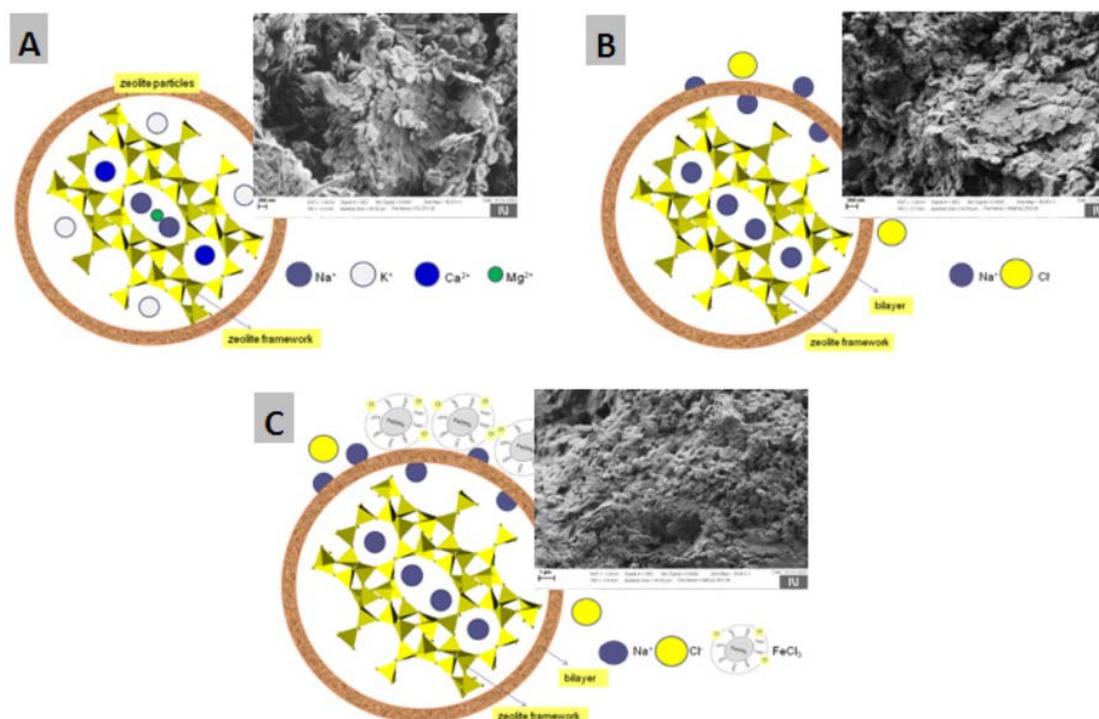


Figure 3.12. Zeolite particles in natural and modified zeolites (Na and Fe forms of clinoptilolite from Serbia) and SEM image of zeolite surface after the implementation of chemical modification [30]

In the current work, different modifications with inorganic salts; namely manganese chloride (MnCl_3), iron chloride (FeCl_3) and aluminium chloride (AlCl_3) are studied. First clinoptilolite was converted into the sodium form, and then it was modified. Experiments with natural non treated clinoptilolite were also conducted to corroborate that the inorganic salt modification is an interesting way of improving the ion exchange capacity, economically and technically.

3.3.3.2. Modification with acid/basic treatment

This treatment is among the most common methods to enhance the cation exchange capacity of the zeolite. It can be modified either with basic solutions, for instance sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)_2), or with acid solutions, for example hydrogen chloride (HCl) or nitric acid (HNO_3) [30].

Not only is the zeolite structure modified, but also its chemical and physical properties. The aluminosilicate structure interacts with H^+ and OH^- ions in the acidic/basic sites of the zeolite's framework. An important limitation of this method is that a dealumination process where Al^{3+} ions are progressively removed from the structure, thus decreasing the sorption properties. Hence, low dissolution rates of acid/basic solutions are recommended for high-silica zeolites [39].

In the present work, a basic treatment is applied in order to regenerate the clinoptilolite

previously modified with inorganic salts. Many commercial applications of natural clinoptilolite are sold pretreated with acid/basic treatment, commonly known as activated zeolite^f.

3.3.3.3. Hydrothermal treatment of natural clinoptilolite

Hydrothermal treatment is really useful to remove water molecules and organics from pore channels. 10 to 25 % of the total mass of the zeolite is considered to be water molecules. Margeta et al. (2013) recommended a dry heating of approximately 400 °C to remove zeolitic water.

Thermal treatment at high temperature enhances pore volume; however, it is important not to risk the structural stability of the zeolitic materials during the dehydration process. Natural clinoptilolite structural stability is up to 750 °C [29].

In the current work, a thermal treatment at a rather low temperature ($T = 80^{\circ}\text{C}$) is applied in order to dry the zeolitic tuff after each modification. Whether the treatment affect to modified clinoptilolite is not clear.

3.3.4. Aspects that influence ion-exchange on zeolites

3.3.4.1. Type of zeolite

As described above, many different types of zeolites can occur. It has been stressed that the characteristics of a zeolite mineral depend on its origin due to variations during the genesis [32]. Zeolite deposits have been found all over the world; for example in Russia, southeastern Europe, China, Australia, United States, Mexico, South Africa [31].

Purity of the zeolitic material is also an important factor to consider. Other occurring minerals such as quartz, volcanic glass and feldspars might be found in the selected minerals, thus decreasing the zeolite concentration.

Other aspects worth mentioning are the structural imperfections and the variety of exchangeable cations present in the zeolitic material, which may lead to pore blockage and slow diffusion rates. Different structures have distinct dominant mechanisms making them particularly useful for different applications [30].

In this study, a natural zeolite obtained from Slovakian Republic was used.

3.3.4.2. Grain size

As it has been reported by many authors, grain size distribution greatly affects the ion

^f Available from: <http://www.liquidzeolitecompany.com>

exchange capacity of the zeolite. For the ammonium removal, Hlavay et al. (1982) studied three intervals of grain sizes resulting that the smallest fraction, 0,5 to 1,0 mm, presented the highest ammonium exchange capacity. Demir et al. (2002) showed that when the loading was higher, also it was the exchange capacity for the smaller grain sizes. These studies concluded that probably a higher mass transfer into the zeolite happens when using smaller grain sizes.

When using filter beds, the influence of the grain size must be properly assessed. Small filter materials mean fine pores which lead to more friction and therefore a higher head loss; thus recommending minimum grain sizes of 0,3 to 0,4 mm [32].

In the present work the selected grain size was between 0,2 mm and 0,8 mm. This decision was made due to the laboratory material available.

3.3.4.3. Influent concentration

Many authors seem to agree that higher influent concentrations lead to higher ammonium uptake on the zeolite. As a result of the diffusion mechanism, greater influent concentrations result in a larger amount of exchanged ammonium [40].

In this report, the influent concentration of nutrients was selected to resemble the typical concentrations of nitrogen and phosphorus of the sewage from Barcelona just after secondary treatment.

3.3.4.4. Competition

Selectivity is an important parameter to control in water treatment procedures. This property is intrinsic of the ion exchanger which shows preference for particular ions. Besides, it strongly depends on the Si/Al ratio.

Zeolites with high field strength, that is to say higher aluminium content, are more selective toward higher charge density cations; namely, Na^+ and Li^+ . Conversely, zeolites with low field strength, that is to say higher silica content, are more selective toward lower charge density cations; namely, K^+ , NH_4^+ , Ag^+ and Cs^+ [30].

Natural clinoptilolite Si/Al ratio is reported to range between 2,7 and 5,7 [41]. This means that it is a zeolite with higher silica content. As clinoptilolite as an ion exchanger has been thoroughly studied, its selectivity is well known.

Table 3-D Selectivity of natural clinoptilolite, main competitors of ammonium and phosphate ions in ion-exchange systems

Group	Competitors	Reference
Alkali metals	$Cs^+ > K^+ > Rb^+ > Na^+ > Li^+$	[30]
Alkaline earth metals	$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$	[30]
Heavy metal ions	$Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Cr^{2+} > Zn^{2+} > Mn^{2+}$	[42]
Anions	$SO_4^{2-} > I^- > NO_3^- > HCrO_4^- > Br^- > Cl^- > OH^-$	[38]

In the present study, no competitors were intentionally included into the solution. Nevertheless, during the adsorption processes the clinoptilolite could release some of the above commented ions, especially Na^+ and Cl^- . This ionic species may somehow compete with ammonium and phosphate for the vacant cavities.

3.3.4.5. pH

After reading Sections 3.1.2 and 3.2.2 it seems clear that pH is a crucial factor when considering ammonium sorption. Sarioglu (2006) stated that the optimum pH for the removal of ammonium ion was 6 [43].

Two sceneries arise in pH extreme conditions. Under acid conditions, H^+ ion seems to be a serious competition for the exchange sites. On the other hand, under basic conditions ammonium ion is converted to ammonia gas which cannot be adsorbed by the zeolite [40].

Very few authors have studied phosphate exchange capacity of natural zeolite. Lin et al. (2014) were some of them. They discovered that under basic conditions, $pH > 10$, phosphate adsorption skyrockets. Also, another relevant discovery was that ammonium ion enhances the phosphorus removal at higher pH. However, as it is explained above, the ammonium exchange capacity plummets since ammonia gas cannot be exchanged [44].

Since this work intends to remove simultaneously two different ion species; an optimal pH for the exchange of both species does not exist. The decision of focusing on the ammonium removal was made and the pH was not regulated, leaving it around 6.

3.3.4.6. Column process, filtration velocity and retention time

Considering that under dynamic conditions the ion exchange onto the zeolite is higher than under static conditions [28], the present work deals only with a packed column system.

The hydraulic retention time influences the operating ammonium exchange capacity when filtering wastewater through a zeolite packed column. A hydraulic retention time of less than three minutes is not recommended due to a fast breakthrough occurring; eventually a five-minute hydraulic retention time is considered optimal [45].

In the current report, general tendency was to stabilize this flow rate in range of 1,4- 1,8 mL/min since fluctuations in this parameter were constant.

3.3.4.7. Temperature

Koon and Kaufmann (1975) discussed how the temperature affected the mechanisms of ammonium uptake from the natural zeolite. Their study claim that a temperature between 10°C and 20°C does not impact on the ammonium ion sorption. Even though the hypothesis of temperature independence in water treatment methods, using zeolites as ion exchangers, is gaining force [40].

In the present work, temperature was not regulated. Since the experimentation was conducted between October and December, it decreased from 22°C to 13°C. Temperature at night was unknown.

3.3.4.8. Scale

As we can see on *Table 3-E*, most studies were conducted at a very small scale (laboratory scale). Literature about experiments done in pilot-plant size systems has not been found. Given that usually up-scaling seems to have negative unexpected results, laboratory scale results are nothing more than an optimistic approach to the possibilities that ion exchange offers.

3.3.5. Zeolites as ion exchangers

A brief review of some studies on natural zeolites as effective adsorbents for ammonium and phosphate removal in water and wastewater treatment is presented in *Table 3-E*. These reports have been the cornerstone to my research; the experimentation was based on the results that the next authors, and many others, had extracted.

Table 3-E Brief review of the main studies on natural zeolites as effective adsorbents for ammonium removal in water and wastewater treatment

Author	Year	Ref	Study
Lahav et al.	1997	[33]	Ammonium removal from secondary effluent by zeolite followed by bioregeneration was studied. The proposed process uses ion exchange material, zeolite, as a carrier for the nitrifying biomass.
Demir et al.	2002	[45]	Factors affecting the ammonium-exchange capacity; zeolites' particle size, loading flow rates and impact of a number of regenerations upon the ion-exchange capacity were studied.
Sprynskyy et al.	2005	[34]	Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite was studied under dynamic conditions. Both recycling and preliminary studies were conducted.
Sarioglu	2006	[43]	In batch studies, effects of stirring time and initial ammonium concentration on removal efficiency and adsorption isotherms were investigated. In column studies, effects of flow rate, pH, initial ammonium concentration, washing with acid and regeneration on the ammonium adsorption capacity of the zeolite were determined.
Marañon et al.	2006	[46]	Influence of contact time, pH, ammonium concentration, presence of other cations and anion species. Comparison of Romanian volcanic tuff with synthetic zeolites used for ammonium removal.
Rozic et al.	2006	[39]	The Croatian zeolite clinoptilolite and Croatian bentonite clay from the Kutina area were used as natural filtration materials. Alkaline and acid modification of natural clay was performed.
Rahmani et al.	2009	[6]	Investigation of clinoptilolite natural zeolite regeneration by air stripping followed by ion exchange for removal of

			ammonium from aqueous solutions in continuous system. Also, the effects of biofilm and nitrifying bacteria as regeneration mechanisms are studied.
Mikkers	2009	-	Chemical regeneration studies were conducted in order to determine the effect of multiple regenerations on the ion exchange capacity of the zeolites and test the effectiveness of two types of regenerant (NaOH and NaCl).
Margeta et al.	2013	[30]	Review on natural zeolites in water treatment. The recent development of natural zeolites as effective adsorbents. The properties, modifications and processes are discussed.
Wang et al.	2010	[28]	Literature review. The effects of relevant parameters, such as contact time, initial ammonia concentration and particle size of clinoptilolite, were examined. Different kinds of clinoptilolite are analyzed for the ammonium removal.
Lin et al.	2014	[44]	Studies on natural zeolite as adsorbent for the simultaneous removal of N and P and P only. In P only tests, pH>9 is favorable to P removal. When N is also present P removal was significantly enhanced.
Lu et al.	2014	[38]	Study used freshly formed metal oxide suspensions usually have high reactivity. Fe-Mn binary oxide (FMBO) was prepared for the phosphate removal. The results were compared with a mixture of ferric oxide and manganese oxides (FMMO), a hydrous ferric oxide (HFO) and a hydrous manganese oxide (HMO). Phosphate removals followed this trend: FMBO>FMMO>HFO>HMO.

4. MATERIALS & METHODS

4.1. ZEOLITIC MATERIALS

4.1.1. Zeolite preparation

A natural zeolite obtained from Zeocem Company was used. The deposits are located in the Slovakian Republic. The mean diameter of the natural clinoptilolite was in the range of 200 μm – 800 μm .

The selection of the upper limit of this range was mainly based on the investigation by Lahav et al. (1997), which concluded that grain sizes above 1,0 mm drastically decreased the ammonium exchange capacity [33]. On the other hand, the selection of the lower limit of this range was based on the investigation of Dehmir et al. (2002), which showed that the smaller the grain size, the higher ammonium exchange capacity due to a higher mass transfer into the zeolite [45]. By selecting this range, the intention was to obtain particles that could be used in a fixed bed system without exercising an excessive pressure drop while optimizing the ammonium uptake.

The non treated zeolite was added to a 0,8 mm sieve and then, the filtered product was added to a 0,2 sieve. Afterwards, all three particle sizes were classified into groups; >200 μm , 200 - 800 μm and <800 μm . The clinoptilolite with the above-mentioned particle size was washed with water Milli-Q® to remove any fines, as well as impurities and dust. To remove the excess of water, the zeolite was left overnight in the oven at a temperature of 80°C.

4.1.2. Modification with inorganic salts

Many authors claim that chemical modification with inorganic salts give to improve zeolite properties and increase its efficiency in water treatment. An adaptation of the process reported by Jiménez-Cetillo et al. (2009) was used to modify the natural clinoptilolite [47]. The selected procedure consists in two sequential procedures.

First, 30 g of the zeolite were put in contact with 300 mL of NaCl solution with a concentration of 0,1 M. This mixture was left 4 h in a combined heater application keeping the temperature below 80°C. This procedure forces the cation exchange between the ions in the zeolitic framework, which are unknown, and the ions in the solution, viz. Na^+ and H^+ . Then, the 300 mL of NaCl solution were carefully replaced by fresh new 300 mL of NaCl solution, and the system was left overnight to complete the cation exchange.

Second, the sodium-modified zeolite was put in contact with 300 mL of MeCl_m with a

concentration of 0,1 M; where Me was either iron (Fe), manganese (Mn) or aluminium (Al).

The procedure described above was repeated for both aluminium chloride solution and manganese chloride solution; while iron chloride solution required a different method. Anhydrous iron III chloride is a fairly strong Lewis acid which could destroy the zeolitic framework; as it is explained in *Chapter 3: Literature review*. That is why 30 g of iron-modified clinoptilolite were not left overnight without supervision. Instead, the 4 h treatment with heat was repeated.

Finally the modified clinoptilolite was washed with 2 L of Milli-Q® water to remove the excess of chloride that the zeolite had been uptaking during both treatments. Then it was left to dry in the oven for 24 h at a maximum temperature of 80 °C. Afterwards, the zeolite was stored.



Figure 4.1 Compacted samples of zeolite before and after treatment with synthetic waste water. Natural non-treated (Z-N), Mn-modified (Z-Mn), Fe-modified (Z-Fe), and Al-modified (Z-Al) clinoptilolite.



4.2. CHEMICALS

In this study, all chemicals were purchased from Scharlab (reagent analytical grade) and were prepared using Milli-Q® water. During the experimentation, seven types of chemicals were used:

- Sodium chloride (NaCl) was used to condition the zeolite previous to the modification.
- Aluminium chloride (AlCl₃) was used to prepare the modifying solution.
- Manganese chloride (MnCl₃) was used to prepare the modifying solution.
- Iron chloride (FeCl₃) was used to prepare the modifying solution.
- Ammonium chloride (NH₄Cl) was used to prepare both the simulated swine wastewater and the ammonium stock standard solutions.
- Anhydrous potassium dihydrogen phosphate (KH₂PO₄) was used to prepare both the simulated swine wastewater and the potassium stock standard solutions.
- Sodium hydroxide (NaOH) was used to prepare the regenerating solution.

Moreover, other chemicals were employed during the determination of nutrients in different analytical methods, including: bicarbonate, hydrogen carbonate, metasilicic acid, vanadomolybdophosphoric acid and nitric acid concentrated. All the safety data sheets (SDS) were consulted.

To wash the glassware used for solution preparations and sample storage neither detergent nor solvent was employed; only water and Milli-Q® water were used. The main reason was because any trace of phosphorus in the glassware could interfere in phosphate analyses.



Figure 4.2 Effects of the chemicals in the glassware

4.3. EXPERIMENTAL METHODS

As it is explained in *Chapter 2: Project aims*, four experiments were designed to study different modifications of natural clinoptilolite. The objective was to discover which performed better in the simultaneous removal of nutrients. Also, the regeneration capacity of each modification was studied.

To accomplish this task, three cycles were passed through each column. One cycle consisted in two different stages; a loading stage followed by a regeneration stage. Hereonby, each cycle will be commented as two separated stages.

Columns (15 mm inner diameter and 100 mm length) were filled completely with approximately 12 g of selected clinoptilolite and equilibrated with Milli-Q® water during an hour. The backwash operation was repeated after every adsorption and desorption. Between cycles, the column was drained and left inactive a minimum of 12 hours.

In adsorption stages, column was contacted with a 4 L solution containing both ammonium and phosphate ions. The concentrations were 100 ppm (1,52 g of NH_4Cl) and 10 ppm (0,20 g KH_2PO_4), respectively. These concentrations were selected because are thought to be representative of the normal range find in Barcelona's sewage treatment plants⁹.

In regeneration stages, column was contacted with the 0,1 M and 0,05 M NaOH solution for the natural clinoptilolite and the modified experiments, respectively. The elution consumed about 1 L of the solution to accomplish the task; that is to say, until there were neither ammonium nor phosphate ions in the effluent. Then the column was considered fully regenerated. After treatment with the basic solution, the clinoptilolite column was immediately washed with distilled water to remove all the excess OH^- ions.

After the third regeneration, the glass column was painstakingly cleaned. Meanwhile, the zeolitic material was introduced in the oven and left 24 hours at an approximate temperature of 80°C. Once all the experimentation was conducted, samples from the exhausted columns were analyzed by a field emission scanning electron microscope (SEM) (JEOL JSM-7001F).

The experiments were conducted with an intended constant flow rate of 1,5 mL/min; in practice, achieving a constant flow rate was really difficult. *Figure 4.3* illustrates one of the eventualities. More information regarding the filtration velocity can be found in *Chapter 3: Literature Review*.

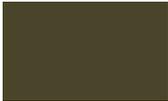
⁹ Available from: <http://www.amb.cat/s/web/medi-ambient/aigua/cicle-de-l-aigua/sanejament.html>





Figure 4.3. Non idealities of the flow, 3rd cycle adsorption of the Fe-modified clinoptilolite.

Figure 4.4 shows the laboratory assembling used to conduct the experiments. A color code is used to define each component of the montage.

	Adsorption: synthetic wastewater 100 ppm NH ₄ ⁺ and 10 ppm PO ₄ ³⁻ (4 L) Regeneration: 0,1 or 0,05 M NaOH solution (1 L)
	Peristaltic pump (Gilson Minipuls 3)
	Glass column (Omnifit 150 mm × 10 mm: 42 bar)
	Fraction collector (Gilson FC 204)

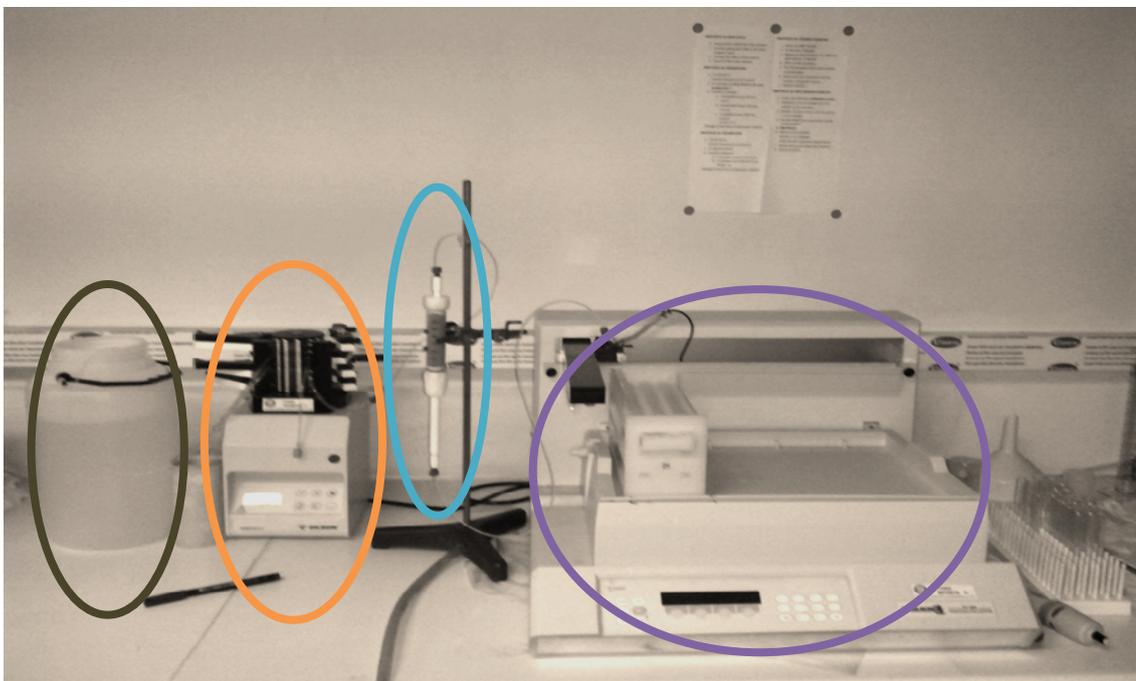


Figure 4.4. Photography of the laboratory assembly.

4.4. ANALYTICAL METHODS

4.4.1. Ammonia concentration determination

To analyse the total content of ammoniacal nitrogen, viz. NH_3 and NH_4^+ , different methods were used. On one hand, in adsorption experiments ammonia analyses were conducted using ionic chromatography. On the other, in desorption experiments different systems were tested; these are ionic chromatography and ammonia ion selective electrode (ISE).



Figure 4.5. Ammonia depletion

During the regeneration studies, ammonia gas was trapped in the test tubes and was accumulated in form of gas bags that pressed the Parafilm® sealant.

4.4.1.1. Ionic chromatography

This technique was used to analyse ammonium ion concentration in the adsorption studies and, also, in the regeneration studies for the manganese, iron, and aluminium-modified columns.

The equipment used was a Thermo Scientific Ionic Chromatograph (Dionex ICS-1100 and ICS-1000). The data system that computed all the information in the column was a software program named Chromleon. In *Figure 4.6* the flow diagram of a typical ionic chromatographer is described.



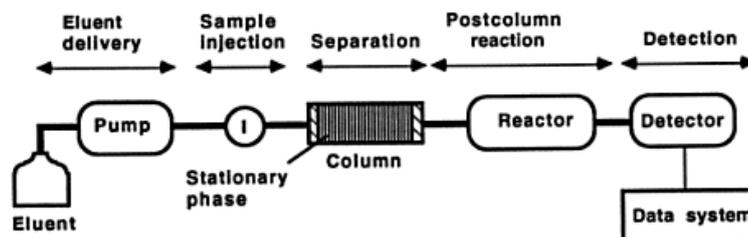


Figure 4.6. Ion chromatographer functioning diagram [48]

Ionic chromatography is a process that allows the separation of ions and polar molecules from a sample. The mobile phase; viz. methasulfonic acid eluent, leads the sample to the cation CS16 analytical column that contains some form of stationary phase material. Then, the target analyte; namely ammonium, is retained on the stationary phase.

This method is applicable up to 300 ppm limit. The samples must be ultra-filtrated and between 3 and 5 mL of sample are needed. When detected, cations appear in this sequence: Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} at approximately 5, 7, 8, 11, 20 min of contact time.

For the adsorption stage, the expected concentration would not rise above the inlet concentration of 100 ppm; whereas for the regeneration stage, the outlet concentration could skyrocket in the initials samples. Hence, sample distillation was needed for the regenerated samples. Three factors of dilution were used; 1/24, 1/16, and 1/7 for the first samples.

4.4.1.2. Ammonia ISE

Only the experimentation with the natural clinoptilolite; or better said, the ammonium ion elution curve was analyzed with this technique. Many authors had detected ammonium ion with this method; however, the equipment that was available presented some failures and it eventually collapsed.

The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia ($\text{NH}_3(\text{aq})$ and NH_4^+) is converted to $\text{NH}_3(\text{aq})$ by raising pH to above 11 with a strong base, viz. 750 μL of sodium hydroxide 10 M. $\text{NH}_3(\text{aq})$ diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode [49].

This method is applicable to the measurement of 0.03 to 1400 ppm . Color and turbidity do not affect the measurement; however, temperature does affect the readings of the electrode. It is recommended to use solutions and samples that have the same temperature and contain about the same total level of dissolved species [49].

Since high concentrations of dissolved ions affect the measurement, sample distillation was necessary in the first samples to avoid, on one hand ammonia values above 1000 ppm and, on the other sodium or chloride interference during the measurement. The ammonia-selective electrode proved to respond slowly below 1 ppm; hence, longer times of electrode immersion (2 to 3 min) were needed to use in order to obtain stable readings.

4.4.2. Phosphate concentration determination

Phosphate from both adsorption and desorption experiments was measured using a Shimadzu UVmini-1240 Spectrophotometer by the Vanadomolybdophosphoric Acid Colorimetric Method.

Colorimetric techniques are always used to determine the concentration of colored compounds in solution. The principle of the Vanadomolybdophosphoric Acid Colorimetric Method is that in a dilute phosphate solution, ammonium molybdate reacts under acid conditions to form a heteropoly acid; namely, molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to phosphate concentration.

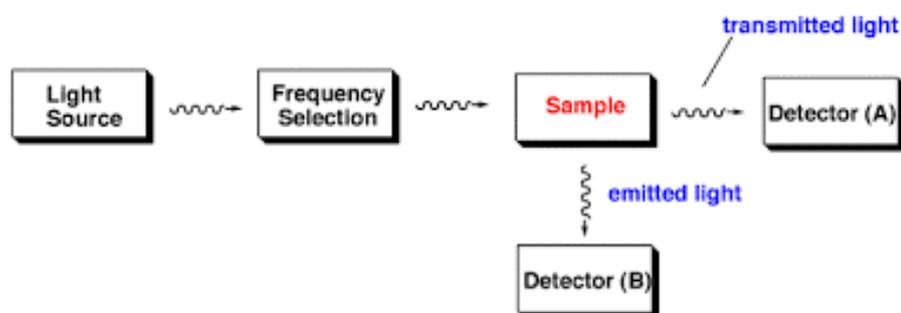


Figure 4.7 Spectrophotometer UV flow diagram [50]

A calibration curve was prepared by using suitable volumes of standard phosphate solution. Since the maximum theoretical concentration of phosphate was 10 ppm for the adsorptions, the standards were picked in this range. At the beginning of each set of analysis, the calibration curve was prepared. Moreover, one standard was analyzed at least with each set of samples.

The fact that samples volume was no more than 8 mL made impossible to follow strictly the



recommended analysis procedure. 3,5 mL of sample and 0,5 mL of Milli-Q® water were placed in a test tube. Then 1 mL of vanadate-molybdate reagent was added and the color yellow appeared. A blank was prepared replacing the normal 3,5 mL of sample for 3,5 mL of Milli-Q® water. Another blank containing only Milli-Q® water was also prepared. At a wavelength of 420 nm, both blanks, the standards of the calibration curve and the samples were analysed. The color was stable for days and its intensity was unaffected by variation in room temperature as it is appreciable in *Figure 4.8*.



Figure 4.8. Sample preparation for the colorimetric method

Other aspects had to be taken into account before start using this technique. Even though some authors reported that ferric ion interfered positively, in iron-modified zeolite experiments ferric ion did not seem to interfere.

Table 4-A. Range of wavelengths to detect the yellow color of the phosphate [50]

P Range Wavelength	
mg/L	nm
1.0– 5.0	400
2.0–10	420
4.0–18	470

A problem aroused when analyzing the samples from the regeneration of the column. Especially in the beginning of the column elution, the quantity of phosphate desorbed by the clinoptilolite was higher than 10 ppm. Moreover, last samples of the regeneration were smaller than 2 ppm. Summarizing, the range of phosphate concentrations during the regeneration was relatively wide, so it was decided to work always with a constant wavelength of 420 nm.

Another concerning matter was the necessity of pH adjustment during the desorption experiments. As the regeneration was conducted with a strong basic solution, these samples presented a pH greater than 10. Between 3 and 5 drops of HNO₃ (63% concentrated) were added to the desorption samples to force the pH below 9.

5. RESULTS

All columns packed in a glass column. The feed solution composition was: ammonium (100 ppm) and phosphate (10 ppm). One bed volume (1 BV), defined as the minimal volume to wet an amount of sorbent, was 13,3, mL. Synthetic wastewater was supplied through the column at an intended constant flow rate of 1,5 mL/min (6,8 BV/h). After saturation on nutrients, the columns were regenerated with either 0,1 M or 0,05 M NaOH solution.

As fluctuations in flow rate were recurrent, general tendency was to stabilize this parameter in range of 1,4- 1,8 mL/min. Also, a terminology to identify which experiments presented flow rate instabilities was adopted. When a ``*`` mark accompanies a numerical value, it indicates that variations in the filtration velocity occurred during the experiment.

Data processing was conducted with MatLAB, MathWorks®, because it provided a range of numerical computation methods. A problem with data integration was that some curves were described poorly thus estimating wrong integration areas.

The performance of the ion exchange columns in all cases is expressed in terms of the column breakthrough. That is to say the point at which the exit concentration from the column starts to rise rapidly, indicating that the column is close to full loading with the inlet ion. In this paper the breakthrough is considered to happen when the effluent concentration expressed in terms of the inlet concentration (C_t/C_0) is 1%. The mathematical concept is presented in equation 1.

$$\text{Breakthrough Capacity} = \frac{(V_t - \int_0^{V_t} C_t dV) C_0}{m_s} \quad \text{Eq. 1}$$

The performance of the regeneration is expressed in terms of the elution curve, where the eluent used was sodium hydroxide slightly concentrated. Mathematical concept is presented in equation 2.

$$\text{Mass recovered} = \int_0^{V_t} C_t dV \quad \text{Eq. 2}$$

This chapter is dedicated to present the results of the fixed bed ion exchange studies in four sections, one for each type of zeolite. At the beginning of each section a table can be found summarizing the observable working conditions of the column, as well as the range of feed compositions. Then the removal of both pollutants is discussed separately. Following the results on the ion exchange capacity are presented and commented.



5.1. NATURAL CLINOPTILOLITE

After five weeks testing the experimental system, determining failures and writing protocols; on the 17th of October the natural clinoptilolite studies began. The first run lasted 3 days, 60 h for the adsorption and 12 h for the regeneration. The second run lasted 3 days, 46 h for the adsorption and 10 h for the regeneration. Finally, the third run lasted 3 days, 50 h for the adsorption and 10 h for the regeneration.

Table 5-A. Natural non-treated clinoptilolite. Working conditions of the three service cycles and both nutrients inlet concentrations.

MASS OF NATURAL CLINOPTILOLITE (g)		12,1			
	Inlet concentration (ppm)		Flow rate (BV/h)		
	NH ₄ -N	PO ₄ -P	Adsorption	Regeneration	
1 st CYCLE	152,3	9,7	6,3	6,3	
2 nd CYCLE	114,2	9,7	6,8	7,3	
3 rd CYCLE	117,8	10,2	6,1	6,3	

5.1.1. Ammonium ion

5.1.1.1. Adsorption studies

Figure 5.1 shows the breakthrough characteristics in three consecutive cycles for the ammonium uptake onto natural clinoptilolite. In the first run the breakthrough occurs almost immediately within the first 10 bed volumes; whereas in the second and third runs the column broke through after approximately 100 bed volumes.

Focusing in the first run, it seems clear that the natural non-treated clinoptilolite is not an effective ion exchanger. These results are in line with Lahav et al. (1997) that reported this same behavior. Since then, many studies together with the current one have corroborated that natural clinoptilolite has some ion-exchange properties. [28], [30], [33]

As expected, following runs performed much better uptaking ammonium than the first run. This is due to the effect of the sodium hydroxide during the regeneration stage. As it is explained in *Chapter 3: Literature review*, zeolite structure and its physical properties can be modified with inorganic basic solutions. Hence, we can assume that treatment with basic solution activates the zeolite, thus enhancing greatly the ammonium uptake.

One unexpected observation about *Figure 5.1* is that no loss of capacity is found between the

second and the third runs. Both breakthrough curves are really similar which seems to point that several loading cycles can be performed before the total exhaustion of the clinoptilolite.

Several authors have studied regeneration with basic solutions. This results are in line with Mikkers et al. (2009) who stated that natural clinoptilolite can be regenerated a great number of times; particularly she regenerate it 10 times. However, this conclusion differs from Sariglu (2006) who stated that ion-exchange capacity slowly decreases and, eventually, the exhaustion of natural clinoptilolite occurs. [43].

5.1.1.2. Regeneration studies

Figure 5.2 shows the elution curve for the first two regenerations of the natural clinoptilolite. The elution was conducted using 0,1 M NaOH. The third run was lost due to failure of the equipment. As explained in *Chapter 4: Materials and methods*, for the elution of the natural clinoptilolite the analyzing method was the ammonium ion selective electrode. The Ammonium ISE collapse may have affected the experimental data shown. Nevertheless, it surely did not affect any other experiment contained in this report since the ammonium analyzing method changed. From that moment on the ammonium detection technique used was ionic chromatography.

Almost the whole column was regenerated after the first 20 bed volumes. The maximum of the first pick and also the second pick is 1800 ppm.

Although the flow rate was relatively different, little change is observed between the two curves. This may suggest that the ammonium ISE was already presenting dysfunctions while operating.



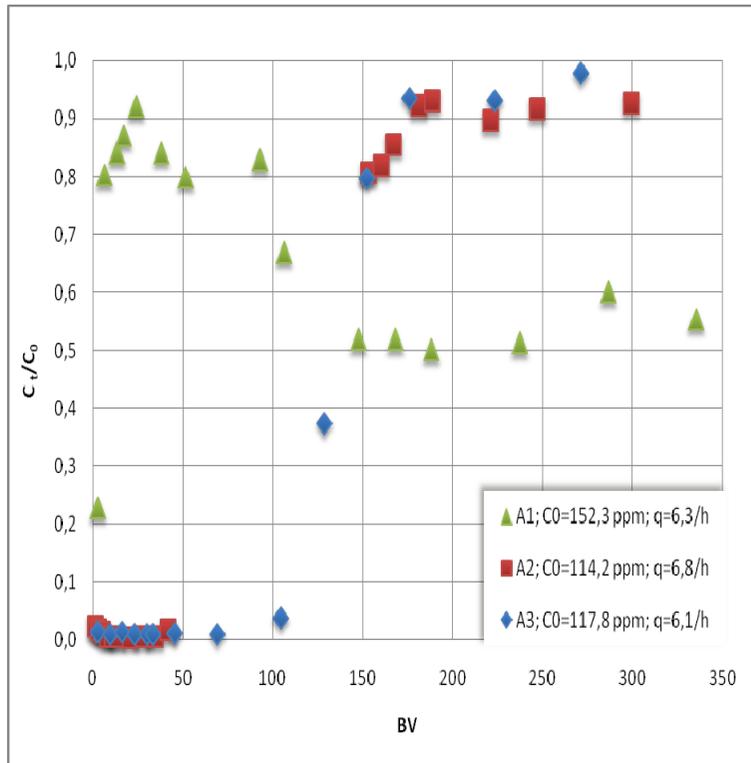


Figure 5.1. $\text{NH}_4\text{-N}$ breakthrough curve. Sorption onto natural non-treated clinoptilolite in three consecutive cycles.

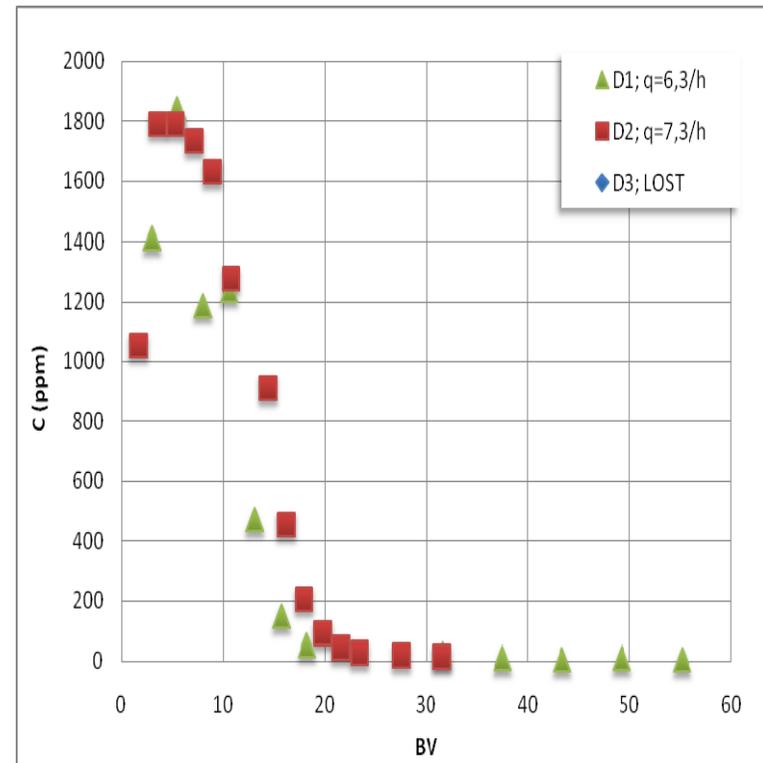


Figure 5.2. $\text{NH}_4\text{-N}$ elution curve. Regeneration of natural non-treated clinoptilolite in three consecutive cycles using 0,1 M NaOH solution.

5.1.2. Phosphate ion

5.1.2.1. Adsorption studies

Figure 5.3 shows the breakthrough characteristics in three consecutive cycles for the phosphate uptake onto natural clinoptilolite. Graphically, seems clear that natural clinoptilolite does not adsorb phosphorus. Unlike the ammonium case, the regenerant did not enhance the phosphate uptake.

Nevertheless, Lin et al. concluded that ammonium assists phosphate removal from high-strength wastewaters by natural zeolite [44]. This differs from this report's results given that the outlet concentration from the samples that exited the column was very much alike the inlet concentration from the synthetic wastewater. However, pH conditions were not alike, and also, inlet concentration in Lin et al. studies was much higher.

One of the strangest observations is the fact that during the second run the outlet concentration is, almost in every sample, higher than the inlet concentration. The most probable explanation is mistaking data in calibration curve.

5.1.2.2. Regeneration studies

Figure 5.4 shows the elution (0,1 M of NaOH solution) results of the three cycles.

As happens with the other nutrient elution, almost the complete regeneration is achieved after the first 20 bed volumes. Then, it slowly diminishes until the outlet concentration of phosphate ion is proximate to zero, meaning that the column has desorbed all the phosphate that had been taken from the influent.

The most important difference between the elution of both ions, namely NH_4^+ and PO_4^{3-} , is that in the phosphate ion case a peak is not plotted; a negative exponential shape is observed instead.

Another aspect worth noticing is the fact that consecutive regenerations remove little more than the previous ones. During the first elution less than 1 ppm was recovered from the column. This is in line with the assumption that the natural clinoptilolite absorbs slightly anything of phosphate ion. The problem is that the second elution removes about 6 ppm of phosphate ion and the third elutes almost 35 ppm of this nutrient.

A reasonable explanation may be that the natural clinoptilolite slowly adsorbs phosphate ion, so in every loading cycle the removal is not noticeable but real. This way, in the 3rd cycle the column would contain much more phosphate than in the other cycles.



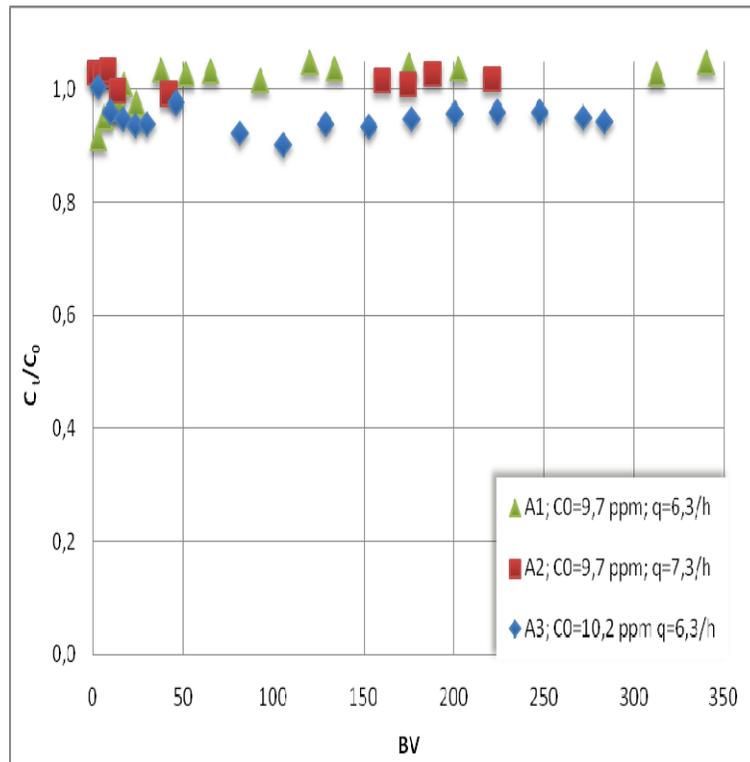


Figure 5.3. $PO_4\text{-P}$ breakthrough curve. Sorption onto natural non-treated clinoptilolite in three consecutive cycles.

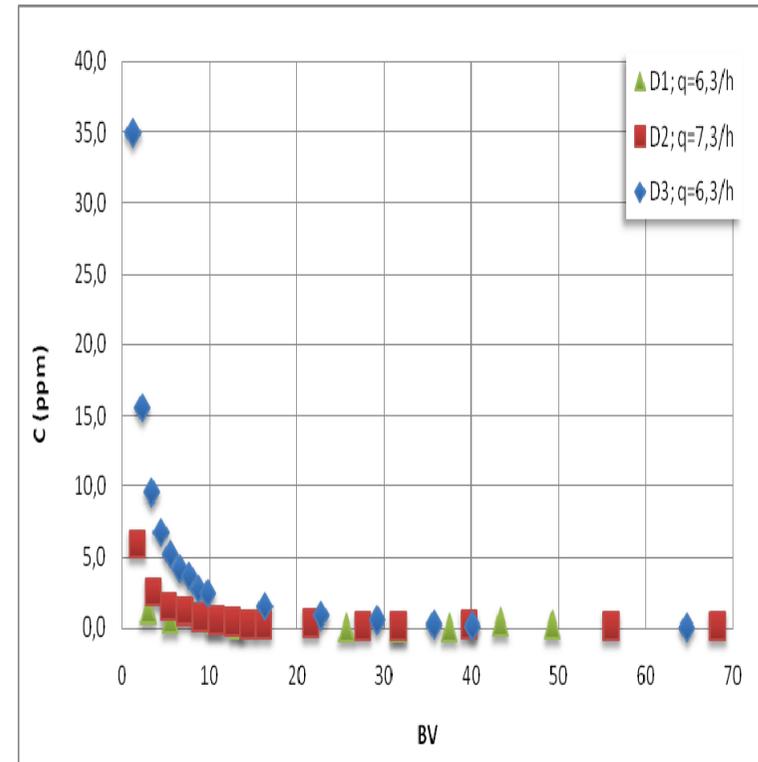


Figure 5.4. $PO_4\text{-P}$ elution curve. Regeneration of natural non-treated clinoptilolite in three consecutive cycles using 0,1 M NaOH solution.

5.1.3. General discussion: mass balance

Table 5-B. Mass balance and capacity results for the 1st cycle of natural non-treated clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	0,2	mg
Desorption	0,2	g	0,2	mg
Capacity	17,2	mg/g	0,0	mg/g

Table 5-C. Mass balance and capacity results for the 2nd cycle of natural non-treated clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	0,0	mg
Desorption	0,2	g	0,3	mg
Capacity	16,2	mg/g	0,0	mg/g

Table 5-D. Mass balance and capacity results for the 3rd cycle natural non-treated clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	2,2	mg
Desorption	-	g	1,3	mg
Capacity	16,9	mg/g	0,2	mg/g

These results both differ and agree with Wang et al. (2010). On one side, they are in line with the 1st cycle capacity value. It is within the range of his studies; Croatian clinoptilolite was reported to have an ammonium adsorption capacity of 7,7-17,6 mg/g. On the other side, the capacity results for the 2nd and 3rd cycles deviate from the range Wang defined for the NaOH activated clinoptilolite; 7,3-8,4 mg/g [37].

It is true that no other study has conducted the regeneration with a lower concentrated basic solution. Further research to increase the number of regenerations before exhausting the zeolite should optimize the concentration of the basic solution.

As phosphate sorption regards, the phosphate uptake is barely noticeable. The pH conditions were not the optimal for the removal of this nutrient [44]; hence, this results corroborate that natural clinoptilolite does not have high selectivity towards phosphate ions.



5.2. MANGANESE-MODIFIED CLINOPTILOLITE

The experiments with the manganese-modified clinoptilolite started the 3rd of November and lasted for ten days. The first run lasted 2 days, 38 h for the adsorption and 8 h for the regeneration. The second run lasted 2 days, 35 h for the adsorption and 8 h for the regeneration. Finally, the third run lasted 3 days, 40 h for the adsorption and 10 h for the regeneration.

Table 5-E. Mn-modified clinoptilolite. Working conditions of the three service cycles and both nutrients inlet concentrations.

MASS OF Mn CLINOPTILOLITE (g)	11,9			
	Inlet concentration (ppm)		Flow rate (BV/h)	
	NH ₄ -N	PO ₄ -P	Adsorption	Regeneration
1 st CYCLE	111,4	9,9	6,4	8,0
2 nd CYCLE	115,5	9,9	7,8	7,8
3 rd CYCLE	109,6	10,0	7,3	6,8

5.2.1. Ammonium ion

5.2.1.1. Adsorption studies

Figure 5.6 shows the breakthrough characteristics in three consecutive cycles for the ammonium uptake onto natural clinoptilolite modified with manganese chloride salt.

The most significant observation is that it presents the slowest breakthrough among the experiments conducted. In all three service cycles, it starts approximately around 40 bed volumes and last until the 200 bed volumes. No loss of capacity is apparently observed within the three runs.

Another relevant observation is that after each run the end of the breakthrough occurs nearer to 1. In the 1st cycle, the column seems exhausted after 200 bed volumes; however, the concentration rate (outlet concentration expressed in terms of inlet concentration) stabilizes at around 0,8. This means that the column is still exchanging some ammonium even though the breakthrough has already occurred. This behavior is typical of the natural non-treated clinoptilolite, but in the Mn-modified experiments this aspect is less noticeable may be because the breakthrough is clearer.

On the other hand, in the 3rd cycle the end of the breakthrough curve is closer to 1, meaning

that ammonium from the influent is not being removed after the breakthrough. Conclusions about this matter cannot be taken regarding the 2nd cycle. The end of the breakthrough is not clear enough to determine whether it still adsorbs once the breakthrough has occurred or not.

5.2.1.2. Regeneration studies

Figure 5.7 shows the elution curve for the three regenerations of the manganese-modified clinoptilolite. The ammonium analyzing method was ionic chromatography. A factor of dilution relatively high was used due to the specifications of the chromatographer^d.

The elution was conducted using 0,05 M NaOH. This change in the concentration of the eluent was adopted after checking the results of the firsts tests with clinoptilolite modified with inorganic salts. The characteristic pick of the elution curve appeared too soon to appreciate the rising of the curve. That is the reason why all the columns containing clinoptilolite modified with inorganic salts were regenerated using sodium hydroxide poorly concentrated as a solvent.

Almost all ammonium is recovered within 40 bed volumes. The highest ammonium concentration obtained in the analyses is 800, 900 and 850 ppm for the 1st, the 2nd, and the 3rd cycle, respectively.

Regarding the influence of the flow rate, even though it diminishes cycle by cycle, little change is observed in the curves. The first and the third runs are practically the same while the second run seems to remove more ammonium than the other two. This eventuality is not reported in any of the literature consulted.

^d See Chapter 4: Materials and methods.



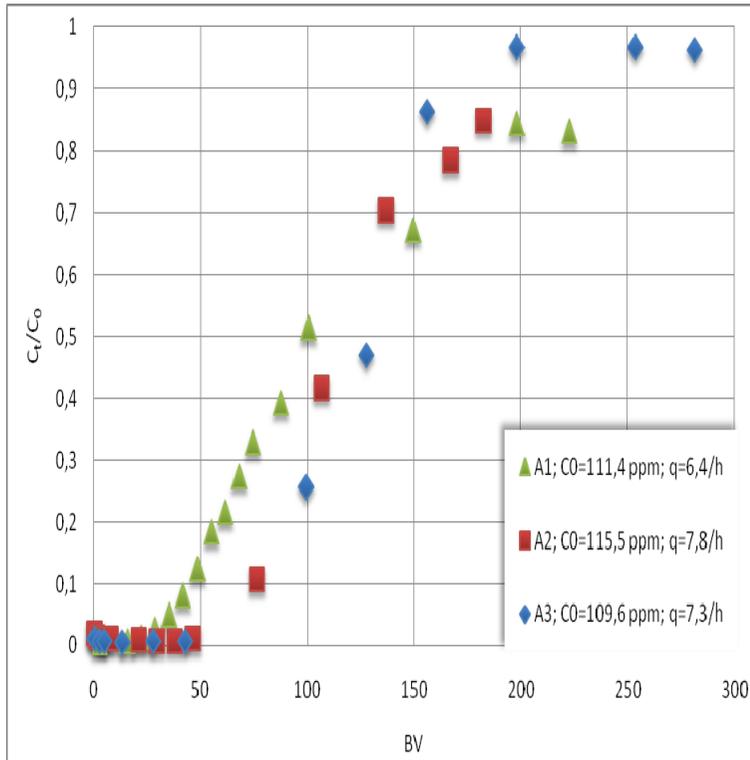


Figure 5.5. NH₄-N breakthrough curve. Sorption onto Mn- modified clinoptilolite in three consecutive cycles.

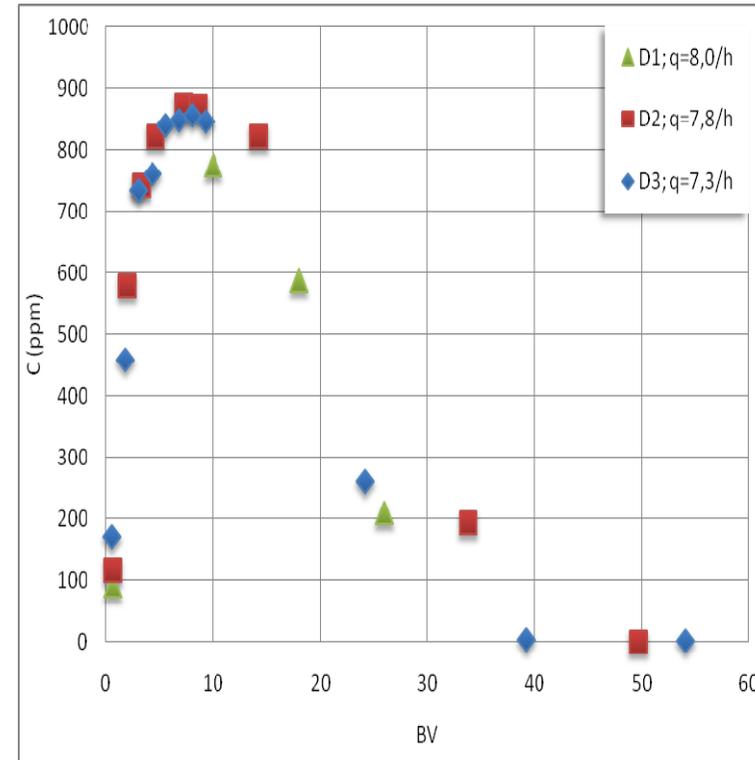


Figure 5.6. NH₄-N elution curve,. Regeneration of Mn- modified clinoptilolite in three consecutive cycles using 0,05 M NaOH solution.

5.2.2. Phosphate ion

5.2.2.1. Adsorption studies

Figure 5.8 shows the breakthrough characteristics in three consecutive cycles for the phosphate uptake onto natural clinoptilolite modified with iron chloride salt. Everything suggests that the modification with manganese enhances very little phosphate sorption capacity. All breakthrough curves start immediately after the loading.

The first run is the one that performed better removing phosphate ion. The column exhaustion occurs after 50 bed volumes. However, unlike the ammonium case, it stabilizes when the outlet concentration is equal to the inlet concentration, meaning that no more phosphate is being absorbed by the column.

Focusing on the second and third runs, it seems right to assume that the elution with sodium hydroxide did not properly regenerate the manganese chloride column. Even though the third run uptakes something more than the second run, less than 10 bed volumes are necessary to exhaust the column.

Another observation worth studying is the fact that in the second and third run, about 70 bed volumes after the breakthrough occurs the manganese-modified clinoptilolite starts adsorbing little phosphate again and for the next 100 bed volumes. This behavior must appear because of the interaction between the basic solution and the clinoptilolite that activated the zeolite.

5.2.2.2. Regeneration studies

Figure 5.9 shows the three service cycles phosphate desorption profiles. The elution was conducted using 0,05 M of NaOH. Even though the basic solution concentration was reduced to half in order to observe clearly each pick, for phosphate studies in this experiment any pick could be observed.

In all three service cycles, the sample that presents the maximum phosphate ion concentration is the first. This value is 2, 4, and 13 ppm for the 1st, the 2nd, and the 3rd cycles, respectively. Even though these results are slightly higher than the ones reported from the natural clinoptilolite, in economical terms this increase is not interesting enough.

The shape of the curves looks very much alike the results of the phosphate elution of the natural clinoptilolite. Also the increment of the quantity desorbed each service cycle is linkable. Hence, the same conclusions should be taken.



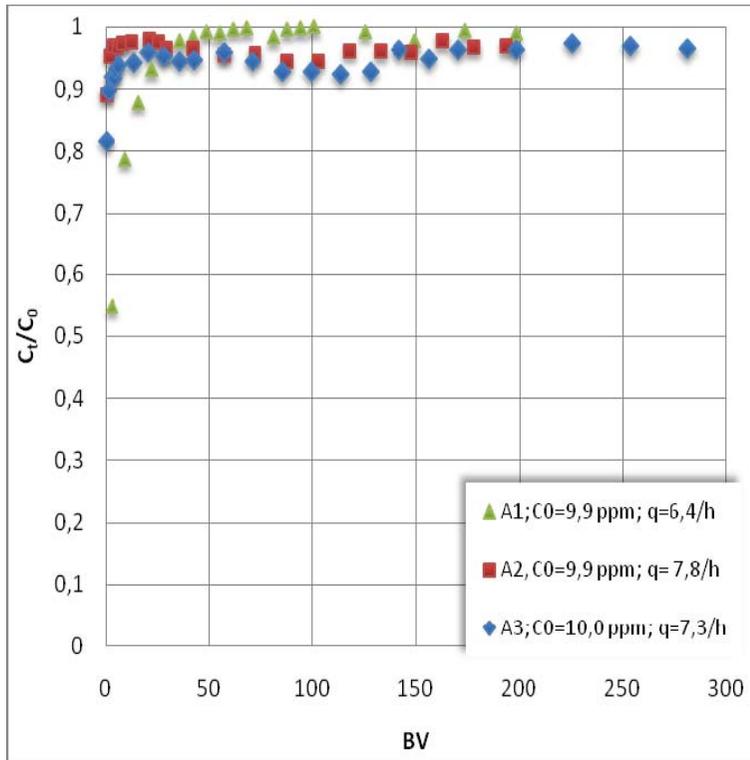


Figure 5.7. PO_4 -P breakthrough curve. Sorption onto Mn- modified clinoptilolite in three consecutive cycles.

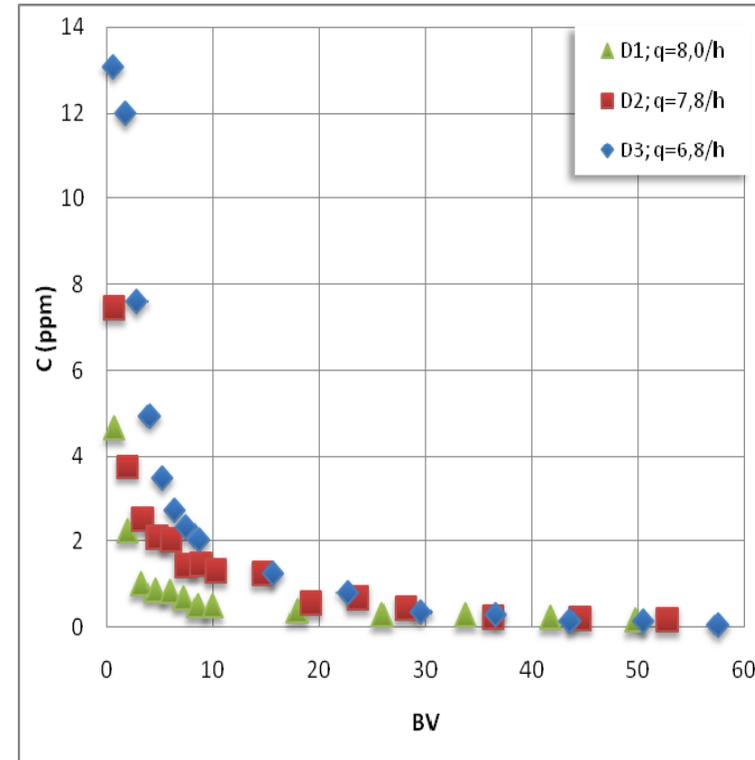


Figure 5.8. PO_4 -P elution curve. Regeneration of Mn- modified clinoptilolite in three consecutive cycles using 0,05 M NaOH solution.

5.2.3. General discussion: mass balance

Table 5-F. Mass balance and capacity results for the 1st cycle of Mn-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	0,8	mg
Desorption	0,2	g	0,3	mg
Capacity	14,0	mg/g	0,1	mg/g

Table 5-G. Mass balance and capacity results for the 2nd cycle of Mn-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	1,1	mg
Desorption	0,2	g	0,6	mg
Capacity	15,7	mg/g	0,1	mg/g

Table 5-H. Mass balance and capacity results for the 3rd cycle Mn-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	1,8	mg
Desorption	0,2	g	1,0	mg
Capacity	14,7	mg/g	0,2	mg/g

No loss of ammonium exchange capacity is found in the manganese-modified clinoptilolite. Ammonium sorption capacity increases 12% between the 1st and 2nd cycles. On contrast, it decreases 6% between the 2nd and 3rd cycles.

Precipitation, as a phosphate removal mechanism, may rule during the 2nd and 3rd cycles and it is more efficient than ion exchange. Even though, phosphate sorption capacity is too low to consider this modification a feasible solution for the simultaneous removal of nutrients.



5.2.3.1. The effect of the regeneration with basic solution onto the clinoptilolite

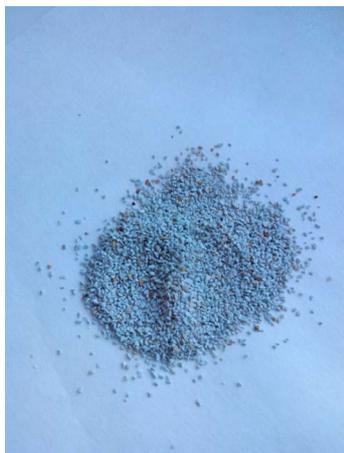


Figure 5.9. Mn-modified clinoptilolite after MnCl₃ modification



Figure 5.10. Mn-modified clinoptilolite after 3rd cycle regeneration

Lu et al. (2014) reported that freshly formed manganese oxides are an approach for the phosphate removal from waste water [38]. *Figure 5.11* shows a black precipitate in the surface of the zeolite. Basic pH, OH⁻ ions and O₂ are responsible.

During the regeneration stage Mn²⁺ could be replaced by Na⁺ in the solution easily. Then, manganese hydroxides (Mn(OH)₂) could precipitate. Alkaline pH and availability of oxygen could oxidize Mn(OH)₂ to MnO₂ and, eventually, MnO₄. Since manganese oxides are black compounds, this hypothesis match with the observable data.

5.3. IRON-MODIFIED CLINOPTILOLITE

The experiments with the iron-modified clinoptilolite started the 21st of November and lasted for twelve days. The first run lasted 3 days, 42 h for the adsorption and 14 h for the regeneration. The second run lasted 3 days, 52 h for the adsorption and 12 h for the regeneration. Finally, the third run lasted 3 days, 60 h for the adsorption and 12 h for the regeneration.

Table 5-1. Fe-modified clinoptilolite. Working conditions of the three service cycles and both nutrients inlet concentrations.

	Inlet concentration (ppm)		Flow rate (BV/h)	
	NH ₄ -N	PO ₄ -P	Adsorption	Regeneration
1 st CYCLE	108,7	10,0	7,3	5,0*
2 nd CYCLE	130,6	10,0	6,8	6,7
3 rd CYCLE	135,9	10,0	6,8*	6,8

MASS OF Fe CLINOPTILOLITE (g)

11,8

5.3.1. Ammonium ion

5.3.1.1. Adsorption studies

Figure 5.13 shows the breakthrough characteristics in three consecutive cycles for the ammonium uptake onto natural clinoptilolite modified with iron chloride salt.

This particular modification of the natural clinoptilolite presents a rather strange behavior. Both 2nd and 3rd cycles breakthrough occur in 60 and 100 bed volumes, respectively. Conversely, the 1st cycle breakthrough occurs immediately. As a result, shape of the first curve resembles to the one characteristically of the phosphate adsorption onto modified clinoptilolite.

One remarkable observation about this experiment is that the iron-modified clinoptilolite quickly loses its sorption capacity. Only two regenerations are needed to decrease its capacity about 40 %. Graphically, the drastic change of slope in the second run starts after 100 bed volumes; whereas in the third run it starts just after 50 bed volumes.



Fluctuations during the first 50 bed volumes of the 3rd cycle are due to flow rate instabilities. The quicker the synthetic water is passing through the column, the less contact time there is between the zeolite and the solution. Hence, the removal of nutrients is worse. Dependence of zeolite sorption capacity on the filtration velocity; or rather, the residence time is reported by many authors [34], [46].

5.3.1.2. Regeneration studies

Figure 5.14 shows the elution curve for the three regenerations of the iron-modified clinoptilolite. The solvent was sodium hydroxide 0,05 M concentrated solution.

For the first run almost all ammonium is removed during the first 55 bed volumes. In the second and third runs the regenerant volume decreases to 20 bed volumes, The maximum concentration obtained in the analyses is 700, 1000 and 1100 ppm for the 1st, the 2nd, and the 3rd cycle, respectively.

In this experiment the influence of the flow rate can be also observed, this time in the first run. In *Chapter 3: Literature review*, the influence of the flow rate in the ion exchange is commented, and in this case it seems that it may have affected in the first run. 1st cycle flow rate was about 1,5 bed volumes slower, thus displacing the elution curve 20 bed volumes late.

In addition, as happens with the other experiments conducted, first run results indicate that the treated clinoptilolite is more reluctant to exchange ammonium ion for sodium ion. Once the zeolite is activated, it releases higher amounts of ammonium ion.

As regards the other two runs, little differences are observed between the curves. Provided that in the experiments with the manganese-modified clinoptilolite the run which eluted more ammonium was the second; it seems that the higher the velocity of filtration the higher the ammonium desorption. However, this happens only when the selected zeolite has been chemically regenerated.

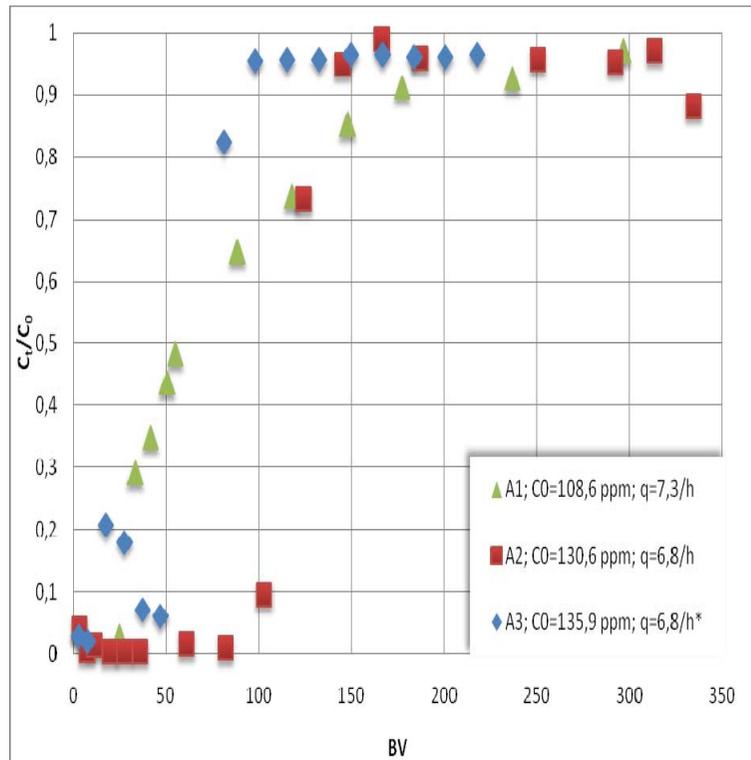


Figure 5.11. $\text{NH}_4\text{-N}$ breakthrough curve. Sorption onto Fe- modified clinoptilolite in three consecutive cycles.

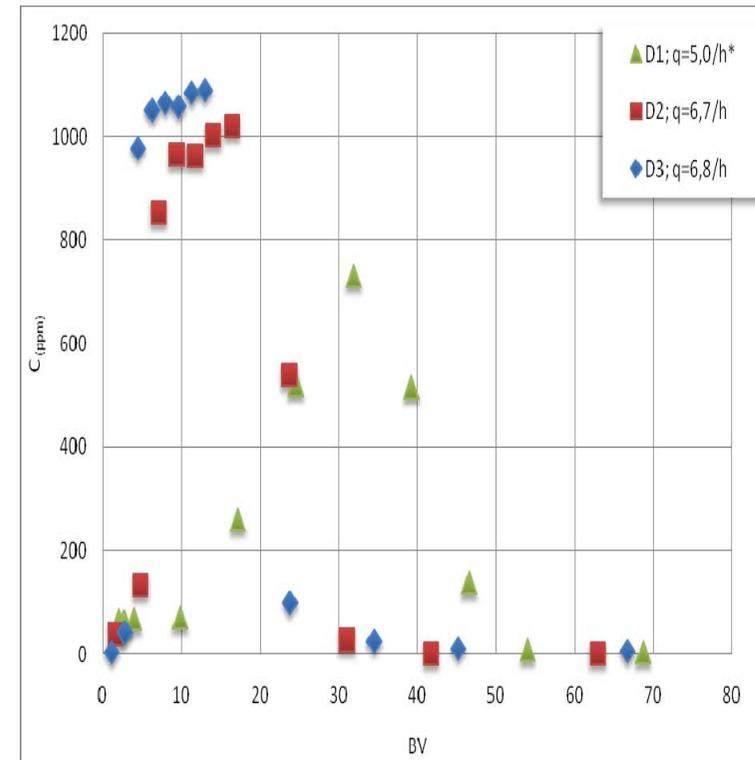


Figure 5.12. $\text{NH}_4\text{-N}$ elution curve. Regeneration of Fe- modified clinoptilolite in three consecutive cycles using 0,05 M NaOH solution.

5.3.2. Phosphate ion

5.3.2.1. Adsorption studies

Figure 5.15 shows the breakthrough characteristics in three consecutive cycles for the phosphate uptake onto natural clinoptilolite modified with iron chloride salt. Everything suggests that the modification with iron enhances phosphate sorption capacity. Still, all breakthrough curves start immediately after the loading.

The first run is the one that performed best removing phosphate ion. Column saturation occurs after 200 bed volumes but it stabilizes when outlet concentration is equal to inlet concentration, meaning that no more phosphate is being absorbed by the column.

As reported in the manganese experiments, the shape of the first run breakthrough curve is not comparable with the ammonium ion case. The column almost immediately reaches breakthrough, but slowly reaches saturation.

Delving into the results of second and third runs, it seems right to assume that the elution with sodium hydroxide did not regenerate the iron chloride column as expected. About 70 bed volumes after the exhaustion of the column, some phosphate is removed again. As reported in *Section 5.2*, the activated zeolite seems to remove phosphate by other mechanisms.

5.3.2.2. Regeneration studies

Figure 5.16 shows the three service cycles phosphate desorption profiles. The shape of each curve does not resemble to the other experiments elution curves mainly because in this case the rising and falling in the concentration is appreciable.

The most significant observation is that the regenerant volume needed to achieve the phosphate ion desorption is not the same for each run. In the 1st cycle the regeneration was not completely achieved; therefore 60 bed volumes of basic solution are not enough. In the 2nd cycle, a depreciable concentration of phosphate is achieved after 55 bed volumes. Finally, in the third adsorption less than 40 bed volumes are necessary to regenerate the column.

Focusing on the quantity of phosphate that is desorbed, a relevant remark would be that the iron modification of the clinoptilolite is more suitable for the phosphate removal than the natural and manganese-modified clinoptilolite. In the first run, the maximum concentration of phosphate ion is about 22 ppm, while in the second and third runs this concentration doubles going up until 44 ppm.

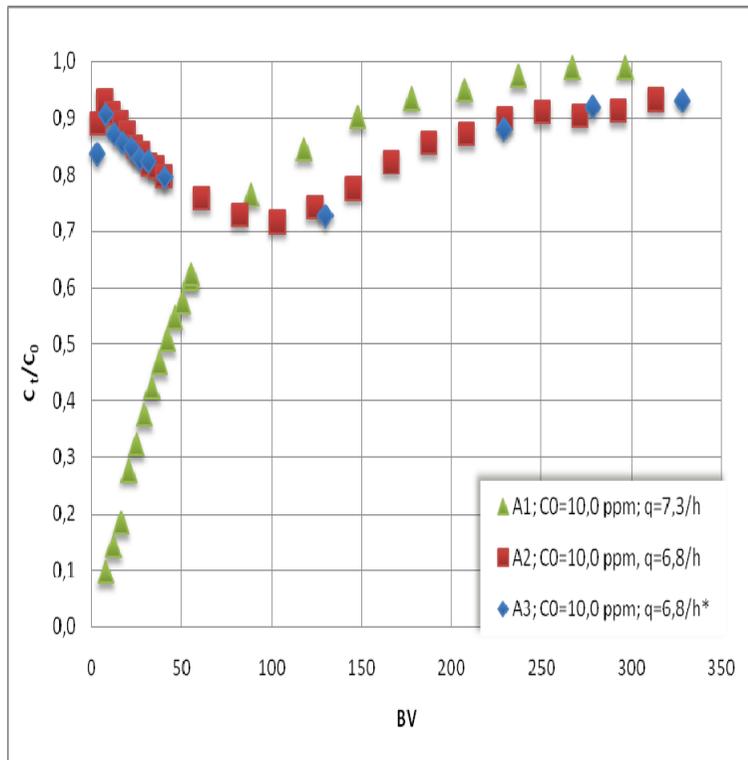


Figure 5.13. $PO_4\text{-P}$ breakthrough curve. Sorption onto Fe- modified clinoptilolite in three consecutive cycles.

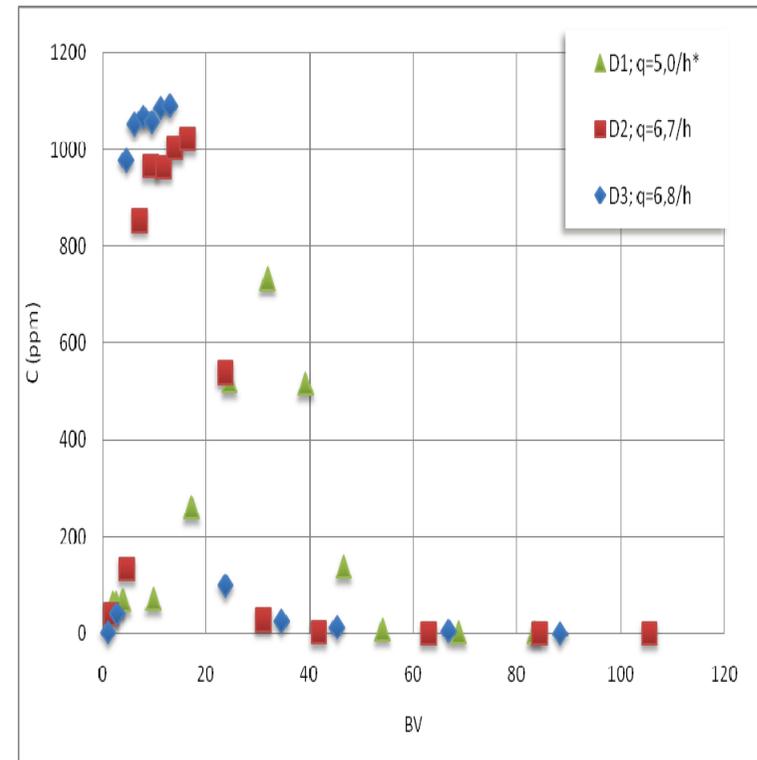


Figure 5.14. $PO_4\text{-P}$ elution curve. Regeneration of Fe- modified clinoptilolite in three consecutive cycles using 0,05 M NaOH solution.

5.3.3. General discussion: mass balance

Table 5-J. Mass balance and capacity results for the 1st cycle of Fe-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,1	g	9,5	mg
Desorption	0,2	g	8,6	mg
Capacity	9,0	mg/g	0,8	mg/g

Table 5-K. Mass balance and capacity results for the 2nd cycle of Fe-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	7,0	mg
Desorption	0,1	g	8,9	mg
Capacity	15,1	mg/g	0,6	mg/g

Table 5-L. Mass balance and capacity results for the 3rd cycle Fe-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,1	g	7,2	mg
Desorption	0,1	g	5,7	mg
Capacity	9,2	mg/g	0,6	mg/g

Iron-modified clinoptilolite is a more interesting approach for the removal of ammonium and phosphate pollutants simultaneously. The ammonium exchange capacity is not constant and it seems that basic treatment in the regeneration stage affected the clinoptilolite. After the second regeneration, the ammonium capacity presents the same value as the fresh column; thus indicating that the column has began to lose the capability to uptake ammonium ion.

However, it must be pointed out that cycles treated with basic solution seem to report better results than the modification with iron chloride. Even in the 3rd cycle, when the column has lost some capacity to uptake ammonium ions, the mass removed from the synthetic wastewater is higher than the 1st cycle recovered mass.

Last but not least, the mass recovered in the 1st cycle is bigger than the mass adsorbed. Causes and consequences of this event are further developed in *Chapter 6: Discussion*.

5.4. ALUMINIUM-MODIFIED CLINOPTILOLITE

Many independent tests were conducted with this particular modification of the natural clinoptilolite. This section delves only into the most recent experiment with this zeolite. The experiments with the aluminium-modified clinoptilolite started the 10th of December and lasted for nine days. The first run lasted 3 days, 43 h for the adsorption and 10 h for the regeneration. The second run lasted 3 days, 40 h for the adsorption and 12 h for the regeneration. Finally, the third run lasted 3 days, 45 h for the adsorption and 12 h for the regeneration.

Table 5-M. Al-modified clinoptilolite. Working conditions of the three service cycles and both nutrients inlet concentrations.

MASS OF Al CLINOPTILOLITE (g)		12,1		
	Inlet concentration (ppm)		Flow rate (BV/h)	
	NH ₄ -N	PO ₄ -P	Adsorption	Regeneration
1 st CYCLE	129,7	10,6	8,1	7,6
2 nd CYCLE	138,2	10,0	7,2	6,7
3 rd CYCLE	140,2	10,7	6,7	6,7

5.4.1. Ammonium ion

5.4.1.1. Adsorption studies

Figure 5.18 shows the breakthrough characteristics in three consecutive cycles for the ammonium uptake onto natural clinoptilolite modified with aluminium chloride salt.

This modification presents a rather erratic behavior. The breakthrough occurs after 60 and 110 bed volumes for the 2nd, and 3rd cycles, respectively. Instead, during the 1st cycle the breakthrough occurs immediately. Since the shapes of the curves resemble so much as the iron in Section 5.3, same comments should be taken.

However some differences exist, the aluminium-modified clinoptilolite keeps adsorbing ammonium ion even though the breakthrough has already occurred. The first run outlet concentration stabilizes before the exhaustion. On the contrary, the runs that have been chemically regenerated present after the breakthrough an outlet concentration in terms of inlet concentration close to 1.



Finally, another significant observation worth studying is that the column seems to enhance its capacity cycle by cycle. No other clinoptilolite reports this behavior.

5.4.1.2. Regeneration studies

Figure 5.19 shows the elution curve for the three consecutive regenerations of the aluminium-modified clinoptilolite. The solvent was a sodium hydroxide 0,05 M concentrated solution. Provided that the adsorption section was rather strange, it is not surprising that the desorption results are erratic, too.

Almost all ammonium is removed during the first 30 bed volumes. The maximum concentration obtained in the analyses is 600, 400 and 900 ppm for the 1st, the 2nd, and the 3rd cycle, respectively.

In order to learn about the influence of the filtration velocity, the second and third regenerations were strictly controlled to keep their flow rate in the same constant value. As a result, in the graphic there is little difference in the width of both curves. There is, however, much difference in the height of both elution curves.

The way the second pick is described points out that these samples lost ammonium ion in form of ammonia gas^h. *Figure 4.15* shows that these phenomena happened to regeneration stage samples.

^h See *Chapter 3: Literature review*

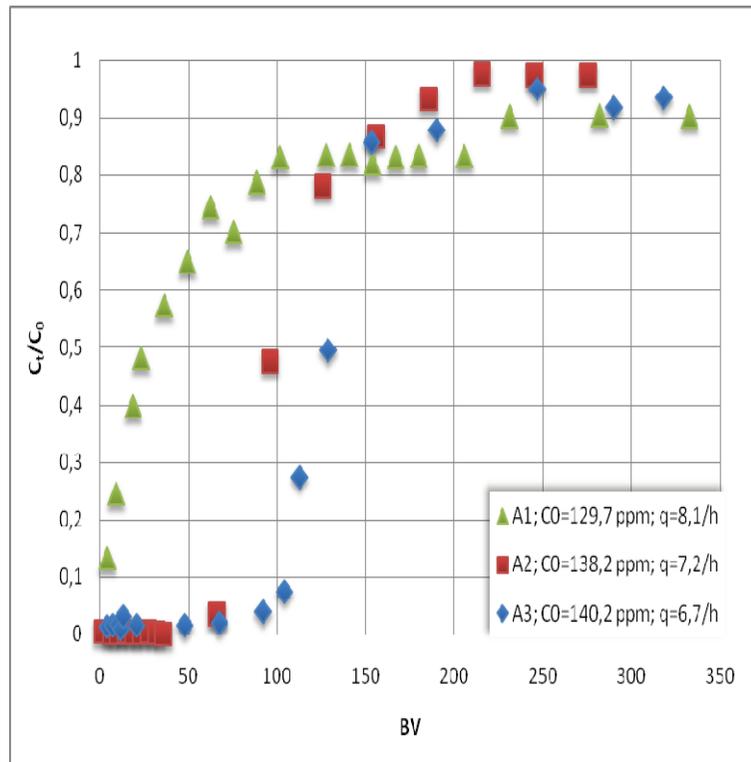


Figure 5.15. $\text{NH}_4\text{-N}$ breakthrough curve. Sorption onto Al- modified clinoptilolite in three consecutive cycles.

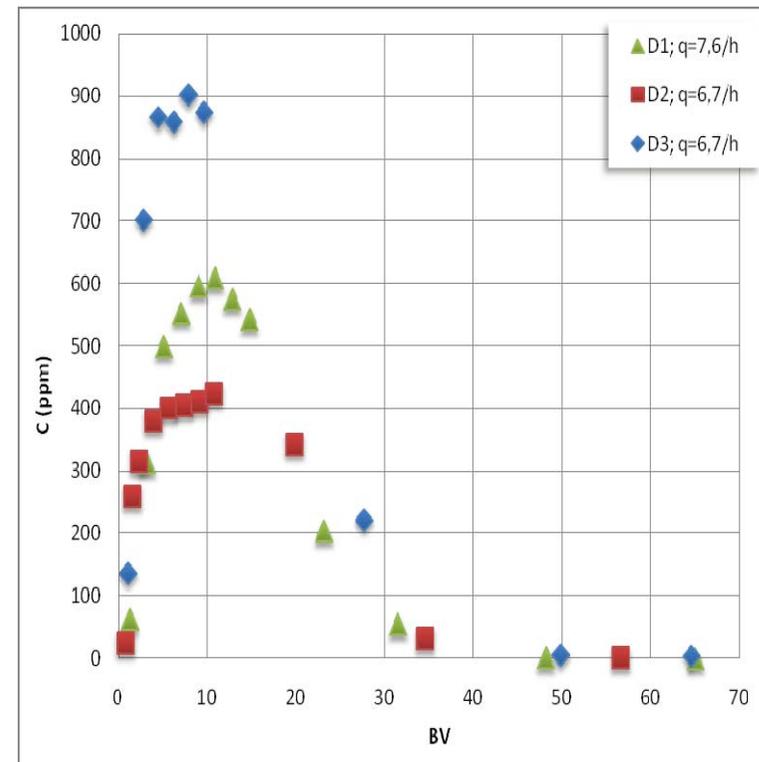


Figure 5.16. $\text{NH}_4\text{-N}$ elution curve. Regeneration of Al- modified clinoptilolite in three consecutive cycles using 0,05 M NaOH solution.

5.4.2. Phosphate ion

5.4.2.1. Adsorption studies

Figure 5.20 shows the breakthrough characteristics in three consecutive cycles for the phosphate uptake onto natural clinoptilolite modified with aluminium chloride salt. Everything suggests that the modification with aluminium enhance the phosphate uptake, as a consequence it performs better than the natural non-treated clinoptilolite.

As reported in the all experiments, the first run breakthrough is immediate after the loading of the column. For the 2nd and 3rd runs no clear breakthrough appears. This is no surprise, these results are recurrent in all experiments of this study.

The first run is the one that performed better removing phosphate ion. The column saturation may occur after 100 bed volumes but, like the iron-modified clinoptilolite studies, it does not stabilize once the breakthrough has happened. The outlet concentration of phosphate continues to grow really slowly and within the 350 bed volumes the maximum concentration did not reach 92% of the inlet concentration.

Focusing on the second and third curves, they present this particular recovery of sorption capacity just after the exhaustion. That is in line with all the clinoptilolite phosphate adsorption results. In this case, the timing of this recovery does not match. For the third run the recovery starts 50 bed volumes after the second run. This may be due to the differences in the flow rate. For example, the studies with iron modification the flow rate is constant at 6,8 BV/h; while in aluminium experiments a difference of 0,5 BV/h exist.

5.4.2.2. Regeneration studies

Figure 5.21 shows the elution results of the three service cycles. The elution was conducted using 0,05 M concentrated NaOH solution.

For the 1st cycle, almost 40 bed volumes of regenerant are required to remove all phosphate. Conversely, for the other runs all phosphate is removed during the first 10 bed volumes. The maximum concentration obtained in the analyses is 47, 38 and 24 ppm for the 1st, the 2nd, and the 3rd cycle, respectively.

The results are really coherent. The first regeneration is one that recovers a more phosphate since the first loading is the only one that reports a nice breakthrough curve. In subsequent runs, the phosphate mechanism of removal may change to precipitation after the breakthrough occurs. Even it seems that aluminium modification does not improve the removal rate.

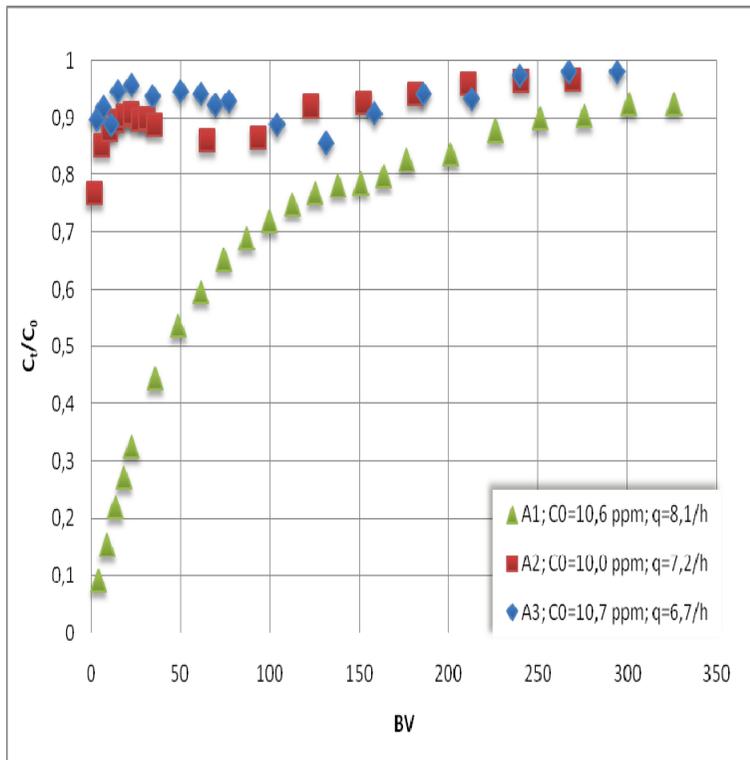


Figure 5.17. $PO_4\text{-P}$ breakthrough curve. Sorption onto Al- modified clinoptilolite in three consecutive cycles.

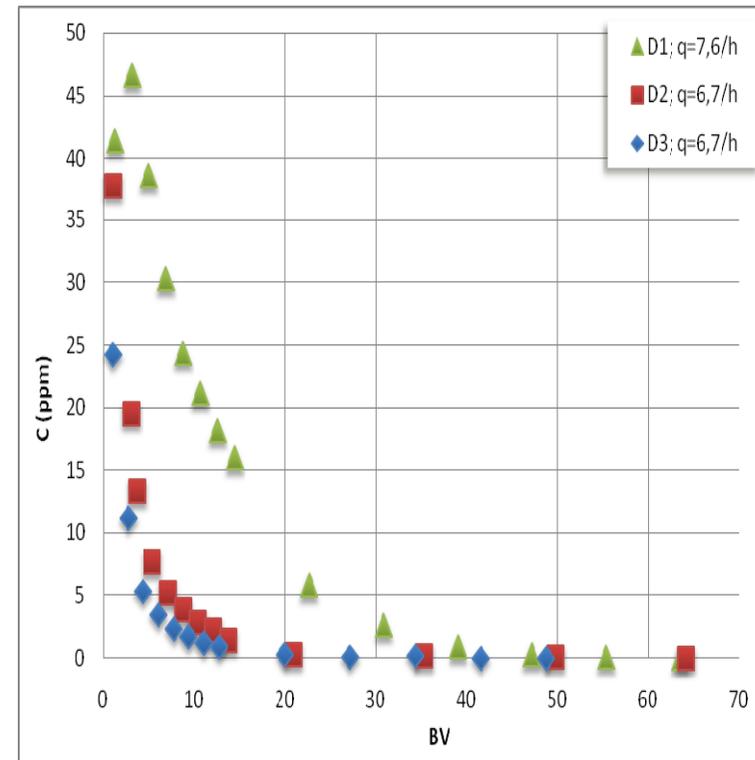


Figure 5.18. $PO_4\text{-P}$ elution curve. Regeneration of Al- modified clinoptilolite in three consecutive cycles using 0,05 M NaOH solution.

5.4.3. General discussion: mass balance

Table 5-N. Mass balance and capacity results for the 1st cycle of Al-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,1	g	10,1	mg
Desorption	0,1	g	6,8	mg
Capacity	8,8	mg/g	0,9	mg/g

Table 5-O. Mass balance and capacity results for the 2nd cycle of Al-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	2,9	mg
Desorption	0,1	g	1,7	mg
Capacity	12,8	mg/g	0,2	mg/g

Table 5-P. Mass balance and capacity results for the 3rd cycle Al-modification of clinoptilolite

MathWorks®	NH ₄ -N		PO ₄ -P	
Adsorption	0,2	g	2,7	mg
Desorption	0,2	g	0,9	mg
Capacity	15,2	mg/g	0,2	mg/g

Unlike Z-Fe experiment, the ammonium exchange capacity increases the ion exchange capacity. It improves 45% and 72 % for the 2nd and 3rd cycles respectively. The ammonium removal is consistent with the mass adsorbed.

The phosphate sorption capacity in the 1st cycle is the highest in this study. However, phosphate removal is also performed by means of chemical precipitation. Modification with aluminium inorganic salt did not enhance the precipitation of cationic species with phosphate ion. Phosphate recovery during the 1st, 2nd, and 3rd regenerations is 68 %, 58 % and 33%, respectively.

Indeed, hydroxyapatite presents high thermodynamic stability and, also, poor solubility [10]. The precipitated compound could be hydroxyapatite, among others. Also, decrease on the percentage of phosphate recovery may be linked to the bad solubility of precipitated phosphate.

6. DISCUSSION

6.1. PERFORMANCE EVALUATION

The best performance of each of the four selected zeolites is compared in *Figure 6.1* which presents the breakthrough curves of the run that reported a higher ammonium adsorption capacity.

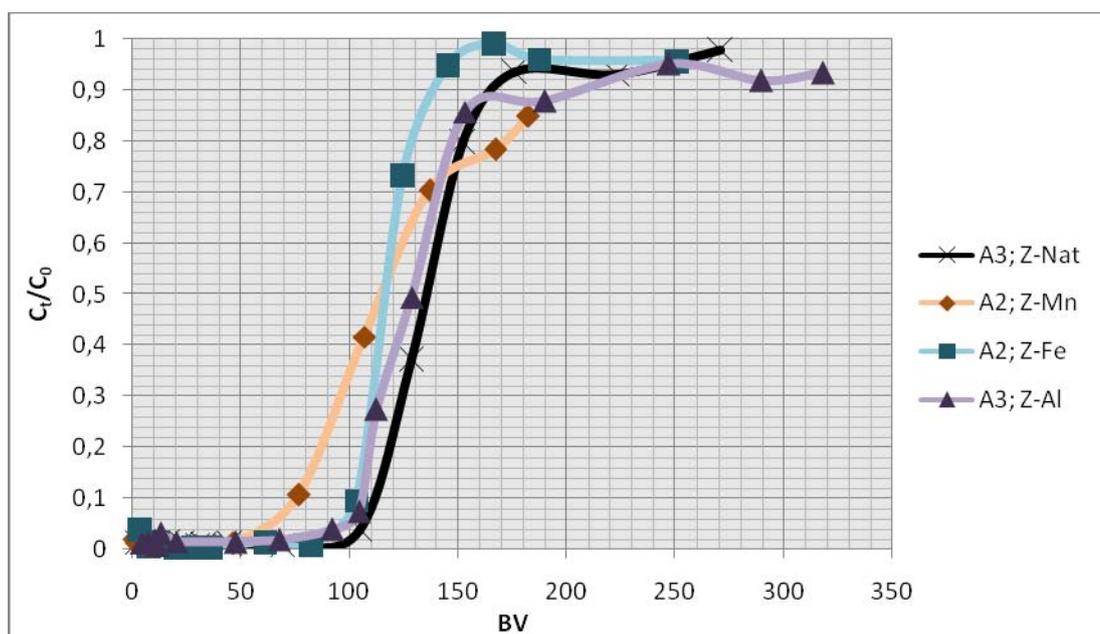


Figure 6.1. Performance comparison. $\text{NH}_4\text{-N}$ best breakthrough curve of each of the four selected zeolites; namely, natural, Mn-modified, Fe-modified and Al-modified clinoptilolite.

An interesting observation is that the 1st cycle is never the selected. The activation of the zeolite by the basic solution used in the regeneration increases, in all studies, the bed volumes needed to reach breakthrough.

Even all four curves resemble, manganese modification of the natural clinoptilolite performs worst. Aluminium-modified and natural non-treated clinoptilolite are the most similar ones. Breakthrough slope, bed volumes treated and exhaustion of both columns are really much alike.

This is logic considering that the natural zeolite possesses an aluminosilicate framework; as consequence of the modification the Si/Al ratio must increase. Whether this increment enhances the ammonium sorption exchange properties is not clear in this study.

The first runs of phosphate adsorption for the modified zeolites are compared in *Figure 6.2*.



The best performance of natural zeolite is also plotted.

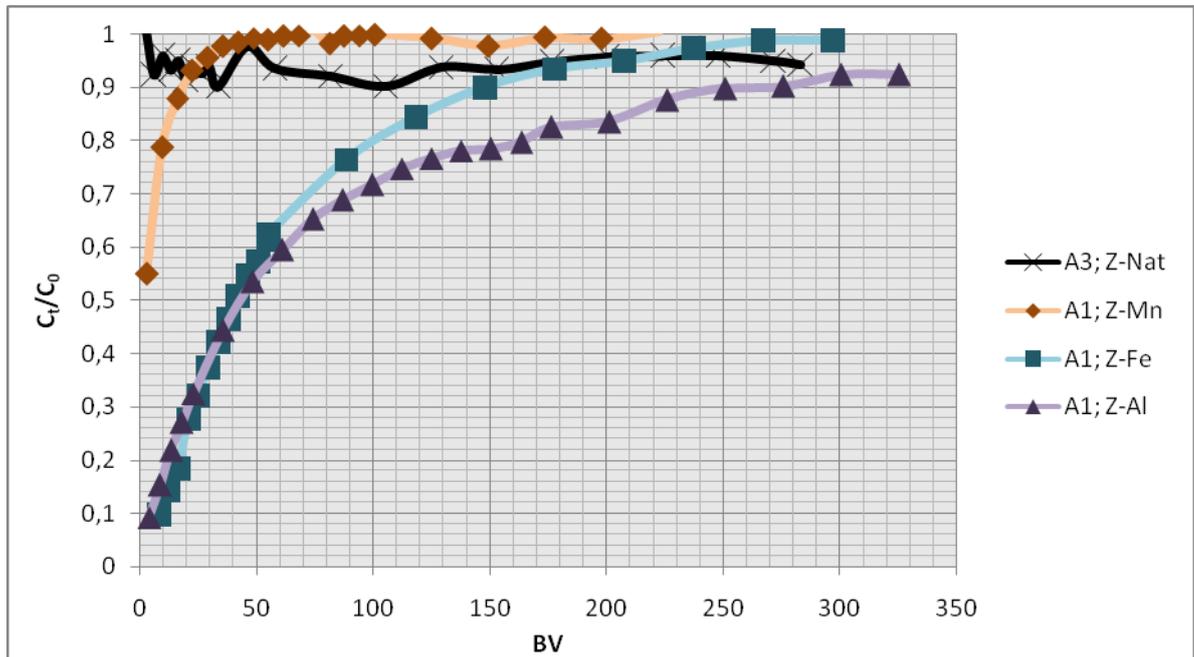


Figure 6.2. Performance comparison. $PO_4\text{-P}$ best breakthrough curve of each of the four selected zeolites; namely, natural, Mn-modified, Fe-modified and Al-modified clinoptilolite.

Although 1st cycle not always performs best, the adsorption mechanism together with the shape of the curve can be seen. In *Chapter 5: Results*, the hypothesis of two distinct phosphate sorption mechanisms emerged; namely adsorption and chemical precipitation.

Lin et al. (2014) proposed that Ca^{2+} from the zeolite exchanges for NH_4^+ and Na^+ from the solution, thus creating hydroxyapatite ($Ca_5OH(PO_4)_3$) in alkaline conditions ($pH > 7$) [44]. The current results are in line with this discovery. Also, phosphate is reported to precipitate in presence of inorganic metal salts such as iron chloride or aluminium chloride. Yeoman et al. (1988) studied this physico-chemical process which is explained in detail in *Chapter 3: Literature review*.

Although chemical precipitation is a flexible approach to phosphorus removal, it produces metal salts within the wasted sludge which are not feasible to recycle. Moreover, the cost and hazard associated to the disposal of these chemicals is high enough to be relevant. That is why other cycles were not analyzed in *Figure 6.2*.

Focusing on the adsorption and ion exchange phosphate removal mechanisms, modification with aluminium salts has the best breakthrough curve.

Focusing on the adsorption and ion exchange nutrient removal methods, these results show

that none of the tested modifications of natural clinoptilolite improve the removal of both ions simultaneously. For instance, manganese-modified clinoptilolite performs adequately while removing ammonium; but, conversely, it is by far the worst while removing phosphate. This is illustrated in *Figure 6.3*. The same seems to happen with clinoptilolite modified with aluminium and iron inorganic salts; however, they perform better in the removal of both nutrients at the same time.

Another important observation is that in the studies with aluminium modification, the clinoptilolite does not completely saturate, that is to say that once the breakthrough is over the ion exchanger still exchanges both nutrients at a lower ratio. This aspect is worth studying too; specially the duration of this phenomenon.

Moreover, phosphate sorption capacity in aluminium studies is three times higher comparing it with the one in manganese modification studies and it seems not to lose much capacity in the three regenerations. Nonetheless, *Figure 5.15* shows clearly that the mechanisms of phosphate sorption between the fresh column and the regenerated ones are different. Hence, the constant uptake of phosphate cannot be attributed only to the adsorption mechanism, the one which this report is interested in.

6.2. CAPACITY COMPARISON

In this section a comparison of the total quantities of ammonium and phosphate ions adsorbed by each column is needed in order to determine which modification is more efficient in the wastewater treatment.

The performance of the natural clinoptilolite is no longer commented due to the bizarre capacity results obtained which led to change the analyzing method. That is another reason why no comparison will be made; the repeatability and reproducibility of an experiment must be taken into account before establishing links between experiments. Also, the fact that a relatively high factor of dilution was applied in the modified clinoptilolite regeneration samples drags a relatively high error that makes any comparison inaccurate.

Following, the ion exchange capacities calculated in each section of this chapter are presented in *Figure 6.3* for both ammonium and phosphate sorption capacity.



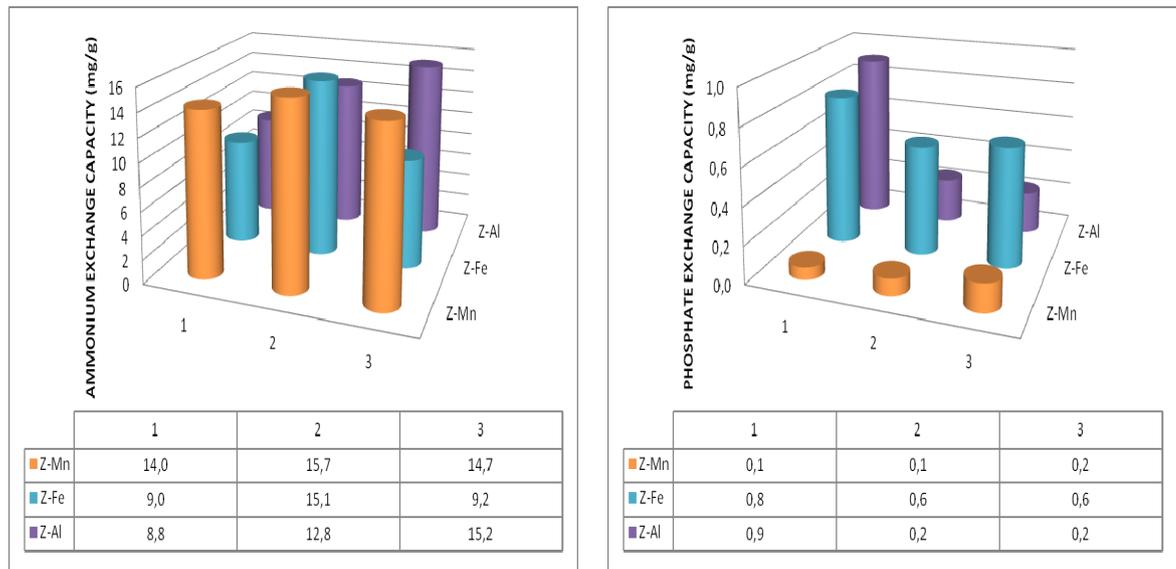


Figure 6.3. Comparison of ammonium ion capacity mg/g (left), phosphate capacity mg/g (right)

After the first regeneration, Z-Mn increased 12% its ammonium exchange capacity; while after the second regeneration it decreased 6%. Z-Mn possesses barely any phosphate sorption capacity, but precipitation mechanism, which is believed to rule over the 2nd and 3rd cycles, reported better results than the adsorption mechanism, which is believed to rule over the 1st cycle.

Z-Fe increased 68% its ammonium exchange capacity after the first regeneration; while after the second regeneration it decreased 39%.

Z-Fe removes some phosphate but, even it presents higher capacity results, less than 1 mg PO₄-P/ g of zeolite are adsorbed in each cycle. Not many differences between adsorption and precipitation removal rates are observed. Precipitation mechanism uptake 25% less phosphate ion than adsorption mechanism.

After the first regeneration, Z-Al increased 45% its ammonium exchange capacity; moreover, after the second regeneration it increased 19%. On balance, all basic treatments onto the aluminium-modified clinoptilolite enhanced 73% its ammonium exchange capacity.

As the other modified zeolitic material results, Z-Al possesses barely any phosphate sorption capacity after the basic treatment. During the 1st cycle the column adsorbed, achieving the highest phosphate sorption capacity (0,9 mg PO₄-P/ g of zeolite) of all experiments conducted. Nevertheless, this modification is not suitable for recycling applications since one cycle is enough to exhaust the zeolite.

6.3. SEM IMAGES & EDDAX RESULTS

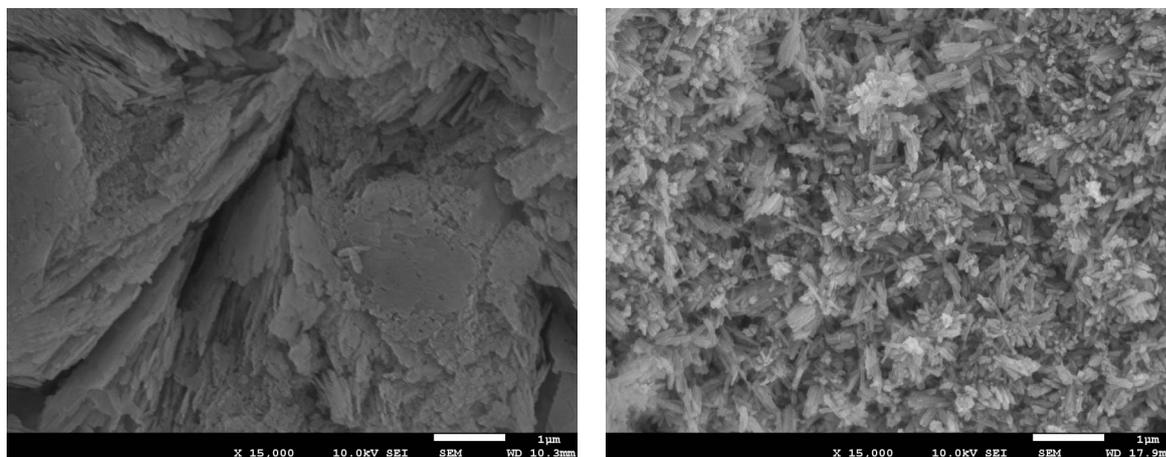


Figure 6.4 SEM images of Z-Al (left) Z-Fe (right) after the third regeneration (x15000)

In left photograph of *Figure 6.4* plate shapes are observed. On contrast, rod shapes are shown in right picture.

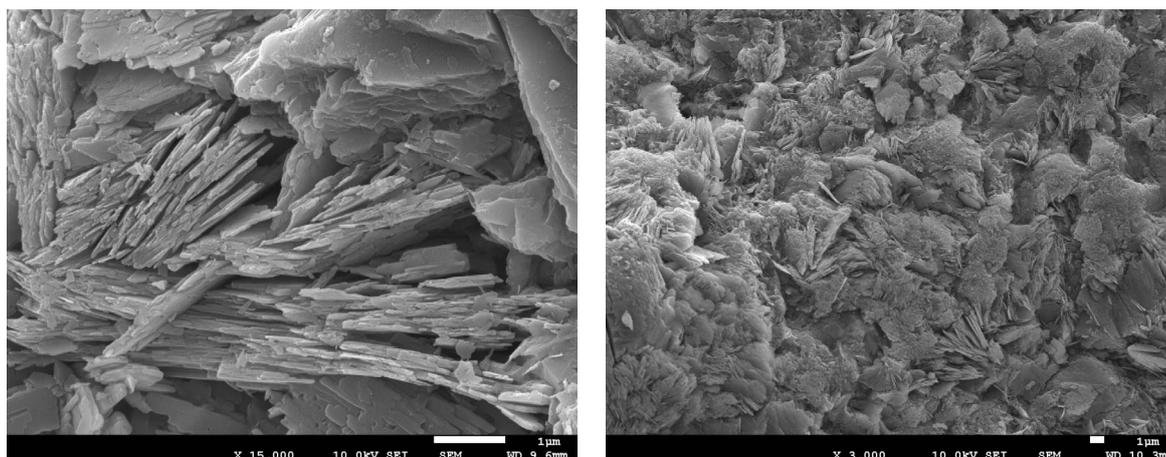


Figure 6.5. SEM images natural clinoptilolite after the third regeneration (x15000 left, x3000 right)

SEM images from *Figure 6.5* reveal that after synthetic waste water treatment the surface of the zeolite is uniformly rough. May be precipitates, for instance manganese oxides or phosphate metallic salts, have accumulated in the surface of the zeolite.

Table 6-A. EDDAX results on clinoptilolite analyses after the third regeneration.

Spectrum	O	Na	Al	Si	K	Ca	Fe	Total
Z-N	54,72	34,59	9,44	34,40	3,96	2,94	N.D.	100,00
Z-Mn	59,21	2,61	5,80	31,08	1,46	N.D.	N.D.	100,00
Z-Fe	37,12	N.D.	1,07	6,48	N.D.	N.D.	53,65	100,00
Z-Al	48,69	3,17	6,16	41,98	N.D.	N.D.	N.D.	100,00



7. FEASIBILITY OF THE PROJECT

7.1. ECONOMICAL FEASIBILITY

Experimentation needs financial aid. Business angels and also public investment funds are the primary means to sustain macro projects such as the one this project participates into.

There are several elements in the budget of this particular project. First, the hours of dedication must be refunded. Considering that UPC recommends students to charge 5€ for working hour, about 350 hours were needed in the laboratory, and 200 hours were needed for the project composition. A total of 3000 € would appear in the budgets as human resources concept.

There are other aspects that affect directly onto the spending budget but they cannot be attributed solely to this project. For instance, approximately 20 g of ammonium chloride and 5 g of anhydrous potassium dihydrogen phosphate were spent during the experimentation. Scharlab® sells this two reactive in containers of 500 g; less than 4% (48 €/container, total of 96 cts) and 1% (89 €/container, total of 89 cts) was used for ammonium and phosphate containers, respectively. For the rest of chemicals used, these percentages plummet because very little amounts were needed.

Many chemical, glassware and other materials were needed; however, their use was not limited to my project. This means that they have been recycled, and they can be recycled. Also, the machinery used in the ammonium and phosphate analyses is also provided for other students that work in the laboratory. In order to account correctly this concept, the amortization of both the chromatographer and the spectrophotometer should be calculated.

As for the analyzing equipment, the electric power consumption needed to work with the machines is the only part of the spending budget that can be attributed to my experiments. Even though, if this was taken into account, many gadgets in the laboratory are needed that consume relevant amounts of energy (lights, pumps, air conditioning, oven...) and, therefore, they should be considered too.

On balance, it is really difficult to delimit these concepts in the economical prospective budget.

Since little more can be said about the economical cost of the experimentation in the laboratory, an overview about the incomes and expenses of a full scale column system is presented in *Table 7-A*.

Table 7-A. Economical assessment. Implantation of an ion-exchange column for the removal and recovery of nutrients in sewage treatment plants.

Expenses	Incomes
Control engineer	Recovery of nutrients as fertilizers
Zeolitic materials and chemicals	Public subsidies
Energy resources	
Equipment (columns, pumps, pipeline...)	

An important part of expenses are associated to installation and are one-time only; leaving two recurring costs, viz. maintenance and raw materials. The key to redeem the associated costs would be to optimize the number of regenerations in order to obtain the highest amount of fertilizer product.

There are several intangible benefits which should be taken into consideration. Improvement on water quality, reduction of biogas storage tanks due to growth of energetic needs, and mitigation of dependence on oil-based fertilizers are some examples.

7.2. ENVIRONMENTAL FEASIBILITY

In every project the environmental impact of itself must be adequately assessed. Any of the laboratory experiments was potentially harmful for the environment. However, by the very nature of laboratory work proper common-sense precautions must be taken. There is a certain unavoidable hazard associated with the use of a variety of chemicals and glassware. Also, there is a great danger related with the disposal of chemicals. Following, general safety guidelines to ensure a safe laboratory environment are presented.

- Human health protection:
 - i. Use of safety goggles and gloves.
 - ii. Use of closed shoes and long pants.
 - iii. Long hair tied back.
 - iv. Use of a lab coat.
 - v. Conduction of authorized experiments only.
- Proper Handling of Chemicals and Equipment:
 - i. Material Safety Data Sheets (MSDS) inform of any hazards and precautions related to any chemical (Annex I).
 - ii. Excess reagents never return to stock bottles.
 - iii. Acid/basic solutions disposal container.
 - iv. Outlet sample disposal container.



Since little more can be said about the environmental impact of the experimentation in the laboratory; an overview about the probable environmental cost of implantation of a full scale column system is presented as follows.

Water treatment regulation is extensive and scattered; including: european policy and national legislation that includes territorial and municipal regulations.

The Water Framework Directive, Directive 2000/60/EC, was adopted in 2000 as a single piece of legislation covering rivers, lakes, groundwater and coastal waters. Its objectives are to prevent further deterioration of waterbodies. Besides, aim of achieving at least good status by 2015 was defined. There are many other legal texts associated with this directive, following mentions concern this project activity: Sewage Sludge Directive (86/278/EEC), Urban Waste-water Treatment Directive (91/271/EEC), Plant Protection Products Directive (91/414/EEC) and Nitrates Directive (91/676/EEC).

Catalan Agency Water (ACA) implements european legislation and has full authority over the hydrological resources in Catalonia. Good quality in Catalan water and waterbodies has not been achieved by 2015. Moreover, ammonium pollutant is located in several fluvio-deltaic (Ter, Fluvià, Baix Besòs and Plain of Barcelona) and, also, in aquifers (Cardó – Vandellós, Montseny – Guillerics, etc.) [51].

The idea is to upgrade a typical water treatment plant. Let us suppose wastewater is, first, pretreated with industrial mechanical filters; then, is subject to a common primary treatment such as coagulation-flocculation; and, finally, a biological treatment is applied to the effluent. Treated water would exit the treatment plan without sufficiently and efficiently removing nitrogen and phosphorus compounds. The proposed solution is to incorporate a set of fix bed columns filled with the studied clinoptilolite. Ammonium and phosphate ions would be taken by the zeolite achieving this way pure clean water that can be safely returned to the environment.

Also, all environmental impact assessments must compare two different scenarios; the past situation and the future situation. The environmental parameters sensitive of change due to either the construction phase or the operational phase of the project are analyzed in *Table 7-B*. For that, a really simple color code is used [52]:

- **GREEN** → a particular parameter is improved with the project.
- **ORANGE** → a particular parameter may be aggravated with the project.
- **RED** → a particular parameter is aggravated with the project.

Table 7-B. Interaction matrix for upgrading a water treatment plant with an ion exchange column system

		ABIOTIC			BIOTIC		SOCIAL ECONOMICAL & CULTURAL				
		LAND FORM	WATER	AIR	PLANT LIFE	ANIMAL LIFE	LAND USE	ECONOMY	UTILITIES	HAZARDS	COMMUNITY REACTION
CONSTRUCTION PHASE	CONTAMINATION			(e)							
	SOIL DISPLACEMENT	(a)	(b)								
	WASTE DISPOSAL		(c)							(i)	
	NATURAL RESOURCES		(d)								
	ENERGY							(f)	(f)		
	PUBLIC SERVICES							(g)			(j)
	CONSTRUCTION COST								(h)		(h)
OPERATION PHASE	REGENERATION							(n)			(q)
	CONTAMINATION		(l)							(q)	
	WASTE DISPOSAL						(m)				
	NATURAL RESOURCES	(k)	(l)								
	ENERGY								(p)		
	QUALITY		(l)								(r)
	N, P REMOVAL		(l)					(o)			
	MANTAINANCE COST							(n)	(h)		(h)

7.2.1. Observations on the interaction matrix

7.2.1.1. Construction phase

- a) Irreversible. Unstable slopes or embankments, as well as extensive disruption to the soil, may occur during the construction phase. Although the system set-up is not particularly large compared with the total extension of the treatment plant, enough space may not be available.
- b) Long term, naturally reversible. Changes in ground contours, shorelines, stream channels or river banks will occur with the incorporation of a tertiary system.
- c) Accidental. Contaminants may be disposed in the wastewater.
- d) Short term. Changes in currents and water movements will occur in the start-up of the system.
- e) Short term, planned. Air pollutant emissions, as well as odors, will be released because of the use of construction machinery.
- f) Indirect. Use of substantial amounts of fuel or energy.
- g) Direct, local, short term. Generate employment.
- h) Long term. Investment that generates well-fare to the local and global population.
- i) Planned. Generation, transport, storage of demolition waste.
- j) Reparable via management practices. Movement of vehicles and construction machinery that may aggravate the traffic circulation. Also, new roads may be constructed.

7.2.1.2. Operational phase

- k) Long term. Depletion of land which may be considered for wilderness.
- l) Cumulative. Improvement of the effluent water with the removal of nutrients that promote eutrophication.
- m) Cumulative, long term. As the system ages, solid wastes like hydroxiapatite and other precipitates may emerge.
- n) Irreversible. Chemical regeneration creates a brine of ammonium and phosphorus that has to be adequately disposed.
- o) Long term. Income of fertilizers sale.
- p) Planned. Need for new utilities; storm sewers, septic tanks and communication systems.
- q) Accidental, local. There is a health hazard associated with the chemical regeneration.
- r) Local, indirect. Aesthetically, a change in the scenic vista open to the public appears.

CONCLUSIONS

Zeolites present both ion exchange and adsorption properties. For this reason they are suitable for many applications in water treatment. Research has been focused on the optimization of surface modification procedures to raise clinoptilolite efficiency and to enhance the capability of regeneration.

Ammonium analyses reported similar behaviors for each tested zeolite. Inorganic salt modification seemed not to increase clinoptilolite ammonium adsorption capacity. On balance, ammonium removals followed this trend: Z-Mn > Z-Al > Z-N > Z-Fe considering process performance in all three cycles.

Conversely, phosphate analyses reported different behaviors for each tested zeolite. Inorganic salt modification increased clinoptilolite phosphate adsorption capacity since natural clinoptilolite possess any selectivity towards phosphate ion. Summarizing, phosphate removals followed this trend: Z-Fe > Z-Al > Z-Mn > Z-N considering process performance in all three cycles.

Generally, ammonium adsorption was high during the first run. However, better ammonium removal from the influent was observed after column regeneration. The basic treatment seems to have activated the zeolite, thus enhancing first run results. Capacity was in range of 9,0-16,0 mg NH₄-N/ g of zeolite. Highest ammonium removal was reported of 0,2 g adsorbed.

In general, phosphate adsorption was low, achieving a maximum removal of 10,1 mg adsorbed by Al-modified clinoptilolite. Two different mechanisms might have been observed before and after basic treatment during elution; adsorption onto the zeolite framework, and partial precipitation with Ca and Mg ions. This theory is buttressed with low percentage of phosphate recovery during the regeneration. In the 3rd cycle regeneration analyses, phosphate recovery percentage was 55%, 79% and 33% for the Mn-modified, Fe-modified, and Al-modified clinoptilolite.

Maybe subsequent research working with these modifications separately and all together in column studies would determine the optimal composition of a zeolite mesh to enhance nutrient removal.

The complexity of aquatic systems demands special attention in the preparation of materials and the selection of conditions for water purification. Further research should be focused on the experimentation with organics and other ion competitors; that is to say, working with real sewage instead of synthetic wastewater.



Zeolitic materials showed varying ion selectivity and competitive adsorption for multi component system. This behavior has presented a difficulty while approximating the total mass of nutrients recovered in every loading cycle. Special attention must be paid if more substances are to intervene in the process.

Influence of flow rate is a limiting factor in the performance of the proposed solution. A slow, constant flow rate is needed to increase the ion exchange. Many problems in this particular aspect were faced during the experimentation. A possible explanation is that the density difference between water from the backwash and sodium hydroxide solution may impede a regular flow. Once all the remaining water exited the column, the basic solution could flow constantly.

Natural zeolites are low cost materials for water and wastewater treatment. However, there are several topics which delimit their economic feasibility at full scale. One is that modification with inorganic metallic salts is needed to remove phosphate, thus increasing the total cost of the material. Another is that the concentrated $\text{NH}_4\text{-PO}_4\text{-Na}$ brine solution from the regeneration stage, which is a basic solution loaded with nutrients, must be treated because it cannot be disposed directly into the environment.

Also, water treatment with ion exchange and adsorption techniques does not substitute other water treatment stages. Preliminary stage, for instance, is necessary because of human obstinacy to use water as a waste dump. Cigarettes' filters, packaging plastics, hygienic products and many other residues are constantly removed from sewage before starting the water treatment itself. This stage that consumes a lot of energy and resources could be easily removed if human being was more conscious of its role in Earth's systems.

Nevertheless, applications in agriculture and gardening exist for the nitrogen and phosphorus recovered; mainly as fertilizers. Subsequent research should be aimed to the study of other regeneration methods in purpose of achieving a low-cost fertilizer.

Global tendency is to guarantee water resources for supply and quality of water within aquatic systems. The proposed cost-effective technique promotes the recovery of nutrients, thus obtaining a potential fertilizer application very attractive to investors and stakeholders. The fact that both nutrients can be recovered from the clinoptilolite makes this procedure environmental friendly since using them for agricultural purposes will decrease human consumption of oil-based fertilizers.

REFERENCES

- [1] A. Tobiesen, "Growth rates of *Heterophrys marina* (Heliozoa) on *Chrysochromulina polylepis* (Prymnesiophyceae)," *Ophelia*, vol. 33, pp. 205–212, 1991.
- [2] E. Impact and A. Report, "Review of Historical Incidents Database," pp. 1–3.
- [3] J. N. Galloway and E. B. Cowling, "Reactive nitrogen and the world: 200 years of change.," *Ambio*, vol. 31, pp. 64–71, 2002.
- [4] J. N. Galloway, F. J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. Cleveland, P. Green, D. M. Karl, A. F. Michaels, J. H. Porter, A. Townsend, and C. Vörösmarty, "Global Nitrogen Cycle – Review Article (," pp. 1–69.
- [5] V. H. Smith, G. D. Tilman, and J. C. Nekola, "Eutrophication: Impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems," in *Environmental Pollution*, 1998, vol. 100, pp. 179–196.
- [6] A. Rahmani, M. Samadi, and H. Ehsani, "Investigation of clinoptilolite natural zeolite regeneration by air stripping followed by ion exchange for removal of ammonium from aqueous solutions," *Iran. J. ...*, vol. 6, no. 3, pp. 167–172, 2009.
- [7] D. Paredes, P. Kusch, T. S. a. Mbvette, F. Stange, R. a. Müller, and H. Köser, "New Aspects of Microbial Nitrogen Transformations in the Context of Wastewater Treatment – A Review," *Eng. Life Sci.*, vol. 7, no. 1, pp. 13–25, Feb. 2007.
- [8] D. S. Baldwin, "Reactive 'organic' phosphorus revisited," *Water Res.*, vol. 32, pp. 2265–2270, 1998.
- [9] G. Hanrahan, T. M. Salmassi, C. S. Khachikian, and K. L. Foster, "Reduced inorganic phosphorus in the natural environment: Significance, speciation and determination," *Talanta*, vol. 66, pp. 435–444, 2005.
- [10] G. K. Morse, S. W. Brett, J. A. Guy, and J. N. U. Lester, "Review□: Phosphorus removal and recovery technologies," 1998.
- [11] H. B. Dharmappa, A. Hasia, and P. Hagare, "Water treatment plant residuals management," in *Water Science and Technology*, 1997, vol. 35, pp. 45–56.
- [12] A. L. Clarke, D. J. Conley, N. J. Anderson, and E. Andre, "Long-term trends in eutrophication and nutrients in the coastal zone," vol. 51, pp. 385–397, 2006.
- [13] S. Yeoman, T. Stephenson, J. N. Lester, and R. Perry, "The Removal of Phosphorus During Wastewater," vol. 49, 1988.
- [14] DHV Consulting Engineers "Crystallisation technique" p031-035.pdf,".
- [15] D. Mara, N. Horan, C. H. Wong, G. W. Barton, and J. P. Barfor, *Handbook of Water and Wastewater Microbiology*. 2003, pp. 427–439.
- [16] C. Fux, K. Lange, A. Faessler, P. Huber, B. Grueniger, and H. Siegrist, "Nitrogen removal from digester supernatant via nitrite--SBR or SHARON?," *Water Sci.*



- Technol.*, vol. 48, pp. 9–18, 2003.
- [17] A. A. Babaei, R. Azadi, N. Jaafarzadeh, and N. Alavi, "Application and kinetic evaluation of upflow anaerobic biofilm reactor for nitrogen removal from wastewater by Anammox process.," *Iranian J. Environ. Health Sci. Eng.*, vol. 10, no. 1, p. 20, Feb. 2013.
- [18] W. Verstraete and S. Philips, "Nitrification-denitrification processes and technologies in new contexts," in *Environmental Pollution*, 1998, vol. 102, pp. 717–726.
- [19] K. A. Third, A. O. Sliemers, J. G. Kuenen, and M. S. Jetten, "The CANON system (Completely Autotrophic Nitrogen-removal Over Nitrite) under ammonium limitation: interaction and competition between three groups of bacteria.," *Syst. Appl. Microbiol.*, vol. 24, pp. 588–596, 2001.
- [20] U. van Dongen, M. S. Jetten, and M. C. van Loosdrecht, "The SHARON-Anammox process for treatment of ammonium rich wastewater.," *Water Sci. Technol.*, vol. 44, pp. 153–160, 2001.
- [21] V. Thomas, J.-F. Loret, M. Jousset, and G. Greub, "Biodiversity of amoebae and amoebae-resisting bacteria in a drinking water treatment plant.," *Environ. Microbiol.*, vol. 10, pp. 2728–2745, 2008.
- [22] D. Mara, N. Horan, C. H. Wong, G. W. Barton, and J. P. Barfor, *Handbook of Water and Wastewater Microbiology*. 2003, pp. 427–439.
- [23] T. Clark, T. Stephenson, and P. A. Pearce, "e r g a m o n IN A BIOLOGICAL AERATED FILTER," 1997.
- [24] F. Helfferich and M. S. Plesset, "Ion Exchange Kinetics. A Nonlinear Diffusion Problem," *J. Chem. Phys.*, vol. 28, p. 418, 1958.
- [25] V. J. Inglezakis, "The concept of 'capacity' in zeolite ion-exchange systems," *J. Colloid Interface Sci.*, vol. 281, pp. 68–79, 2005.
- [26] F. Helfferich, "Ion-Exchange Kinetics," *J. Phys. Chem.*, vol. 69, pp. 1178–1187, 1965.
- [27] IUPAC, "IUPAC Gold Book," *Glossary for chemists of terms used in biotechnology (IUPAC Recommendations 1992, 1992)*. [Online]. Available: <http://goldbook.iupac.org/B00663.html>.
- [28] S. Wang and Y. Peng, "Natural zeolites as effective adsorbents in water and wastewater treatment," *Chem. Eng. J.*, vol. 156, no. 1, pp. 11–24, Jan. 2010.
- [29] C. Baerlocher, L. McCusker, and D. Olson, *Atlas of zeolite framework types*, vol. 12. 2007, pp. 5170–94.
- [30] K. Margeta, N. Z. Logar, M. Šiljeg, and A. Farkaš, "Natural Zeolites in Water Treatment – How Effective is Their Use," 2013.
- [31] B. Bogdanov, D. Georgiev, K. Angelova, and K. Yaneva, "Natural Zeolites: Clinoptilolite Review," *Economics and Society development on the Base of Knowledge*. 2009.

- [32] A. Hedström, "Ion Exchange of Ammonium in Zeolites: A Literature Review," *Journal of Environmental Engineering*, vol. 127, pp. 673–681, 2001.
- [33] O. Lahav and M. Green, "Ammonium removal using ion exchange and biological regeneration," *Water Res.*, vol. 32, pp. 2019–2028, 1998.
- [34] M. Sprynskyy, M. Lebedynets, A. P. Terzyk, P. Kowalczyk, J. Namieśnik, and B. Buszewski, "Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions.," *J. Colloid Interface Sci.*, vol. 284, no. 2, pp. 408–15, Apr. 2005.
- [35] S. Kurajica, V. Vanc, Ā. Ina, Ā. Ic, and M. Roz, "AMMONIACAL NITROGEN REMOVAL FROM WATER BY TREATMENT WITH CLAYS AND ZEOLITES," vol. 34, no. 14, 2000.
- [36] A. Farkaš, M. Rožić, and Z. Barbarić-Mikočević, "Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia," *J. Hazard. Mater.*, vol. 117, pp. 25–33, 2005.
- [37] Y. Wang, K. H. Tng, H. Wu, G. Leslie, and T. D. Waite, "Removal of phosphorus from wastewaters using ferrous salts – A pilot scale membrane bioreactor study," *Water Res.*, vol. 57, pp. 140–150, Jun. 2014.
- [38] J. Lu, H. Liu, X. Zhao, W. Jefferson, F. Cheng, and J. Qu, "Phosphate removal from water using freshly formed Fe-Mn binary oxide: Adsorption behaviors and mechanisms," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 455, pp. 11–18, 2014.
- [39] M. Rožić, Š. Cerjan-Stefanović, S. Kurajica, M. R. Maëefat, K. Margeta, and A. Farkaš, "Decationization and dealumination of clinoptilolite tuff and ammonium exchange on acid-modified tuff," *J. Colloid Interface Sci.*, vol. 284, pp. 48–56, 2005.
- [40] B. A. Hedstro, "I ON E XCHANGE IN Z EOLITES□: A L ITERATURE R EVIEW," no. August, pp. 673–681, 2001.
- [41] M. E. Davis and R. F. Lobo, "Zeolite and molecular sieve synthesis," *Chem. Mater.*, vol. 4, pp. 756–768, 1992.
- [42] N. S. Bolan, C. Mowatt, D. C. Adriano, and J. D. Blennerhasset, "Removal of Ammonium Ions form Fellmongery Effluent by Zeolite," *Commun. Soil Sci. Plant Anal.*, vol. 34, pp. 1861–1872, 2003.
- [43] M. Sarioglu, "Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite," *Sep. Purif. Technol.*, vol. 41, no. 1, pp. 1–11, Jan. 2005.
- [44] L. Lin, C. Wan, D.-J. Lee, Z. Lei, and X. Liu, "Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite," *Sep. Purif. Technol.*, vol. 133, pp. 351–356, Sep. 2014.
- [45] A. Demir, A. Günay, and E. Debik, "Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite," vol. 28, no. 3, pp. 329–336, 2002.
- [46] E. Marañón, M. Ulmanu, Y. Fernández, I. Anger, and L. Castrillón, "Removal of ammonium from aqueous solutions with volcanic tuff," *J. Hazard. Mater.*, vol. 137,



- pp. 1402–1409, 2006.
- [47] M. J. Jiménez-Cedillo, M. T. Olguín, C. Fall, and A. Colín, “Adsorption capacity of iron- or iron-manganese-modified zeolite-rich tuffs for As(III) and As(V) water pollutants,” *Appl. Clay Sci.*, vol. 54, pp. 206–216, 2011.
- [48] J. J. Shea, “Handbook of Instrumental Techniques for Analytical Chemistry,” *IEEE Electr. Insul. Mag.*, vol. 14, 1998.
- [49] H. Company, “Ammonia Gas Sensing Combination Electrode,” 2001.
- [50] W. E. Federation, “Standard Methods for the Examination of Water and Wastewater Standard Methods for the Examination of Water and Wastewater,” no. 1, 1999.
- [51] J. W. Friend, “Catalonia,” pp. 1–100, May 2012.
- [52] C. Town, “196 5.1.3,” no. 2, pp. 196–203, 1986.

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