Chapter 5

Zeolites for the nutrient recovery from wastewater

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Abstract

The recovery of nitrogen (N) and phosphorus (P) from alternative sources and their reuse to increase soil fertility is of paramount importance due to the increased demand for food resulting from the growing world population and the depletion and unbalanced global distribution of phosphorus mines. Zeolites are suitable materials for the adsorption of nutrients from treated municipal wastewater. Zeolites are microporous crystalline tectosilicates with a net negative charge balanced by exchangeable cations. They are commonly used for ammonium recovery, although several studies have shown simultaneous recovery of ammonium and phosphate from wastewater using modified zeolites. Once the zeolites are exhausted, they can be regenerated thus being reused for ammonium recovery, or to be applied to the soil as slow-release fertilizers.

Keywords: ammonium adsorption, phosphorus recovery, resource recovery regeneration, enriched zeolites, biochemical and chemical soil properties

1. Introduction

To meet the growing food demand of the world population, excessive use of chemical fertilisers is occurring to improve soil fertility and crop production. The excessive use of chemical fertilisers is not economically and environmentally sustainable. Indeed, from one hand, due to the increasing demand of fertilisers is rising their costs whereas, on the other hand, the accumulation of fertilisers in wastewaters is altering the homeostasis of the ecosystems thus causing serious damages to human health [1,2]. The recovery of nutrients, such as nitrogen (N) and phosphorus (P), from wastewaters is a good option to counteract both economic and environmental issues raised by the excessive use of fertilisers [3]. Adsorption is among the most widely used methods for nutrient recovery from wastewaters due to its efficiency and simplicity. The choice of appropriate adsorbent materials is a key issue for ensuring high performance and low costs of the process [4]. Over the years, several materials have been studied to absorb nutrients from wastewaters. Zeolites, both natural and modified, have attracted great attention due to their relevant specific capacity, selectivity, safety, and stability [5]. However, considering that in municipal effluents the inorganic P exists as the anionic forms of dihydrogen or monohydrogen phosphates ($H_2PO_4^-$ and HPO_4^{2-}; respectively) and N in both cationic (ammonium, NH_4^+) and anionic (nitrate, NO_3^-) form [6], natural zeolites can be only used for the direct recovery of NH_4^+. This derives from the chemical properties of zeolites, which consist of an aluminosilicate structure comprising a tridimensional tetrahedral arrangement of silicon cations (Si_4^+) or aluminium cations (Al_3^+) each surrounded by four oxygen anions (O_2^-). Some Si_4^+ ions are substituted by Al^{3+} ions, resulting in the imbalance of net negative charges in the structure of the tectosilicate [7].

Thus, thanks to their negative charges, zeolites can adsorb cations from the surrounding environment. In recent years, also P recovery by zeolites has been studied, focusing on the possibility of simultaneous N and P recovery. In fact, being the NH_4^+ adsorption from wastewaters by zeolites mainly based on exchange reactions, other cations are released into the solution, thus potentially leading to synchronous phosphate (PO_4^{3-}) precipitation [8]. The simultaneous recovery of N and P by zeolites can be also obtained by improving their affinity for PO_4^{3-} through their activation by aluminium salt solution [9]. Once recovered, the nutrients can be reused as a soil fertiliser within a circular economy vision [10]. In fact, it is possible to reuse both the nutrients desorbed from the zeolites after regeneration through the production of fertilisers or by applying the enriched zeolites directly to the soil. This second option of reusing the recovered nutrients is possible because zeolites are considered one of the natural inorganic soil conditioners widely used to improve the physical and chemical properties of the soil; moreover, when enriched, they are able to retain the most important nutrients for plants, making them available when they are required by the plants themselves thus acting as a slow-release fertilizer (De Campos Bernardi et al., 2013).

In the present chapter, firstly, the chemical composition, structure and properties of zeolites are reported and, thereafter the differences between natural and synthetic zeolites and their main fields of use are discussed. Finally, the possibility of using zeolites for the recovery of nutrients from wastewaters, the mechanisms that allow the nutrient adsorption, the methods of regeneration and reuse of recovered nutrients and enriched zeolites in agriculture are discussed.

2. Structure and chemical composition of zeolites

2.1 Chemical composition and structure of Zeolites

The name "zeolite" was proposed by the Swedish mineralogist Crönstedt in 1756. He observed that these minerals (especially stilbite) emit bubbles due to the release of interstitial water when heated, without changing the aluminosilicate structure. This characteristic gives rise to the name Zeolite from ζέω (boil) e λίθος (stone) in Greek [12].

Zeolite is a crystalline hydrated aluminosilicate. Its basic structure consists of an interconnected tetrahedral arrangement in which silicon (Si^{4+}) and aluminium (Al^{3+}) cations placed in the centre of each tetrahedron coordinate four oxygen anions (O^{2-}) placed at the vertexes. Each oxygen atom is shared by two tetrahedra thus connecting them and resulting in inorganic macromolecules with a unique three-dimensional framework. The resulting Si (or Al) to O ratio is 1:2. The isomorphic substitutions of some Si^{4+} by Al^{3+} ions determine a net negative charge in the structure of the zeolites, arising from the difference in formal valence between the tetrahedra $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ and normally found on one of the oxygen anions connected to an aluminium cation. Such negative charges are balanced by alkaline earth metals, such as sodium (Na^+), potassium (K^+) or calcium (Ca^{2+}); also, lithium (Li^+), magnesium (Mg^{2+}), strontium (Sr^{2+}) and barium (Ba^{2+}) can be found in some zeolites [13], beyond water. These ions are found on the external surface of zeolite, bound with the aluminosilicate structure by weaker electrostatic bonds [14,15]. The zeolite framework contains open cavities in the form of pores, channels and cages that host the water molecules and cations, but only those of appropriate molecular size to fit into the pores are admitted. The framework can be interrupted by (OH, F) groups; these occupy the vertexes of a tetrahedron and are not shared with adjacent tetrahedra [16].

The chemical composition of a zeolite can hence be represented by a formula of the type:

$$|M_{x/n,}\,(H_2O)_z|[AlO_2)_x\,(SiO_2)_y]\ (1)$$

where M is an extra-framework cation with valence n, and x, y are pertinent values of molar concentrations of Al and Si in the zeolite framework, and z is molar concentration of H_2O [17].

2.1.1 Primary and Secondary Building Units of Zeolites

The crystal structure of zeolite is usually divided into Primary Building Unit (PBU) and Secondary Building Unit (SBU). The PBU framework is a TO_4 tetrahedron, where the central T-atom is usually Si or Al, and the outer atoms are O.

****Insert Fig. 5-1.HERE****

The simple geometric shape is formed by the interconnection between two or more tetrahedra. Therefore, the formed link is called the Secondary Building Unit (SBU). The complexity of SBU starts with simple rings, double rings, polyhedra, and even more complex units linked together. The unit cell of zeolite always contains an integer number of SBUs [18].

****Insert Fig. 5-2.HERE****

In addition to the above-mentioned PBU and SBU, the zeolite can also contain other components, such as prisms and cages, which are called Composite Building Units (CBU). The cage is defined as a polyhedron whose largest ring is not enough to allow molecules larger than water to pass through. They appear in several different framework structures and can be useful in identifying relationships between framework types [7]. CBUs are therefore a grouping of finite and infinite building units and involve various forms, such as SBUs, polyhedra such as the sodalite unit (β cavity) and chains of tetrahedra [18,19]. To date, 253 different zeolite framework types have been identified in natural or synthetic zeolites, and the International Zeolite Association (IZA) has assigned a three-letter code for each; this short note is used to describe the pore system [20]. Each porous network is characterized by the direction of the channel, the number of atoms in the pore, and the crystallographic free diameter of the pore (in

Å), the number of asterisks indicating whether the system is one-, two- or three- dimensional [21].

2.1.2 Pores, cages, and channels

The structure of zeolites is characterised by tetrahedra bond in different ways thus producing different types of tetrahedral structures. Each tetrahedron is composed of TO_4 (T=Si, Al and P, among others). This structure contains open cavities in the form of pores, channels, and cages. These are usually occupied by H_2O molecules, and by extra-framework alkali metal ions or organic amines which can be removed during the ion exchange process. The pores in zeolites are classified according to their diameter into micropores, mesopores or macropores (Table 1). A cage is a polyhedral pore whose faces are so narrow that cannot host species larger than a water molecule, while a cavity is the pore with at least one face large enough to host a water molecule. In practice, a cage has no face larger than 6 rings (a ring is usually referred to as a cycle of tetrahedrally coordinated silicon or aluminium and oxygen atoms), whereas a cavity has at least one. Channels, that are infinitely large in one dimension, are large enough to allow the spread of host species (i.e., larger than six rings).

The internal cages and channels of zeolites depend on the specific arrangement of the SBUs and are organised according to a hierarchical structure, which gives zeolites adsorption, catalysis, and ion exchange properties [22–26].

****Table 1****

2.1.3 Cation Exchange Capacity of Zeolites

Natural zeolites have different properties, one of these is the cation exchange capacity (CEC), that represents the theoretical quantity of cations that can be exchanged per mass of zeolite at a given pH. The CEC is reported to range between 60 and 230 $cmol_{(+)}\ kg^{-1}$ and depends on the amount of negative charge resulting from the isomorphic substitution of Si by Al [27]. Generally, the process takes place with the uptake of one or more cationic species, that in the natural zeolites are usually represented by: Na^+, K^+, Mg^{2+}, and Ca^{2+} [7], and the simultaneous displacement of an equivalent amount of one or more other cationic species [28].

The cation exchange process may be presented by the following equation:

$$Z_A {B_{(z)}^{Z}}^{+B} + Z_B {A_{(s)}^{Z}}^{+A} \leftrightarrow Z_A {B_{(s)}^{Z}}^{+B} + Z_B {A_{(z)}^{Z}}^{+A} \quad (2)$$

where: z_A and z_B represent the A and B exchangeable ion charges and the coefficients (z) and (s) refer to zeolite and to aqueous solution, respectively. The reaction proceeds until equilibrium is attained [29]. Due to such property, zeolites have been found to be a good adsorbent of gases and liquids materials thus being useful to separate them from the surrounding environment. Furthermore, the cation exchange has been identified as the mechanism for NH_4^+ adsorption.

2.1.4 Selectivity of Zeolites

Selectivity is defined as the affinity or preference of certain types of materials for certain ions [30]. It depends on the interaction of materials and ions in relation to ionic radius (molecular sieve), ion hydration energy and electrostatic bond energy [31].

Shape selective adsorption is a process that separates molecules based on inclusion or exclusion from specific zeolite pores. This phenomenon is possible because the large structural cavities and the entry channels leading into them contain water molecules, which form hydration spheres around exchangeable cations. On removal of water by heating at 350–400°C, small molecules can pass through entry channels, but larger molecules are excluded—the so called ‘‘molecular sieve’’ property of crystalline zeolites [32]. The ion exchange selectivity usually depends on the hydrated ionic radius of cations, i.e. on the number of water molecules that surrounds the cations. An example of cation selective sequence in natural zeolite is, as reported by Sarioglu [33]:

$$K^+ > NH_4^+ > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} \quad (3)$$

3. Natural Zeolites and Synthetic Zeolites

Many zeolites are found naturally as minerals and are mined extensively in many parts of the world. Others are synthetic and manufactured commercially for specific uses or produced by scientists trying to improve their chemistry.

3.1. Natural Zeolites

Natural zeolite is found all over the world. Although there are no accurate data on the total amount of zeolites, it is reported that they occur on all continents with different mineral concentrations and types [34]. Natural zeolites are produced by the interaction of volcanic rock and volcanic ash with alkaline groundwater, usually related to mountainous areas such as the Caucasus and Balkans. Deposits have also been found in the Himalayas, near the Gulf of Mexico, Switzerland, and the United States [29,35]. They can occur in the crystalline form found in igneous and metamorphic rocks, as well as in smaller-diameter crystal grains accumulated in sedimentary rocks [30,36]. Indeed, the performance of a natural zeolite depends on several factors including structure, size and shape, the charge density of the anionic framework, and the ionic charge and concentration of the external electrolyte solution [31].

Among all the natural zeolites discovered (over 60), only six are abundant in natural deposits worldwide: Analcime (ANA), Chabazite (CHA), Clinoptilolite (HEU), Erionite (ERI), Mordenite (MOR) and Phillipsite (PHI). The most common natural zeolite can be purchased at very low cost, making it an economical alternative to synthetic zeolite [32].

Due to its characteristics, natural zeolite is used as soil amendment, animal feed additives, ion exchangers in industrial, agricultural, and municipal wastewater treatment, Sr and Cs radioisotope absorbents in the nuclear industry, and nuclear accident clean-up (Chernobyl), soil replacement in horticulture, veterinary and medical applications [33]. Natural zeolites are used for wide applications due to its low cost and availability, on the other hand, the industrial application of natural zeolite is limited because, as mentioned above, its properties strictly depend on its crystal structure. The main disadvantage is that the channel diameter is too small to absorb larger gas molecules and organic compounds [34]. Furthermore, zeolites, due to the very different conditions under which they are formed in nature, are rarely pure but contaminated to varying degrees by other minerals, metals, quartz, or other zeolites [7].Therefore, natural zeolite is excluded from many important commercial applications where uniformity and purity are essential [35]. It is important to clarify that zeolite deposits are non-renewable resources.

3.1.1 Most important Natural Zeolites

Clinoptilolite-Heulandite

Clinoptilolite is one of the most common natural zeolites. It is easily obtained from mines and is suitable for use as an adsorbent due to its characteristics. Although many researchers classify it as Heulandite, its Si/Al ratio and thermal stability make it different from Heulandite ($4 \leq$ $Si/Al < 5.2$ and $Si/Al < 4$ at 750–800 and 450–550 °C, respectively [35,37]. The Heulandite group minerals are classified according to the main exchangeable cations as follows: K-, Na-, Ca- and Sr-heulandite and K-, Na- and Ca-clinoptilolite [18,38]. The IZA identification code is HEU and the chemical formula is $(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O)$.

Chabazite

Chabazite is a zeolite with the chemical formula $CaAl_2Si_4O_{12} \cdot 6H_2O$, which consists of a hydrated calcium and aluminium silicate contained in white to yellow or red creamy glass crystals. It has small pores with an effective pore size of about 4 Å and a good cation exchange capacity. Nowadays, due to their unique properties, chabazites are widely used to remove trace gases and as a water softener [39,40]

Phillipsite

The name Phillipsite is derived from the name of the English mineralogist William Phillips. It is a mineral belonging to the group of zeolites, potassium and calcium silicate, with the formula $(K,Na,Ca)_{1}$-$_{2}(Si,Al)_8O_{16}\cdot 6(H_2O)$. It crystallizes in the monoclinic system and forms pseudo-rhombic, colourless, brittle and twin crystals. It is often found in leucitic and tefritic rocks, and less frequently in basalts. Major deposits of phillipsite occur at Aci Castello in Sicily and at Capo di Bove near Rome in Italy [41].

3.2 Synthetic Zeolites

Synthetic zeolites, like natural zeolites, have different structures and properties. However, in contrast to the natural zeolites, the synthetic ones being obtained under controlled conditions, have standardized and pure form (e.g., pores diameters are known), and better adsorption performance and cation exchange capacity thus being more useful for industrial applications[42]. Synthetic zeolite properties can be improved by physical and chemical treatments (hydrothermal synthesis, molten salt method, fusion method, alkali activation, microwave-assisted synthesis, synthesis by dialysis [42] thus increasing the hydrophilicity/hydrophobicity towards many ions or organic adsorbents [36,43]. Considering the industrial importance of zeolite, and due to its structural complexity and inherent scientific interest in its chemistry, a lot of effort has been made for zeolite synthesis [44]. The history of artificial zeolite can be traced back to the levynite produced in the laboratory claimed by St.

Claire Deville in 1862. However, the zeolite synthesis as known today originated from Richard Barrer and Robert Milton. They showed that the final product can be obtained by heating the aluminosilicate raw material in the presence of an alkaline solution within a few hours or days, depending on the type of raw material and the process conditions (temperature, pressure) [45].

Among all the methods, hydrothermal method is effective, cheap, easiest, and commonly adopted by IZA (International Zeolite Association). It usually takes place in an alkaline (high pH) medium, in which an amorphous reagent containing silica and aluminium is mixed with a cation source. This aqueous mixture is then heated in an autoclave at temperatures above 100°C. Initially, after raising the synthesis temperature (induction period), the reactants maintain an amorphous composition and following this it is possible to detect the products, i.e. the crystalline zeolites that have formed. Subsequently, all the amorphous materials are replaced by a single and equal mass of zeolite crystals, which are recovered by a process of filtration, washing, and drying [46,47].

3.2.1 Most important Synthetic Zeolites

More than 150 zeolites have been synthesized, the most common are zeolites A (commonly used as a laundry detergent), X and Y (two different types of faujasites, used for catalytic cracking), ZMS-5 (a branded name for pentasil-zeolite).

Zeolite A

Zeolite A has a framework structure called Linde A (LTA), which consists of sodalite (SOD) cages connected by four rings and has a Si/Al ratio of 1:1. The SOD units are combined to produce an alpha cage with a diameter of 11.4 Å (a large cavity in the centre of the structure), and two channel systems are connected to allow movement of Na^+ ions and water molecules [45]. It is characterized by the formula $|(Na_{12}^+(H_2O)_{27}|_8[Al_{12}Si_{12}O_{48}]_8$.

Zeolite X and Zeolite Y

Zeolite X and zeolite Y belong to the family of aluminosilicate molecular sieves with faujasite type structure (FAU). The chemical formula is $|(Ca,Mg,Na_2)_{29}\ (H_2O)_{240}|[Al_{58}Si_{134}O_{384}]$– FAU (IZA). Faujasite is a rare zeolite, although its synthetic counterparts Linde X and Linde Y are widely used as adsorbents and catalysts. The difference between zeolite X and zeolite Y is determined from their Si/Al atomic ratio (usually between 1 and 1.5 for X and higher for Y zeolite) [48].

Zeolite ZMS-5

ZMS-5 is the prototype high silica zeolite ZSM-5, which was discovered in 1972. ZSM-5 belongs to the molecular pentasil (MFI) family, and its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ (n is between 0 and 27).   The catalyst is called ZSM-5 because its pore size is 5Å (Angstroms) and it has a Si/Al ratio of more than five [49].

Table 2

4. Applications of Zeolites

Due to its characteristics, zeolite is one of the most important inorganic cation exchangers used in catalysis, agriculture, water and wastewater treatment, as well as in industrial applications, nuclear waste, animal feed additives and biochemical applications [50].

Catalysis

In terms of value, the consumption of zeolite catalysts accounts for about 27% of the global zeolite market, but this percentage may increase [51]. In fact, zeolites are used as catalysts in the oil refining and petrochemical industry because of their superiority performance, stability and selectivity in large conversion and upgrade processes compared to their amorphous equivalents. The action of catalysts takes place within the pores of zeolites selected on the basis of their unique characteristics of structure, morphology and composition [52,53]. The compatibility of the zeolite as a catalyst with the specific reaction can be considered the key to the economic success of this method [54]. Two important processes involving the use of zeolite as a refinery catalyst are fluid catalytic cracking (mainly gasoline production process) and hydrocracking (mainly middle distillate production process) [55].

Agriculture

Zeolite is commonly used in agriculture to improve physical and chemical properties of the soil, such as water and nutrient retention capacity, electrical conductivity, soil aggregation, permeability, infiltration rate and saturated hydraulic conductivity [56]. This is because of the unique characteristics of zeolites such as high pore volume, low bulk density and cation exchange capacity [57].Ravali et al. [58]found the application of 7.5 t ha^{-1} of zeolite, sieved at 2 mm, increases CEC by 37% compared to the untreated soil. CEC increase is of paramount importance because in turn affects nutrient retention capacity. MacKown and Tucker [59] found that the application of zeolites reduces nitrate leaching in sandy soils probably due to a decrease of the nitrification process. Indeed, clinoptilolite is able to slow down the NH_4^+ oxidation by nitrifying bacteria [56]. With regard to the effect of zeolite on water infiltration rate in soils, Xiubin and Zhanbin [60], in a study conducted under laboratory and field conditions, observed that natural mordenite with a particle size lesser than 0.25 mm, increased infiltration by 7-30% on gentle slope soils and more than 50% on steep slope soils. In addition, they found that soil moisture could increase by 0.4-1.8% in extreme drought conditions, and by 5-15% in general situation. It is undoubtedly that zeolite ameliorate physical and chemical properties of soils as demonstrated by the larger number of studies. However, more studies are needed to elucidate the effect of the soil quality improvement on crop grown and productivity.

Fig. 5.1.HERE

Industrial Wastewater treatment

Heavy metals are classified as metal elements with a relatively high density (> 5 g cm^{-3}) that are hazardous and harmful to human health, including impaired growth and development, cancer, organ damage, nervous system damage, and even, in extreme cases, death. Industrial wastewaters containing heavy metals comes from different industries [36]. A large number of elements fall into this category, but the most environmentally relevant elements are Cd, Cr, Cu, Ni, Zn, Pb and Hg [61]. Natural zeolites as adsorbents for heavy metals have attracted great interest due to their valuable ion exchange capacity. In fact, they can exchange or adsorb various cations such as cesium (Cs) and strontium (Sr), and heavy metals such as cadmium (Cd), lead (Pb), nickel (Ni), manganese (Mn), zinc. (Zn), chromium (Cr), iron (Fe) and copper (Cu) [62].

5. Use of Zeolite for nutrients recovery

One of the main fields of use for zeolites is the recovery of nutrients from wastewaters. This capacity depends on the negative charges of the zeolites, which allows them to adsorb the cations from the surrounding environment. They have been used mainly to recover NH_4^+ from wastewater as this is one of the cations for which zeolites have the greatest selectivity. In recent years, the use of zeolites is also being extended to the recovery of PO_4^{3-} from wastewaters, using modified zeolites.

5.1 Nutrients recovery mechanism

Over the years, several studies have been conducted to evaluate the application of zeolite in NH_4^+ adsorption, with a particular focus on operational capacity. The ability of zeolite to adsorb NH_4^+ depends on several factors such as initial NH_4^+ concentration, medium size, contact time and temperature [27,63]. Currently, the most used ion exchange media for NH_4^+ removal is the natural zeolite clinoptilolite (in the activated Na-form) which has been shown to have NH_4^+ an exchange capacity of 29 mg N-NH_4^+ g^{-1} in single NH_4^+ solutions and 23 mg N-NH_4^+ g^{-1} in treated wastewater simulating up-concentration effluent at pH 8 [64]. However, most of the latest research on NH_4^+ removal in the ion exchange process is limited to laboratory-scale analyses, and to the best of our knowledge, only one full-scale application has been performed worldwide in the last half century. This is the Battelle Northwest/South Tahoe Public Utility District treatment unit, created to protect the quality of the water of the Truckee River in California. This unit includes a 22,500 m^3 d^{-1} facility in California for the removal of NH_4^+ from domestic wastewater and is the only industrial facility using natural zeolite in the world [65]. However, unfortunately no data are available in literature regarding the performance of such full-scale treatment plant. The transition from batch testing to full testing is of great importance because allows to assess other parameters in the NH_4^+ adsorption by zeolite. For example, the mechanical strength of the medium that is considered to be the key characteristics to prevent the breakdown and disintegration of the medium during the ion exchange process. The mechanical strength of the zeolites refers to the resistance of the media to friction and compression. Friction resistance is correlated with turbidity measurements, following the principle that increasing turbidity was related to media disintegration over time. This parameter was recently studied by Guida et al.[66]. In their batch study, six synthetics (named progressively from Zeolite1 to Zeolite6), one natural (clinoptiolite), and one engineered (Zeolite-N) zeolites were analysed. They observed that after the first 2 hours of stirring, the disintegration values ranged from 17.5 NTU h^{-1} to 2.7 NTU h^{-1}. Clinoptilolite showed the best friction resistance together with other two natural zeolites. To evaluate compression, the different zeolites were subjected to increasing load pressure and recording the force at the breaking point. Zeolite-N resisted to a pressure up to 7.9 N before fracture, synthetic zeolites 4 and 5 resisted a load up to 11.3 N and 16.5 N, respectively, for the other synthetic zeolites the average load before fracture was between 3.9-5.7 N. Among all, clinoptilolite showed the highest compressive strength with a loading pressure of 38.6 N before fracture. This variability in the mechanical strength of synthetic zeolites was attributed to the difference in the manufacturing process (temperature, time, and furnace size during calcination), which could explain the higher strength of natural zeolite.

Recently, zeolites have been investigated also to recover PO_4^{3-} from wastewater. Natural zeolites usually have little or no affinity for anions such as PO_4^{3-} because of its net negative charge [67]. Therefore, natural zeolite may demonstrate only low adsorption capacity for PO_4^{3-} [68]. To overcome this limit, several studies have analysed the possibility to modify zeolites to improve their ability in recovering PO_4^{3-} from water. Onyango et al. [9] studied the removal of inorganic PO_4^{3-} from aqueous solutions by improving the affinity of zeolite for PO_4^{3-} through its activation by aluminium salt solution. In their study, they used the synthetic zeolite HSZ 330 HUD (Si/Al ratio: 2.75-3.25) and its Al^{3+}-activated form (Al HUD). Equilibrium and kinetic experiments were performed to investigate the effects of operating conditions such as adsorbent mass, solution pH, coexisting ions, and initial PO_4^{3-} concentration on the ability or rate of PO_4^{3-} adsorption by zeolites. Activated zeolite was prepared by adding 50 g of HUD to 1 L of 0.075 M aluminium sulphate solution, the mixture was stirred for 2 days and then washed several times with demineralized water to lower the electrical conductivity. Finally, the Al^{3+} -activated HUD zeolite was air-dried at room temperature for 2 days. The ability of the HUD and Al-HUD zeolites to remove PO_4^{3-} was tested by varying the masses of the zeolite at a fixed PO_4^{3-} concentration of 100 mg L^{-1}, at room temperature of 25°C and, pH of 5.7. Zeolite activated with Al^{3+} (Al-HUD) showed higher removal efficiency; indeed, 150 g of Al-HUD lowered the PO_4^{3-} concentration below 10 mg L^{-1}, whereas HUD zeolite was not able to low the PO_4^{3-} concentration below 20 mg L^{-1} under the same experimental conditions. Furthermore, it was observed that the efficiency of PO_4^{3-} removal by zeolite increased by increasing the mass of the adsorbent and decreasing the pH of the solution. Other studies have focused on the simultaneous recovery of N and P from wastewater by zeolite. In a study conducted by Karapinar [69], natural zeolite was studied in lab scale using a batch system to remove NH_4^+ and PO_4^{3-} in two steps. Specifically, zeolite with an average particle size of 13 μm was used as adsorbent for NH_4^+ and then as a seed material for the precipitation of calcium phosphate [$Ca_3(PO_4)_2$]. The Author found that zeolite and NH_4^+ did not affect the amount of calcium phosphate precipitated. On the other hand, phosphate precipitation increased with rising pH and was achieved at low super saturations (pH 6.9 – 7.5) through secondary nucleation and crystal growth. Thus, this study pointed out that zeolite can be appropriately used as an adsorbent/seed material for the removal of both NH_4^+ and PO_4^{3-} nutrients from wastewater. Lin et al. (2014) in their study for the first time used natural zeolite in batch and continuous tests to simultaneously remove P and N from orthophosphate and ammonium-nitrogen laden wastewaters with a pH range from 3–11. They used an unmodified Chinese natural zeolite formed from clinoptilolite-Na, heulandite, and quartz, with a specific surface area of 14.33 m^2 g^{-1}, sieved to 0.8-1.43 mm, with a CEC of 0.092 $cmol_{(+)}$ g^{-1}. They found that P removal was efficient only at pH > 9, decreasing from 102 to 14.5 mg L^{-1}. Moreover, when ammonium was also present, P removal was enhanced by about 60%. They suggested that ammonium was first adsorbed onto the zeolite via ion exchange to release Ca^{2+} ions from the zeolite lattice [70]. This ion exchange reaction was independent on the presence of P. Then the released Ca^{2+} ions precipitated the dissolved phosphate, which was greatly dependent on the concentration of ammonium.

More recently You et al. [71] investigated the performance of three synthetic Na-zeolites, modified in Ca- and Mg-zeolites, for the simultaneous removal and recovery of NH_4^+ and PO_4^{3-} from synthetic solutions, simulating wastewater treatment effluent. The simultaneous removal of NH_4^+ and PO_4^{3-} can occur through two mechanisms: 1. ion exchange and formation of calcium phosphate minerals in the case of Ca-zeolite, and 2. precipitation of struvite ($MgNH_4PO_4$) in the case of Mg-zeolite. Results suggested that the activation of Na-zeolite in calcium and magnesium forms improved the PO_4^{3-} adsorption capacity of zeolite. The maximum adsorption capacities obtained were 123 mg NH_4 g^{-1} and 119 mg PO_4 g^{-1} in an ammonium/phosphate binary system for Ca-zeolite, whereas Mg-zeolite adsorbed while 55 mg NH_4^+ g^{-1} and 60 mg PO_4^{3-} g^{-1}. However, the sorption process was faster for Mg-zeolites and the sorption mechanism that controls the overall process, for both zeolites, was diffusion into the particle.

5.3 Regeneration of Zeolites

Once saturated, the zeolite can be regenerated or used as slow-release fertilizer. Regeneration is the biggest obstacle to the widespread use of zeolite-based wastewater treatment on a large scale; indeed, it is estimated to account for up to 80% of the total operating cost of zeolite use, which is why it is necessary to develop a method that is economically feasible [65]. For this reason, it is crucial to assess the potential applicability of a zeolite for industrial or large-scale applications and to study the possibility of its regeneration in order to consider its use in multiple cycles. Regeneration allows the zeolite to be reused for several cycles until when the adsorption capacity decrease towards levels no more sustainable from an economic point of view. Regeneration can be carried out by various techniques such as chemical, acid, heating and biological regeneration [72]. However, the most used regeneration methods are chemical and biological ones. Chemical regeneration is commonly achieved using high strength ionic brines, e.g. aqueous sodium chloride (NaCl), where Na^+ ion replaces the NH_4^+ adsorbed liberating it into the liquid phase [65,73].

The desorption and regeneration are based on the following cation exchange equation [74]:

$$NH_4\text{-zeolite} + Na^+ \rightarrow Na\text{-zeolite} + NH_4^+ \quad (4)$$

The concentrated regenerating solution, after increasing its pH above 9.3 (pKa of the NH_4^+-NH_3 system), can be stripped from the air of its ammonia content and the brine can be recovered [75]. The NH_3 gas can be further absorbed into a solution of H_2SO_4 or HNO_3. In addition, the H_2SO_4 solution absorbed by NH_3 could be used as a fertilizer.

Widiastuti et al. [15] studied the desorption and regeneration of zeolite in a batch experiment using a 1% NaCl solution. Their results showed that the NH_4^+ desorption was up to 97% depending on contact time, zeolite loading, initial NH_4^+ concentration and pH of the solution and that the adsorption and desorption efficiency decreased by increasing the cycle numbers. In fact, the adsorption of NH_4^+ on the zeolites decreased from 4.49 mg g^{-1} in the first cycle to 3.71 mg g^{-1} in the third cycle, whereas the desorption decreased from 4.27 mg g^{-1} in the first cycle to and 3.57 mg g^{-1} in the third. However, although NH_4^+ is selectively adsorbed by zeolite, its desorption was sufficiently high following the treatment with NaCl that is the most widely used method mainly for the low cost of the NaCl. Also, Li et al. [76] carried out column experiments and batch tests to test the efficiency of Silicate-Carbon Modified Zeolite (SCMZ) in removing NH_4^+ from drinking water with a concentration ranging from 2.5 to 10 mg NH_4^+ L^{-1} and how this efficiency varies when regenerated by NaCl solution. They observed that the NaCl regeneration method had good regeneration capacities for NH_4^+ adsorption of SCMZ. Indeed, NH_4^+ adsorption capacity was 0.1117 mg L^{-1}, at the first regeneration cycle and 0.11047 mg L^{-1} at the third regeneration cycle, both values close to those of fresh SCMZs (0.1155 mg L^{-1}). Finally, Deng et al. [77] conducted both batch and column test to recover NH_4^+ from zeolite with NaCl solution at different pH (9-12) and salt concentration (20 to 160 g L^{-1}). In the batch study, they achieved 95% of regeneration efficiency after only 1 h at NaCl concentration of 80 g L^{-1}. Interestingly, the regeneration efficiency was 96% at the low NaCl at pH 12 in 2 h. Results from the column study, on the other hand, suggested that an optimum NaCl concentration for regeneration of exhausted zeolite determined in batch tests cannot represent that in continuous zeolite columns, due to different volumes. Indeed, at pH 9, the maximum RE was 76% at NaCl concentration of 160 g L^{-1}, while it was only 38% and 13%, respectively, at NaCl concentration of 80 and 20 g L^{-1}. The Authors [77] attributed the low regeneration efficiency of NH_4^+ in the continuous column compared with in batch studies to the small mass ratio of Na^+ to Zeolite-NH_4^+–N in the column during regeneration. Thus, based on results of Deng et al. [77] the maximum regeneration efficiency (85%) of zeolite in column test can be achieved within 2 h of reaction time at pH 12 using low NaCl dosages from 10 to 40 g of NaCl L^{-1}. Besides to NaCl, also other salts can be used to recover NH_4^+ from zeolite. Czárán et al. [78], for example, suggested KCl solution at pH ranging from 9 to 11 to regenerate zeolite. Indeed, KCl should be preferred to NaCl due to the much higher selectivity of clinoptilolite toward K^+ than Na^+; on the other hand, it is less used due to its cost. On the other hand, Metcalf et al. [79] recommended calcium hydroxide for the regeneration of zeolite, although this method waste time, energy, and chemical reagents, causing secondary pollution that requires further treatment.

The direct result of zeolite regeneration is the desorption of NH_4^+, which can be recycled and used for other purposes, such as fertilizer.

In some cases, however, if the aim is not to reuse the zeolite, it may be possible to desorb the nutrients without regenerating the zeolite itself. Cyrus and Reddy [80] proved that adsorbed NH_4^+ can be desorbed by washing the zeolite with water for 250 hours; however, a large amount of N (> 20%) is retained in the zeolite column. This experiment suggested that NH_4^+ enriched zeolite can be a suitable medium to slowly release N in the soil.

An alternative to the chemical regeneration is the biological regeneration, a two-mode process consisting of aerobic nitrification and further processing of NO_3^- products [81]. Biological regeneration occurs putting in contact the NH_4-zeolite with nitrifying bacteria. In this system, a solution containing cations is recirculated through the bed of zeolite to desorb NH_4^+ into the solution:

$$Z\text{-}NH_4^+ + Na^+ \leftrightarrow Z\text{-}Na^+ + NH_4^+ \quad (5)$$

The effluent containing the displaced NH_4^+ is then oxidized to NO_3^- by nitrifying bacteria in presence of oxygen.

$$NH_4^+ + 2O_2 \leftrightarrow NO_3^- + 2H^+ + H_2O \quad (6)$$

The NO_3^- brine, after a clarification process, is easy to dispose of or can be mixed with raw wastewater and denitrified into harmless N gas [82].

5.4. Reuse of enriched Zeolites

Zeolite cannot be regenerated indefinitely. After a certain number of regeneration cycles, they are exhausted. Several studies have been performed with the purpose of evaluating after how many cycles of use the ammonium exchange capacity (AEC) of regenerated zeolites is significantly reduced, compared to virgin zeolite. Deng et al. [77] evaluated the AEC of four natural zeolites, breakthrough time, in a continuous zeolitic column fed with anaerobic membrane bioreactors permeates and NH_4Cl solution to optimize the operating conditions and evaluate the effect of competitive cations on the AEC. Regeneration was performed using 1% NaCl solution at pH 12. They observed that the AEC decreased by 13% after the first cycle (from 3.1 to 2.7 mg N g^{-1} zeolite). After the third and fourth cycles the AEC was reduced by 12.5% compared with virgin zeolite. After the fifth cycle, the AEC started to decrease until it reaches a plateau of about 1.8 mg N g^{-1} zeolite after the eighth cycle. Thus, the regeneration efficiency of the first five cycles were almost constant at 84% and then slowly decreased to about 70%. In another study, Guida et al. [66] evaluated the regeneration capacity of zeolites over multiple cycles using wastewater. Of the eight zeolites analysed, including six synthetics (Zeolite1, Zeolite2, Zeolite3, Zeolite4, Zeolite5, Zeolite6), one natural (clinoptilolite), and one engineered (Zeolite-N), the latter showed the highest AEC, with a 6% decrease between the first and tenth cycles. Zeolite-N also presented the highest regeneration capacity which increased by 7% between the first and tenth cycles, achieving a regeneration efficiency of 90-100%. For clinoptilolite and Zeolite2, after 10 cycles, the AEC decreased by 15% and 3%, respectively, and the regeneration capacity also decreased by 11% and 3%, respectively, while no clear pattern in the variation of AEC and Q_{reg} was identified for the other zeolites.

Non-regenerated enriched zeolite, however, can be reused for other purposes, such as slow-release fertilizer in agriculture, in which case, the enriched zeolite is applied directly to the soil. Based on the high affinity of Ca/Mg zeolites for NH_4^+ and PO_4^{3-} and the slow release of NH_4^+ and PO_4^{3-}, especially when removed through the formation of Ca and Mg-phosphate minerals, You et al. [71] suggested the use of these materials as potential nutrient carriers for soil quality improvement. Several studies have been conducted to investigate this possible alternative use of zeolite. Kocatürk-Schumacher [83] conducted a pot experiment with ryegrass to test the ability of zeolite clinoptilolite enriched with digestate nutrients to supply nitrogen when used as fertilizer. Clinoptilolite had particle size of 1-3 mm, pH of 8.5, with 150-210 $cmol_{(+)}$ kg^{-1} cation exchange capacity, and 35.5 m^2 g^{-1} specific surface area. Nutrient-enriched clinoptilolite, and quartz sand, was used to fill in pots to have 15 or 45 mg N per pot. Pots with the lowest N resulted in more than a twofold increase in yield and more than a threefold increase in N uptake when compared to the control (untreated) clinoptilolite treatment. The increases were even greater when nutrient-enriched clinoptilolite was added to reach 45 mg N per pot, with almost a fourfold and sixfold increase in yield and N uptake.

Guaya et al. [6] activated a natural clinoptilolite in its potassium form with hydrated metal oxides (Fe, Mn, Al) and used it to recover nutrients from wastewater. Then, the nutrient-enriched zeolites were used as a soil conditioner in sandy and clay soils for the growth of sunflower (Helianthus annuus) plants. They observed that enriched zeolites as soil conditioner improved sunflower production by more than 50% (Table 4), thus confirming the reasonable use of enriched zeolites as a slow nutrient release avoiding, at the same time, nutrient leaching and the consequent environmental issue.

****Table 3 ****

6. Future perspectives

It should be mentioned that there are still immediate challenges for further successful environmental applications of this interesting class of natural materials. Future research should find sustainable methods to increase the operating capacity and mechanical strength of natural zeolites to enable their use in large-scale plants. Therefore, it is essential to find zeolites with a good adsorption capacity and capable of maintaining this capacity after several regeneration cycles, thus ensuring the sustainability of the process. Furthermore, after their depletion, enriched zeolites can be applied to the soil as slow-release fertilisers. The possible use as large-scale fertilisers may increase their possibilities for environmental application but has to be deeply investigated.

7. Conclusions

Due to its physical and chemical properties, natural abundance and low cost, zeolite is widely used for its catalytic abilities, cation exchange capacity, and application potential in various industrial processes. Due to the high CEC, zeolite can be used for the recovery of nutrients, e.g., NH_4^+, from treated wastewater. In addition, zeolite can also be modified to recover negatively charged nutrients such as PO_4^{3-}. Furthermore, zeolite can also be used as a soil conditioner to improve the physic-chemical characteristics of soils, such as nutrient retention capacity. Finally, the application of nutrient-enriched zeolite can be a suitable option as a source of nutrients for plants in a circular economy perspective. The use of zeolites is set to increase significantly due to the various fields in which they can be used.

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References

[1] Polat, E., Karaca, M., Demir, H., and Onus, a N. (2004) Use of natural zeolite (clinoptilolite) in agriculture. *Journal of Fruit and Ornamental Plant Reserarch*. 12 (December 2004), 183–189.

[2] Bashir, M., Ali, S., A.Izni, and Harun, R. (2013) Impact of excessive nitrogen fertilizers on the environment and associated mitigation strategies. *Asian Journal of Microbiology, Biotechnology and Environmental Sciences*. 15 213–221.

[3] Mannina, G., Badalucco, L., Barbara, L., Cosenza, A., Di Trapani, D., Gallo, G., et al. (2021) Enhancing a transition to a circular economy in the water sector: The eu project wider uptake. *Water (Switzerland)*. 13 (7), 1–18.

[4] Wang, H., Gui, H., Yang, W., Li, D., Tan, W., Yang, M., et al. (2014) Ammonia nitrogen removal from aqueous solution using functionalized zeolite columns. *Desalination and Water Treatment*. 52 (4–6), 753–758.

[5] Okoniewska, E., Lach, J., Kacprzak, M., and Neczaj, E. (2007) The removal of manganese, iron and ammonium nitrogen on impregnated activated carbon. *Desalination*. 206 (1), 251–258.

[6] Guaya, D., Mendoza, A., Valderrama, C., Farran, A., Sauras-Yera, T., and Cortina, J.L. (2020) Use of nutrient-enriched zeolite (NEZ) from urban wastewaters in amended soils: Evaluation of plant availability of mineral elements. *Science of The Total Environment*. 727 138646.

[7] Moshoeshoe, M., Silas Nadiye-Tabbiruka, M., and Obuseng, V. (2017) A Review of the Chemistry, Structure, Properties and Applications of Zeolites. *American Journal of Materials Science*. 2017 (5), 196–221.

[8] Wan, C., Ding, S., Zhang, C., Tan, X., Zou, W., Liu, X., et al. (2017) Simultaneous recovery of nitrogen and phosphorus from sludge fermentation liquid by zeolite adsorption: Mechanism and application. *Separation and Purification Technology*. 180 (C), 1–12.

[9] Onyango, M.S., Kuchar, D., Kubota, M., and Matsuda, H. (2007) Adsorptive Removal of Phosphate Ions from Aqueous Solution Using Synthetic Zeolite. *Industrial & Engineering Chemistry Research*. 46 (3), 894–900.

[10] Oladoja, T.D.S.N.A. (2021) Nutrient recovery from wastewater and reuse in agriculture : a review. *Environmental Chemistry Letters*. (0123456789),.

[11] De Campos Bernardi, A.C., Anchão Oliviera, P.P., de Melo Monte, M.B., and Souza-Barros, F. (2013) Brazilian sedimentary zeolite use in agriculture. *Microporous and Mesoporous Materials*. 167 16–21.

[12] Breck, D.W. (1984) Zeolite molecular sieves: structure, chemistry and use. Krieger, .

[13] Ambrozova, P., Kynicky, J., Urubek, T., and Nguyen, V.D. (2017) Synthesis and modification of clinoptilolite. *Molecules*. 22 (7), 1–13.

[14] Farkaš, A., Rožić, M., and Barbarić-Mikočević, Ž. (2005) Ammonium exchange in leakage waters of waste dumps using natural zeolite from the Krapina region, Croatia. *Journal of Hazardous Materials*. 117 (1), 25–33.

[15] Widiastuti, N., Wu, H., Ang, H.M., and Zhang, D. (2011) Removal of ammonium from greywater using natural zeolite. *Desalination*. 277 (1–3), 15–23.

[16] Colella, C. and Wise, W.S. (2014) The IZA Handbook of Natural Zeolites: A tool of knowledge on the most important family of porous minerals. *Microporous and Mesoporous Materials*. 189 4–10.

[17] Bacakova, L., Vandrovcova, M., Kopova, I., and Jirka, I. (2018) Applications of zeolites in biotechnology and medicine-a review. *Biomaterials Science*. 6 (5), 974–989.

[18] McCusker, L.B., Olson, D.H., and Baerlocher, C. (2007) Atlas of Zeolite Framework Types. .

[19] McCusker, L.B., Liebau, F., and Englehardt, G. (2003) Nomenclature of structural and compositional characteristics of ordered microporous and mesoporous materials with inorganic hosts (IUPAC recommendations 2001): Physical chemistry Division commision on colloid and surface chemistry including catalysis. *Microporous and Mesoporous Materials*. 58 (1), 3–13.

[20] Coombs, D.S. (2001) Recommended nomenclature for zeolite minerals: Report of the subcommittee on zeolites of the international mineralogical association, commission on new minerals and mineral names. *Bulletin of Mineralogy Petrology and Geochemistry*. 20 (3), 149–155.

[21] Guisnet, M. (2003) Zeolites for Cleaner Technologies. .

[22] Coronas, J. (2010) Present and future synthesis challenges for zeolites. *Chemical Engineering Journal*. 156 (2), 236–242.

[23] Li, Y., Li, L., and Yu, J. (2017) Applications of Zeolites in Sustainable Chemistry. *Chem*. 3 (6), 928–949.

[24] Kaduk, J.A. and Faber, J. (1995) Crystal Structure of Zeolite Y as a Function of Ino Exchange. *The Rigaku Journal*. 12 (January 1995), 14–34.

[25] Mitchell, S., Michels, N.L., Kunze, K., and Pérez-Ramírez, J. (2012) Visualization of hierarchically structured zeolite bodies from macro to nano length scales. *Nature*

Chemistry. 4 (10), 825–831.

[26] Li, Y. and Yu, J. (2021) Emerging applications of zeolites in catalysis, separation and host–guest assembly. *Nature Reviews Materials*.

[27] Wang, S. and Peng, Y. (2010) Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*. 156 (1), 11–24.

[28] Lok, M. (2009) Coprecipitation. *Synthesis of Solid Catalysts*. 135–151.

[29] Smical, I. (2011) Properties of natural zeolites in benefit of nutrition and health. *Human and Veterinary Medicine*. 3 (2), 51–57.

[30] Semmens, M.J. and Martin, W.P. (1988) The influence of pretreatment on the capacity and selectivity of clinoptilolite for metal ions. *Water Research*. 22 (5), 537–542.

[31] Begzati, A., Berisha, M., Mrasori, S., Xhemajli-Latifi, B., Prokshi, R., Haliti, F., et al. (2012) We are IntechOpen , the world ’ s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %. *Intech*. i (tourism), 38.

[32] Mumpton, F.A. (1999) La roca magica: Uses of natural zeolites in agriculture and industry. *Proceedings of the National Academy of Sciences of the United States of America*. 96 (7), 3463–3470.

[33] Sarioglu, M. (2005) Removal of Ammonium From Municipal Wastewater Using Natural Turkish (Dogantepe) Zeolite. *Separation and Purification Technology*. 41 1–11.

[34] Petranovskii, V., Chaves-Rivas, F., Hernandez Espinoza, M.A., Pestryakov, A., and Kolobova, E. (2016) Potential uses of natural zeolites for the development of new materials: Short review. *MATEC Web of Conferences*. 85 (January),.

[35] Rhodes, C.J. (2010) Properties and applications of zeolites. *Science Progress*. 93 (3), 223–284.

[36] Gribble, A.C.M.C.D. (2010) Minerals and rocks. *Geology for Civil Engineers*. 5–59.

[37] Alietti, A. (1972) Polymorphism and Crystal-Chemistry of Heulandites and Clinoptilolites. *American Mineralogist*. 57 (9–10), 1448–1462.

[38] Armbruster, T. (2008) Natural Zeolites: Cation Exchange, Cation Arrangement and Dehydration Behavior. in: S. V Krivovichev (Ed.), Miner. as Adv. Mater. I, Springer Berlin Heidelberg, Berlin, Heidelbergpp. 1–6.

[39] Du, T., Che, S., Liu, L., and Fang, X. (2017) Preparation of zinc chabazite (ZnCHA) for CO2 capture. *Research on Chemical Intermediates*. 43 (3), 1783–1792.

[40] Mishra, M. and Jain, S.K. (2011) Properties and applications of zeolites: A Review. *Proceedings of the National Academy of Sciences India Section B - Biological Sciences*. 81 (PART3), 250–259.

[41] Kallo D (2001) Natural Zeolites: Occurrence, Properties, Applications. in: Rev. Miner. Geochemistry Mineral. Soc. Am., pp. 519–550.

[42] Król, M. (2020) Natural vs. Synthetic zeolites. *Crystals*. 10 (7), 1–8.

[43] Muscarella, S.M., Badalucco, L., Cano, B., Laudicina, V.A., and Mannina, G. (2021) Ammonium adsorption, desorption and recovery by acid and alkaline treated zeolite. *Bioresource Technology*. 341 (August), 125812.

[44] Yuna, Z. (2016) Review of the natural, modified, and synthetic zeolites for heavy metals removal from wastewater. *Environmental Engineering Science*. 33 (7), 443–454.

[45] Ernst, S. (2011) Zeolites and Catalysis. Synthesis, Reactions and Applications. Edited by Jiri Cejka, Avelino Corma and Stacey Zones. *Angewandte Chemie International Edition*. 50 (24), 5425–5426.

[46] Cundy, C.S. and Cox, P.A. (2003) The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time. *Chemical Reviews*. 103 (3), 663–701.

[47] Cundy, C.S. and Cox, P.A. (2005) The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism. *Microporous and Mesoporous Materials*. 82 (1–2), 1–78.

[48] Julbe, A. and Drobek, M. (2015) Zeolite X: Type. in: E. Drioli, L. Giorno (Eds.), Encycl. Membr., Springer Berlin Heidelberg, Berlin, Heidelbergpp. 1–2.

[49] Widayat, W. and Annisa, A.N. (2017) Synthesis and Characterization of ZSM-5 Catalyst at Different Temperatures. *IOP Conference Series: Materials Science and Engineering*. 214 (1), 1–8.

[50] Pavelić, S.K., Medica, J.S., Gumbarević, D., Filošević, A., Pržulj, N., and Pavelić, K. (2018) Critical review on zeolite clinoptilolite safety and medical applications in vivo. *Frontiers in Pharmacology*. 9 (NOV), 1–15.

[51] Lauriente DH, I.Y. (2005) The Chemical Economics Handbook, SRI consulting. 6–8, 14.

[52] Naber, J.E., de Jong, K.P., Stork, W.H.J., Kuipers, H.P.C.E., and Post, M.F.M. (1994) Industrial applications of zeolite catalysis. in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Hölderich (Eds.), Zeolites Relat. Microporous Mater. State Art 1994 - Proc. 10th Int. Zeolite Conf. Garmisch-Partenkirchen, Ger. 17-22 July 1994, Elsevier, pp. 2197–2219.

[53] Kumar, N., Tiwari, K.R., Meenu, K., Sharma, A., Jain, A., Singh, S., et al. (2019) Utilization of Various Analogy of Synthetic Nanoporous Zeolites and Composite of Zeolites for Decontamination/Detoxification of CWA Simulants—An Updated Review. *International Journal of Nonferrous Metallurgy*. 08 (04), 35–71.

[54] Yilmaz, B. and Müller, U. (2009) Catalytic Applications of Zeolites in Chemical Industry. *Topics in Catalysis*. 52 (6), 888–895.

[55] Vermeiren, W. and Gilson, J.-P. (2009) Impact of Zeolites on the Petroleum and Petrochemical Industry. *Topics in Catalysis*. 52 1131–1161.

[56] Ramesh, K. and Reddy, D.D. (2011) Zeolites and Their Potential Uses in Agriculture. *Advances in Agronomy*. 113 219–241.

[57] Nakhli, S.A.A., Delkash, M., Bakhshayesh, B.E., and Kazemian, H. (2017) Application of Zeolites for Sustainable Agriculture: a Review on Water and Nutrient Retention. Water, Air, & Soil Pollution, .

[58] Ravali, C., Rao, J.K., Anjaiah, T., and Suresh, K. (2020) Effect of Zeolite on Soil Physical and Physico-Chemical Properties. *Journal in Science, Agricultural & Engineering*. X (Xxxiii), 776–781.

[59] MacKown, C.T. and Tucker, T.C. (1985) Ammonium Nitrogen Movement in a Coarse-Textured Soil Amended with Zeolite. *Soil Science Society of America Journal*. 49 (1), 235–238.

[60] Xiubin, H. and Zhanbin, H. (2001) Zeolite application for enhancing water infiltration and retention in loess soil. *Resources, Conservation and Recycling*. 34 (1), 45–52.

[61] Barakat, M.A. (2011) New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*. 4 (4), 361–377.

[62] Chowdhury, S., Khan, N., Kim, G.H., Harris, J., Longhurst, P., and Bolan, N.S. (2016) Zeolite for Nutrient Stripping From Farm Effluents. Elsevier Inc., .

[63] Perera, M.K., Englehardt, J.D., and Dvorak, A.C. (2019) Technologies for Recovering Nutrients from Wastewater: A Critical Review. *Environmental Engineering Science*. 36 (5), 511–529.

[64] Sancho, I., Licon, E., Valderrama, C., de Arespacochaga, N., López-Palau, S., and Cortina, J.L. (2017) Recovery of ammonia from domestic wastewater effluents as liquid fertilizers by integration of natural zeolites and hollow fibre membrane contactors. *Science of The Total Environment*. 584–585 244–251.

[65] Canellas, J. (2018) Tertiary Ammonium Removal With Zeolites. *School of Water, Environment and Energy Research Degree, Cranfield University*.

[66] Guida, S., Potter, C., Jefferson, B., and Soares, A. (2020) Preparation and evaluation of zeolites for ammonium removal from municipal wastewater through ion exchange process. *Scientific Reports*. 10 (1), 1–11.

[67] Huang, H., Xiao, D., Pang, R., Congcong, H., and Ding, L. (2014) Simultaneous removal of nutrients from simulated swine wastewater by adsorption of modified zeolite combined with struvite crystallization. *Chemical Engineering Journal*. 256 431–438.

[68] Markou, G., Depraetere, O., Vandamme, D., and Muylaert, K. (2015) Cultivation of Chlorella vulgaris and Arthrospira platensis with recovered phosphorus from wastewater by means of zeolite sorption. *International Journal of Molecular Sciences*. 16 (2), 4250–4264.

[69] Karapinar, N. (2009) Application of Natural Zeolite for Phosphorus and Ammonium

Removal From Aqueous Solutions. *Journal of Hazardous Materials*. 170 (2–3), 1186–1191.

[70] Lin, L., Wan, C., Lee, D.J., Lei, Z., and Liu, X. (2014) Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite. *Separation and Purification Technology*. 133 351–356.

[71] You, X., Valderrama, C., and Cortina, J.L. (2017) Simultaneous recovery of ammonium and phosphate from simulated treated wastewater effluents by activated calcium and magnesium zeolites. *Journal of Chemical Technology and Biotechnology*. 92 (9), 2400–2409.

[72] Sengupta, S., Nawaz, T., and Beaudry, J. (2015) Nitrogen and Phosphorus Recovery from Wastewater. *Current Pollution Reports*. 1 (3), 155–166.

[73] Koon, J.H. and Kaufman, W.J. (1975) Ammonia Removal from Municipal Wastewaters by Ion Exchange. *Journal (Water Pollution Control Federation)*. 47 (3), 448–465.

[74] Du, Q., Liu, S., Cao, Z., and Wang, Y. (2005) Ammonia removal from aqueous solution using natural Chinese clinoptilolite. *Separation and Purification Technology - SEP PURIF TECHNOL*. 44 229–234.

[75] Liberti, L., Petruzzelli, D., and Florio, L. De (2001) REM NUT Ion Exchange Plus Struvite Precipitation Process. *Environmental Technology*. 22 (11), 1313–1324.

[76] Li, M., Zhu, X., Zhu, F., Ren, G., Cao, G., and Song, L. (2011) Application of modified zeolite for ammonium removal from drinking water. *Desalination*. 271 (1–3), 295–300.

[77] Deng, Q., Dhar, B.R., Elbeshbishy, E., and Lee, H.S. (2014) Ammonium nitrogen

removal from the permeates of anaerobic membrane bioreactors: Economic regeneration of exhausted zeolite. *Environmental Technology (United Kingdom)*. 35 (16), 2008–2017.

[78] Czárán, E., Mészáros-Kis, Á., Domokos, E., and Papp, J. (1988) Separation of ammonia from wastewater using clinoptilolite as ion exchanger. *Nuclear and Chemical Waste Management*. 8 (2), 107–113.

[79] Metcalf, L., Eddy, H.P., and Tchobanoglous, G. (1991) Wastewater engineering: treatment, disposal, and reuse. McGraw-Hill New York, .

[80] Cyrus, J.S. and Reddy, G.B. (2011) Sorption and desorption of ammonium by zeolite: Batch and column studies. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*. 46 (4), 408–414.

[81] Wu, Z., An, Y., Wang, Z., Yang, S., Chen, H., Zhou, Z., et al. (2008) Study on zeolite enhanced contact–adsorption regeneration–stabilization process for nitrogen removal. *Journal of Hazardous Materials*. 156 (1), 317–326.

[82] Rahmani, A.R., Mahvi, A.H. and . A.H.M. (2004) Use of Ion Exchange for Removal of Ammonium: A Biological Regeneration of Zeolite. *Pakistan Journal of Biological Sciences*. 8 (1), 30–33.

[83] Kocatürk-Schumacher, N.P., Zwart, K., Bruun, S., Stoumann Jensen, L., Sørensen, H., and Brussaard, L. (2019) Recovery of nutrients from the liquid fraction of digestate: Use of enriched zeolite and biochar as nitrogen fertilizers. *Journal of Plant Nutrition and Soil Science*. 182 (2), 187–195.

Caption for tables

Table 1: Division of zeolites according to pore size, which influences their properties and fields of use

Table 2: Chemical and physical characteristics of natural and synthetic zeolites.

Table 3: Plant growth indicators take in consideration in the different treatments by Guaya et al. [6]. NEZ – Nutrient Enriched Zeolite CS – Clay Soil, SS – Sandy Soil.

Tables

Table 1: Division of zeolites according to pore size, which influences their properties and fields of use

Category	***Number of rings***	***Diameter***
Small-pore	≤ 8 rings	Having free diameters of 0.30 - 0.45 nm
Medium-pore	10-ring	0.45 - 0.60 nm in free diameter
Large-pore	12-ring	0.6-0.8 nm
Extra-large-pore zeolites	>12-ring	more than 8 nm

Table 2: Chemical and physical characteristics of natural and synthetic zeolites.

Name	**Chemical Formula**	**Si/Al ratio**	**CEC (meq g^{-1})**	**Structure type**	**Application**
Clinoptilolite-heulendite	$(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si1_3O_{36}\cdot 12(H_2O)$	5	2.2	HEU	Different application fields, in particularly is used as an adsorbent due to its natural characteristics
Chabazite	$CaAl_2Si_4O_{12} \cdot 6(H_2O)$	2-5	3.9	CHA	Widely used to remove trac gases and as a water softene
Phillipsite	$(K,Na,Ca)_{1-2}(Si,Al)_8O_{16}\cdot 6(H_2O)$	2	4.5	PHI	Widely used as a water softener
Zeolite A	$Na_{12}[(SiO_2)_{12}(AlO_2)_{12}]. 27\ H_2O$	1	5.3	LTA	Laundry detergent
Zeolite X and Y	$\vert(Ca,Mg, Na_2)_{29}\ (H_2O)_{240}\vert[Al_{58}Si_{134}O_{384}]$–FAU	1.2 – 2.5	3.2 – 4.5	FAU	Catalytic cracking
Zeolite ZMS-5	$Na_nAl_nSi_{96-n}O_{192}\cdot{}_{16}H_2O$ (n is between 0 and 27)	20	2	MFI	Used to convert alcohols directly into gasoline

Table 3: Plant growth indicators take in consideration in the different treatments by Guaya et al. [6]. NEZ – Nutrient Enriched Zeolite CS – Clay Soil, SS – Sandy Soil.

	Evapotranspiration	***Plant moisture content***	***Plant biomass***		***Root/branch ratio***		***Nitrogen and Phosphorus uptake***		***C/N ratio***	
	The incorporation of NEZ systems did not modify the evapotranspiration on both clayey and sandy amended soils.	The addition of the NEZ system changed the plant water contents of sunflowers grown on clay soils but for sandy soils the water content was the same in all treatments.	***CS***	***SS***	***CS***	***SS***	***CS***	***SS***	***CS***	***SS***
NEZ-Al			*+269%*	*+77%*	*-47%*	*+34%*	*+19% N* *+110%P*	*+17% N* *+210% P*	*-1%*	*-10%*
NEZ-Mn			*+401%*	*+131%*	*-13%*	*+17%*	*+44% N* *+77% P*	*+45% N* *+174% P*	*-21%*	*-38%*
NEZ-Fe			*+95%*	*+50%*	*-21%*	*-12%*	*+43% N* *+54% P*	*+5% N* *+140% P*	*-24%*	*-10%*

Caption for Figures

Fig. 5.1.jpg Primary Building Unit of Zeolites

Fig. 5.2.jpg Secondary Building Unit of Zeolites

Fig. 5.3.jpg Mechanism by which zeolites retain nutrients in the soil.

Figures

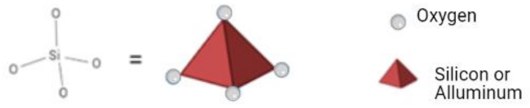

Fig. 5.1.jpg Primary Building Unit of Zeolites

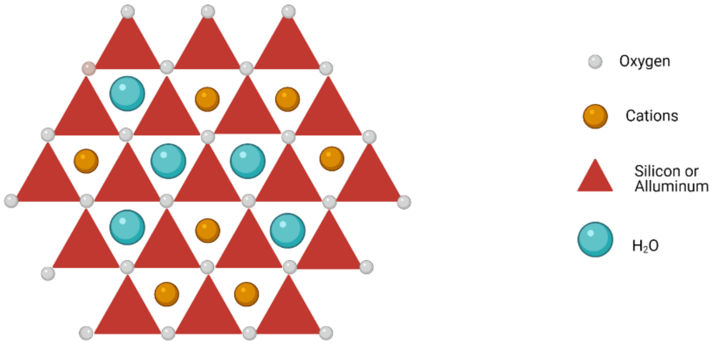

Fig. 5.2.jpg Secondary Building Unit of Zeolites

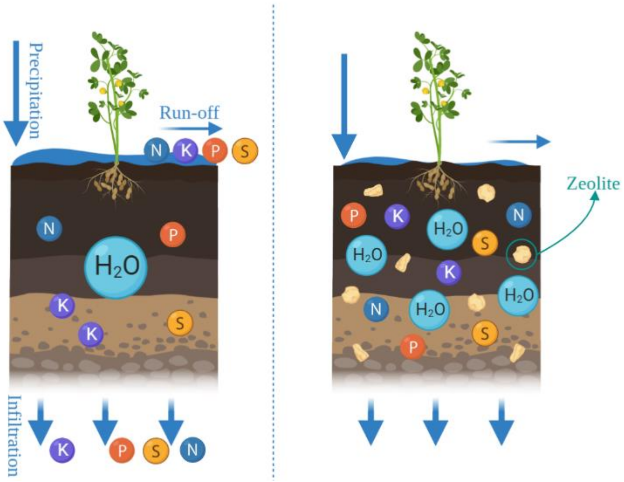

Fig. 5.3.jpg Mechanism by which zeolites retain nutrients in the soil.