Appications of Natural Clinoptilolites Based on Ion Exchange

Subjects: Mineralogy | Chemistry, Physical

Contributor: Inocente Rodríguez-Iznaga , Marina G. Shelyapina , Vitalii Petranovskii

There are many natural zeolites, of which a small number, including clinoptilolite, chabazite, mordenite, erionite, ferrierite, and phillipsite offer the greatest promise for industrial applications. Natural clinoptilolites have been the subject for different modifications in order to improve their use potentialities, where the ion exchange property has been a key role for their different applications. Application of ion exchange to modify clinoptilolites, cation selection, mono- and polycationic exchange to create new functional materials for specific applications are key issues.

clinoptilolite heulandite ion exchange

1. Removal of Cationic Contaminants from Water

1.1. Removal of Heavy Metals

As [1] states, “*The world is so polluted with heavy metals, mainly due to human pollution, that it affects the health of so many people*”. Therefore, research and engineering work to find a way out of this situation must continue intensively so that we are aware of the effects caused by pollution of the biosphere with these metals, the symptoms observed, and ways to remove at least part of the pollution that we have from all heavy metals.

The depletion of water resources and water scarcity have become one of the greatest threats to society today, plaguing the environment [2]. Due to population growth, the demand for water exceeds the amount of available water resources; thus, wastewater treatment becomes indispensable to reduce water scarcity. Removal of heavy metal ions from industrial and domestic wastewater is of paramount importance for the purity of the environment and human health. The presence of heavy metals in wastewater increases with the growth of industry and human activities, for example, in the electroplating industry, electrolysis, metal washing processes, the production of batteries, pesticides, paper, metal smelting, mining, viscose industry, leather industry, textile industry, etc. Heavy-metal-contaminated wastewater enters the environment, threatening human health and the ecosystem. Heavy metals are not biodegradable; thus, the presence of these metals in water in the wrong amounts can lead to critical health problems for living organisms. Various methods have been devoted to the removal of heavy metal ions from various wastewater sources. These methods can be divided into adsorption, membrane, chemical, electrical, and photocatalytic methods. [3] reviews and discusses these methods in terms of removal efficiency, operating conditions, and the pros and cons of each method. The authors point out that the study of heavy metal removal should focus more on using real wastewater rather than synthetic wastewater.

In practice, the term “heavy metal” has come to encompass any metal, exposure to which is clinically undesirable and potentially hazardous [4]. The cited review provides a summary of some general concepts of metal toxicology, and several metals of particular importance are discussed in detail. More information on various aspects of metal toxicity can be found in [1][3]. Nevertheless, metal poisonings constitute an important aspect of toxicology because of their widespread use and availability. Some aspects of human exposure to heavy metals are shown in **Figure 1**.

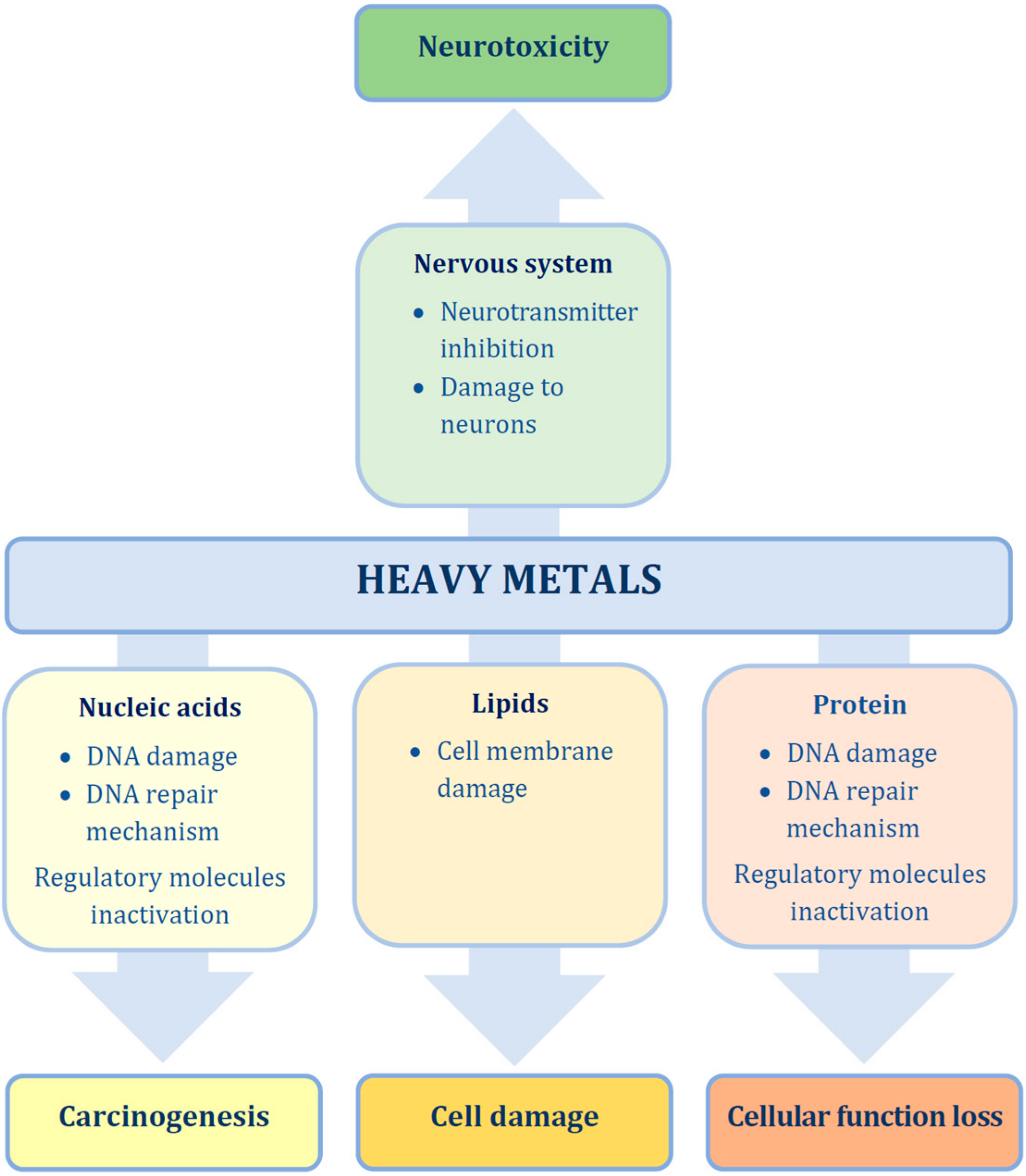

Figure 1. The pathways of heavy metal ions in the human body and their effects. Adapted with permission from Briffa, J. D et al., *Heliyon*; Elsevier Ltd. CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/, 18 November 2022), 2020 [1].

The heavy metals that draw the most attention include V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Sb, Cd, Hg, Pb (and not only), which are arranged in order of their atomic numbers in the above list. Compared to other methods of heavy metal elimination, ion exchange methods for the selective removal of heavy metals are energy efficient and environmentally friendly. In particular, zeolites have been attractive adsorbents for heavy metals since the first attempt to systematically use zeolites for water purification in the 19th century [5]. Many types of zeolites have been tested for the removal of heavy metals, such as zeolites X, Y, A, P (types FAU, LTA, GIS), clinoptilolite, etc. [6]. Recent studies have focused on modifying zeolites with metals or metal oxides to improve their ability to remove heavy metals. For example, iron-coated clinoptilolite showed significantly improved adsorption capacity for heavy metals, especially Pb, compared to uncoated clinoptilolite [7]. This was probably because iron could reduce PbII ions on the clinoptilolite surface to Pb0. Taking advantage of iron's reducing ability, nanoscale zero-valent iron/zeolite composites can be fabricated. Due to the large surface area of iron nanoparticles and the stabilizing effect of zeolites with respect to iron nanoparticles, the absorption of PbII can be greatly improved.

Among the main reports on the use of the natural clinoptilolites as ionic exchanger are industrial wastewater treatment and the pollution removal and industrial wastewater treatments, where special attention is paid to the removal and recovery of heavy metals [8][9][10][11]. Although there are a very large number of reports in the literature devoted to these processes, most of them describe only the removal of impurities to purify the water itself, i.e., without considering the recovery of the valuable metal (by subsequent elution, etc.) and furthermore without any recommendations on how to proceed with the zeolite used.

Rodriguez-Iznaga et al. [10] reported a large-scale study of natural clinoptilolite from the Caimanes deposit, Cuba, modified into its ammonium form by replacing the original mineral cations through ion exchange in a ammonium-concentrate solution (concentrated NH_4OH) and then using the resulting material as an efficient exchanger in cyclic Ni^{2+} removal–elution processes 20 or more times in a row, without significantly degrading both the crystal framework and the Ni^{2+} and NH_4^+ exchange capacity for this modified clinoptilolite. The authors showed that use of this ammonium-rich solution allows ion exchange processes to be carried out that lead to both the recovery of nickel once retained on zeolite phase during its removal from solution and the regeneration of the ammonium–clinoptilolite form for starting a new cycle. Moreover, the Ni^{2+} removal capacity of this clinoptilolite substantially increased due to the OH^- anions from ammoniac solution are retained (adsorbed, occluded) on zeolite phase, and consequently, a low-soluble nickel hydroxide precipitation process takes place parallel to the ion exchange.

Greek natural clinoptilolite, supplied by S&B Industrial Minerals S.A. Zeolite, was treated with different wasters (synthetic aqueous solutions, secondary effluent from system treating municipal wastewater and primary treated wastewater collected from municipal wastewater treatment plant) containing Zn(II) and Pb(II) [12]. The desorption (elution) of Zn(II) and Pb(II) retained on zeolite was evaluated by using solutions of HNO_3, NaCl, KCl and NH_4Cl in batch processes, which lead to test the clinoptilolite regeneration by conducting successive Pb(II) and Zn(II) removal/elution (adsorption/desorption) cycles. The best results in the clinoptilolite regeneration and metal elution were obtained with KCl solutions (3 M KCl solution for lead and 1 M KCl for zinc). However, after nine and four cycles for lead and zinc, respectively, regeneration–elution efficiency decreased by more than 50%, which showed difficulty desorbing the ions that were easily adsorbed. The authors suggest several issues that could affect the regeneration–elution efficiency, such as impurities (carbonates, sulfates, etc.) mainly in the wastewater, replacement of Ca^{2+}, Na^+, Mg^{2+} (native cations in the zeolite) by K^+ and the formation of chloride–metal complexes. In addition to this, it is necessary to take into account that high coordination K^+ cation can achieve with the clinoptilolite framework.

The ion exchange capacity of the Bulgarian natural clinoptilolite to remove Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} from mono- and multi-component solutions was improved after applying a modification pretreatment by Na^+ cation exchange to obtain the exchanged Na-clinoptilolite. However, the reached change had no significant effect on Pb^{2+} removal, which was associated with the fact that Pb^{2+} ion exchange is more related with other cations ($Ca^{2+}$and K^+) different to Na^{2+} [13]. In the same way, the ammonium removal capacity of the natural clinoptilolite from Beli Plast deposit, Bulgaria, was enhanced after modifying this zeolite to its Na- form [14][15]. The effect of pretreatment of Chilean natural zeolite (composed mainly of clinoptilolite and mordenite) with NaCl, NaOH, Na_2CO_3 and NH_4Cl solutions on its capacity to be removed by Mn^{2+} ion exchange was studied [16]. The results showed that the applied pretreatment type led to an increase in the level of manganese removal. The efficiency depends on the applied treatment in the following way: NaCl ~ NaOH > Na_2CO_3 > NH_4Cl > natural clinoptilolite. The level of Ni^{2+} cation removal on natural clinoptilolite from a Serbian deposit was improved by modifying this zeolite through Na^+ ion exchange to its Na-clinoptilolite form [17]. The authors have also reported a low level of nickel removal at room temperature, which can be improved with temperature increases is in line with other reports [8][9].

The ion exchange property has also been used to improve the natural clinoptilolites capacity in removal processes of water pollution that is unusual, difficult to eliminate or that cannot be removed by direct ion exchange, for example metal oxyanions, such as described in [18]. Natural clinoptilolite from Puebla State, México, was exchanged with 0.1 N HCl solution and then treated with silicon in the presence of peroxide and heptane at 70 °C [19]. This leads to the deposit of silicon nanocrystals on the zeolite surface without affecting its crystalline structure and textural characteristics, which could help to improve its capacity to remove Cs and Sr isotopes from pollutant residues. Material of inexpensive cost with increased capacity to remove Cr(VI) in chromate anion form from waters was prepared using natural clinoptilolite from St. Cloud Mine in Winston, NM, Japan, modified by Fe^{3+} ion exchange and then an adjustment of pH to 9 [20]. The authors report that CrO_4^{2-} oxyanion binds with oxy-hydroxides of iron on the zeolite surface, favoring the removal of this anion. This same natural clinoptilolite from St. Cloud Mine in Winston, NM, Japan, but modified by Fe(II) ion exchange, was used as an efficient material to remove chromium in CrO_4^{2-} anions form from watery solution [21]. The Cr(VI) removal in chromate and dichromate form on natural clinoptilolite from Chihuahua, Mexico, was improved by pre-modifying it through applying Na^+ ion exchange and then treated with hexadecyltrimethylammonium bromide (HDTMA-Br) [22]. The modification by ion exchange led to a light increase in the specific surfaces of this zeolite, which could favor the retention of HDTMA-Br on teh clinoptilolite surface and, consequently, increase its capacity to remove Cr(VI).

Natural clinoptilolite from Metaxades deposit, Greece, was evaluated in the removal of Cu^{2+}, Fe^{3+} and Cr^{3+} from nitrate salt solutions (containing KNO_3 too) in the presence of SO_4^{2-} and HPO_4^{2-} anions (as K_2SO_4 and K_2HPO_4) [23]. The authors report that Cu^{2+} removal is significantly affected by both anions, while this negative effect is less significant for Fe^{3+} and Cr^{3+} in the presence of SO_4^{2-} and HPO_4^{2-}, respectively. This was associated with the formation of a metal–anion complex. In the case of Fe^{3+}, the presence of HPO_4^{2-} provokes the iron precipitation that occurs joint to its ion exchange, which results in a higher removal (complete iron removal). Furthermore, a significant level of anion removal was reached.

In addition to the modification of clinoptilolites with single cations (monocationic exchange), there are other reports on modifications with mixed cations (multicationic exchange) that lead to improving its properties for diverse uses, nanospecies stabilizing on natural clinoptilolite matrix, etc. [24][25].

1.2. Removal of Dissolved Ammonia

Dissolved ammonia, the ammonium ion (NH_4^+), is a water pollutant that can enter water bodies continuously and persist for a long time. Natural sources of NH_4^+ in water include decomposition of organic matter, gas exchange with the atmosphere, forest fires, animal and human waste, etc. Another serious cause of ammonium in surface water is anthropogenic activities such as municipal sewage discharge, deposition from the air, and runoff from agricultural land [26]. One of the forms of nitrogen normally presents in aquatic systems at pH below 8.75 [27]; ammonium, however, differs from them in its effects at elevated levels. While high concentrations of other forms of nitrogen can only lead to nutrient overenrichment and indirect effects on hydrobionts, high concentrations of ammonium (particularly ammonium nitrate) have direct toxic effects on aquatic inhabitants [28].

To detect ammonium in aqueous solutions, conductometric sensors have been developed using the intrinsic cation exchange of the natural zeolite clinoptilolite [29]. The sensor recognition element was fabricated with a primary layer of clinoptilolite and a subsequent layer of Nafion on the electrode surface. The protocol for using the sensor included soaking the sensor membrane in 5 mM sodium prior to analysis to ensure optimal conditions for ion exchange in the zeolite. The linear range of the sensor studied for the first time was 0–1.5 mM ammonium. The mechanism of clinoptilolite selectivity to ammonium has been widely studied and is explained by cationic exchange between Na^+ ions, which initially occupy the extra-framework exchange sites of the zeolite, and NH_4^+ from the environment [30]. The optimization data obtained by the authors can be useful for the accurate detection of ammonium by sensors and biosensors based on clinoptilolite. Other features of the optimized ammonium selective sensors described in this work are their low cost, high stability of operation, and stability during long-term storage, which makes these sensors promising analytical devices for analyzing real samples.

The use of clinoptilolite allows for the development of other conductometric sensors. The ion exchange properties of zeolites can be used to accumulate electroactive cations within zeolite particles located on the electrode surface [31]. This is a key starting point for many electroanalytical applications using zeolite-modified electrodes. Highly sensitive conductometric urea biosensors have been developed by exploiting the successful combination of the ion exchange selectivity of clinoptilolite to ammonium with the unique biorecognition ability of urease. To optimize the performance of urea biosensors based on clinoptilolite, the dependencies of their analytical signals on the pH, buffer capacity, and ionic strength of the phosphate-buffered solution were investigated [32].

Due to its high affinity for the ammonium ion, clinoptilolite can be used not only for its determination, but also for its removal from wastewater. This raises the need for the preparation of engineered zeolites having a high ammonium exchange capacity and at the same time mechanical strength and abrasion resistance. Research [33] was devoted to the production and evaluation of synthetic zeolites and comparison with natural clinoptilolite in a demonstration ion exchange plant treating secondary effluents from municipal wastewater treatment plants. Future work should focus on optimizing the granular zeolite production process (temperature, time, and furnace size during calcination) to produce a spherical engineered zeolite that will reduce possible sharp edges that can affect mechanical strength.

1.3. Removal of Contaminants from Organic Solutions

Besides the ion exchange removal processes performed commonly in aqueous solutions, there are other unusual methods such as those where the solvents used are organic. The natural clinoptilolite from the northern part of Greece was used to remove Cu^{2+}, Cr^{3+} and Fe^{3+} cations from nearly pure ethanol and acetone where the cations are in the form of cation–solvent complex [34]. The authors have compared the ion exchange levels in water with respect to those reached in the organic solvents, being observed as satisfactory levels only to Cr^{3+} in ethanol and Cu^{2+} in acetone.

2. Storage and Conversion of Undesirable Gas Emissions into the Atmosphere

The unique and exceptional physical and chemical properties of zeolites in general, and of the heulandite–clinoptilolite family of zeolites in particular, favor their use in many applications, including CO_2 post-combustion adsorption [35]. One of these properties is a high adsorption capacity, which is combined with a molecular sieve effect, which makes it possible to selectively absorb certain gases from mixtures. In combination with ion exchange properties that allow one to control the number and size of cations in the channels of clinoptilolite, such adsorption becomes somewhat controllable.

There are many natural zeolites, a number of which, including clinoptilolite, chabazite, mordenite, erionite, ferrierite and phillipsite, are widely available and are the most promising for gas separation. The results [36] show that these natural zeolites are particularly well suited for the removal of gaseous impurities. Clinoptilolite and chabazite are considered the most versatile.

Separation of mixtures is always necessary in modern industry, especially in the fine chemical, petrochemical, and pharmaceutical industries. The problem of the separation process is usually associated with small molecules with very similar physical and chemical properties. The widely used high-pressure cryogenic distillation process is energy intensive. The adsorptive separation process based on zeolite sorbents is a promising low-energy alternative; however, the efficiency in this case directly depends on the zeolitic material. Review [37] considers separation mechanisms based on steric, equilibrium, kinetic, and other effects and summarizes recent advances in adsorption separation using zeolites, including the separation of CO_2, light olefins, C-8 aromatics, and hydrogen isotopes.

It has been found [38] that in Na- and Ca-clinoptilolites, the diffusion rate of N_2 is much higher than the diffusion rate of CH_4, resulting in excellent separation performance. The separation kinetics for an N_2/CH_4 mixture depend on the cationic composition; in clinoptilolites with Li^+, Mg^{2+}, and Ca^{2+}, N_2 diffuses much faster than CH_4. In addition, a mixed ion exchanged clinoptilolite such as Mg/Na (50/50) exhibits even better kinetic selectivity for N_2/CH_4 separation.

A serious problem is the processing of organic waste. Composting is a promising technology that makes it possible to obtain a humus-like high-quality compost substance that can be used as an organic fertilizer. However, both greenhouse gases (N_2O, CO_2, CH_4) and odorous emissions (H_2S, NH_3) are emitted, which is a serious concern. These secondary pollutants have adverse effects on the environment and human health. It is known that in the process of composting, an important role for the quality of the resulting fertilizer is played by the nitrogen cycle. In review [39], the authors summarized the basics of the nitrogen composting cycle; examined the impact of operating parameters, microbial activity, enzyme functions influencing the nitrogen cycle; and discussed strategies to mitigate nitrogen losses. Operating parameters such as humidity, oxygen content, temperature, C/N ratio and pH play an important role in the nitrogen cycle, and adjusting them is the simplest method to reduce nitrogen losses. Furthermore, the addition of biochar, and especially clinoptilolite, helps control nitrogen losses, which has a beneficial effect on the quality of the compost and controls air pollution.

An even more serious problem is the food waste digestate (FDP), which is high in NH_4^+-N and difficult to compost due to higher NH_3 emissions (and loss of nitrogen from the resulting fertilizer). The study [40] used clinoptilolite as a physical additive for ammonia retention. The results showed that the addition of zeolite had a positive effect, since at dosages of additives of 5%–10%, nitrogen losses decreased by 34%–39%. At the same time, the addition of zeolite increased the decomposition rate by 30%–32%.

3. Production of Catalysts and Photocatalysts

All people and animals need access to clean water in their daily lives. Unfortunately, we face water shortages all over the world. At the same time, however, we inevitably pollute water in various ways. Population growth, globalization and industrialization are generating more and more wastewater that contains pollutants such as organic substances, metal salts, agrochemicals, herbicides, pesticides, antibiotics, dyes, radioactive pollutants, etc. This whole range of pollutants can cause various diseases in humans and animals, as well as damage to the environment. In addition to existing contaminants, a number of new pollutants are now being produced by developing industries. To solve this problem, we need new effective tools and materials to remove impurities from wastewater. Photocatalysis can often be very effective for the removal of complex organic substances, especially under the influence of natural sunlight. However, zeolite itself shows little photocatalytic efficiency; thus, zeolites, using their ion exchange potential, are enriched with various photoactive materials to increase their photocatalytic efficiency. The production of such zeolite-based composites is developing.

Natural clinoptilolite can be used as support for immobilization of TiO_2 nanoparticles [41][42][43]. Moreover, it was found that the efficiency of this composite for photocatalytic degradation of organics under sunlight irradiation was significantly improved [41]. TiO_2 supported on alkaline clinoptilolite followed by NH_4NO_3 treatment exhibited its effectiveness in hydrogen production by photocatalytic water splitting [43]. The results obtained suggest that the ion exchange alkaline treatment of clinoptilolite along with providing strong basic sites creates mesoporosity; altogether, this improves the photocatalytic activity of TiO_2/clinoptilolite composites for hydrogen evolution.

The photocatalytic activity of CuS in the composition of clinoptilolite during the bleaching of a mixture of methyl orange and bromocresol green under sunlight irradiation was investigated in [44]. The degree of discoloration was estimated from the residual concentration spectrophotometrically and was confirmed by the reduction in chemical oxygen demand (COD). The formation of catalytically active copper and nickel nanoparticles on natural zeolites for the complete oxidation of hydrocarbons was studied in [45][46]. A combination of green chemistry and nano-engineering is needed to produce minimal waste, using simpler and safer products, and new technologies. Dyes have a complex structure, an intractable/recalcitrant nature and a greater number of intermediates. Various attempts to degrade dyes in textile wastewater using various advanced oxidation processes are being made everywhere. Treatment technology can be improved by advanced oxidation processes [47]. These processes are efficient, inexpensive, and environmentally friendly methods of decomposing toxic pollutants. Advanced oxidation processes (AOPs) are broadly defined as a set of chemical treatment procedures designed to remove organic pollutants. AOPs are classified as non-photochemical and photochemical processes. Various technologies such as ozonation, Fenton oxidation, wet-air oxidation, electrochemical oxidation, and photocatalytic oxidation can be included. The production of highly reactive free radicals is the main goal of the AOP process. The production of free radicals is increased by a combination of two or more AOP processes, resulting in higher oxidation rates.

The review [48] highlights the types and mechanisms of synthesis of zeolite-based materials for wastewater treatment and analyzes the gaps in current research, which gives a qualitative background of world research on this topic.

In [49], Aguiñaga et al. reported that natural mixed clinoptilolite–mordenite tuff is an effective photocatalyst. Pretreatment of the sample consisted of acid etching. The rock was crushed and sieved to obtain grains with sizes of 2.38 and 3.36 mm. The particles were treated in 1 M aqueous hydrochloric acid for 8 h at 60 °C, thus obtaining protonated zeolite. The results obtained were compared with those for titanium dioxide particles, and it was found that under similar conditions, both zeolite and TiO_2 require the same time to completely degrade caffeine. On the basis of spectroscopic analysis of UV–Vis spectra of the materials obtained in this work, it was found that the absorption bands in the range of 200–500 nm refer to different states of iron, and in natural zeolites, the presence of iron is common.

In the case of clinoptilolites, it is iron that often becomes the active centers in photocatalysis and catalysis. For example, in [50], the natural form of clinoptilolite was similarly protonated. Both the initial and H-forms were then subjected to mechanochemical treatment in water and air. XRD, FTIR, SEM, XPS and UV–Vis spectroscopy were used to examine both the initial and milled samples. The authors showed that dry milling leads to destruction of the crystal structure, whereas milling in water partially preserves the crystal structure; however, a meso-macroporous structure is formed in both cases. The surface of these materials was enriched with oxygen-containing particles of iron compounds that served as photocatalytic centers. These samples exhibit increased photocatalytic activity in the degradation of rhodamine B under the action of visible light [50].

Natural zeolite with a crystalline framework of heulandite type was modified with iron and tested as a catalyst for selective catalytic reduction of nitrogen oxides by ammonia (NH_3-SCR) in the temperature range of 150–450 °C [51]. The activity of the catalyst was tested under industry conditions using tail gases from a pilot nitric acid plant. The effect of temperature, catalyst loading, and amount of reducing agent (ammonia) on the NOx reduction process was investigated. The results of the catalytic tests showed that Fe-clinoptilolite showed about 58% NO conversion at 450 °C. In addition, it was noted that the ratio of N_2O concentrations after and before the catalytic bed was below 1, indicating that the catalyst exhibited activity in both the de-NOx and de-N_2O processes.

The authors [52] prepared protonated clinoptilolite as a catalyst carrier and then subjected it to ion exchange with salts of Fe, Cu, and Co. Their experimental protocol included repeated ultrasound treatment at various stages of preparation. The zeolite catalysts obtained were used for biomass conversion. The following organic acids were obtained during conversion: lactic acid, formic acid, pyruvic acid, acetic acid, and levulinic acid. The highest yield of lactic acid (66.2%) was achieved with Co-clinoptilolite, formic acid (93.6%) with Cu-clinoptilolite, and acetic acid (87.4%) with Fe-clinoptilolite.

The property of ion exchange has found wide application in the preparation of catalysts. Transition metals, their oxides and ionic compounds are known to be very effective catalysts. Their use applied to zeolites creates interesting opportunities for nanoengineering solutions when cations are distributed over the carrier surface. The use of natural clinoptilolite as a support matrix modified by ion exchange with cations such as Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, etc. led to the development of low-cost NO_x reduction catalysts [51][53][54][55]. The authors call attention to the substance (e.g., salts) used as a precursor of the cation active in the catalytic reaction and complete removal of its residue on the zeolite support after ion exchange, which can affect the activity of the developed catalyst. A review of studies on samples of HEU-type zeolites, both pure and modified with transition elements of d- and f-blocks and Pb, is given in [56]. The interest in such modified zeolites is mainly due to their use for pollution control and their potential catalytic properties. Detailed information on the crystal structure of HEU-type crystals fully subjected to cation exchange shows that the ions mainly occupy two out-of-frame positions: one in the center of the ten-membered ring, octahedrally coordinated with six H_2O molecules, and one in the eight-membered ring, coordinated with framework oxygen and additional H_2O. Additional microscopic, spectroscopic, and thermal data for heulandite and clinoptilolite interacting with these ions showed non-homoionic and non-stoichiometric metal loading. Excessive accumulation on the crystal surface due to adsorption and deposition phenomena on the surface was usually observed. Only a very low incorporation of trivalent lanthanide/rare Earth element ions into the clinoptilolite channel system was experimentally achieved.

Despite the fact that the use of natural raw materials as catalysts causes a number of problems related to their non-homogeneous composition, the efforts to create such materials continue. This is due to the fact that synthesis of zeolites generates rather large volumes of aggressive high-alkali wastes, and synthetic zeolites themselves due to prices for raw materials and energy turn out to be rather expensive. Modernization processes in the chemical industry over the past few years have increased concerns about the sustainable use of natural resources and the introduction of solvent-free and toxic synthesis processes. In addition, the development of new catalysts capable of minimizing or even eliminating harmful substances commonly used in the chemical industry is receiving increasing attention in academia and the industry in the context of "green chemistry," based on the search for products and processes that can reduce or even eliminate the use of hazardous substances. Review [57] describes the main classes of green catalysts, their main characteristics, and various synthesis methods.

4. Bioactive Materials

Reviews on medical and veterinary applications of different natural clinoptilolite-based materials as well as their safety can be found in [58][59]. Modification of natural clinoptilolite by ion exchange with certain cations known for their oligodynamic activity, such as Zn^{2+}, Cu^{2+}, Ag^{+}, etc., makes it possible to obtain materials and products with biocide activity for different interest fields [58][60][61]. In [62], the authors reviewed the bioactive properties of exchanged natural Ag-clinoptilolites, its activity mechanism, antimicrobial agent and biomedical applications. Studies of Mexican natural clinoptilolite from Etla, Oaxaca, showed that *Escherichia coli* and *Salmonella typhi* bacteria experience a rapid reproduction on this zeolite [63]. However, when this clinoptilolite is modified by using it first with Na^{+} ion exchange, followed by Ag^{+} exchange and finally thermal reduction, it is transformed into a material efficient enough to eliminate both bacteria.

The natural clinoptilolite from Sardinia, Italy, was modified by ion exchange with Zn^{+} cations and erythromycin, resulting in a patented product [64] with the potential for biomedical application in the topical treatment of acne, where the combination of zinc and erythromycin is effective against resistant strains of *Propionibacterium* [61]. The antibacterial activity against *Escherichia coli* (Gram-negative bacteria) and *Staphylococcus aureus* (Gram-positive bacteria) of the natural clinoptilolite from Zlatokop, Serbia, modified with Cu^{2+}, Zn^{2+} and Ni^{2+}, was tested in different liquid media (namely Luria Bertani, synthetic wastewater and real effluent water from the secondary stage of the biological wastewater treatment plant) [63]. The only Cu- and Zn-clinoptilolite forms showed important activity against these pathogens, which reduced the bacterial numbers for six orders of magnitude in effluent water. Ni-clinoptilolite showed weak antibacterial activity, which was associated with a high leaching of Ni^{2+} from the zeolite phase to solution. Chilean natural clinoptilolite supplied by Minera Formas, Chile, was subjected for several size reduction processes to obtain it in nanoparticle form with an average diameter of 37.2 ± 15.8 nm, which then was chemically treated with HCl solution and finally modified to its copper form by using Cu^{2+} ion exchange [65]. This Cu-nanozeolite showed antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, primary pathogens that are present in food and that are resistant to multiple drugs. In addition, the authors have outlined that its nanometric size increase the available surface area and leads to its applicability in different matrices. Exchanged Ag-, Zn- and Cu-clinoptilolite were the obtained forms of natural clinoptilolite from Vranjska Banja deposit (Serbia) by using ion exchange, first with Na^{+} ions and then with Ag^{+}, Zn^{2+} and Cu^{2+} cations, respectively, and they were tested as antibacterial agents for wastewater treatment in a batch and bead filter system [66]. Ag-clinoptilolite showed higher antibacterial activity, which was outstanding in the bead filter system against hospital pathogenic bacterium *Acinetobacter baumannii,* completely removing the pathogenic carbapenem-resistant bacteria from real effluent wastewater.

Based on Cuban natural clinoptilolite modified by Zn^{2+} ion exchange, a zeolitic product ZZ$^{@}$ was developed, which has microbicidal properties against bacteria, yeasts, and protozoa [60]. ZZ$^{@}$ has been used in different drinking water purification systems (domestic and collective) and preparation of other microbicidal products. Its microbicidal action consists in the controlled release of Zn^{2+} cations into contacting media (for example, water), which have a wide spectrum of bactericidal effects on pathogenic microorganisms, suppressing their infectious effect on humans. The levels of zinc achieved in this way in water are below those recommended by the Guidelines for Drinking Water Quality (<5 ppm) [67]. Furthermore, zinc is an essential element for human and animal life. This element, sometimes referred to as the spark of life, is effective against a wide variety of pathogens, mostly those living in water that commonly cause gastrointestinal, lung, and skin infections in humans.

5. Agricultural Applications

Among all the zeolites used in agriculture, natural clinoptilolite stands out because it is the most used and contributes to the improvement of some soil properties [68][69][70][71]. Cuba is among the countries with major natural reserves of zeolites, included clinoptilolite [72][73]. Their deposits are distributed along this Caribbean island [71]; coincidently, its most productive agricultural crop areas are in the vicinity of clinoptilolite deposits. In this sense, it is appropriate to note that silicon, the main component of zeolites, is also considered an important element due to its significant role in the physiology and biochemistry of the crop plants [74][75][76].

Of all the nitrogen fertilizers commonly used in agriculture, urea is the most widely used in agriculture worldwide, where a high nitrogen content (46%) is of great importance. However, its application in soils is accompanied by high losses and low utilization efficiency (<50%), mainly associated with ammonia volatilization and nitrate leaching. These processes represent severe environmental risks, manifested in the degradation of soil and underground water quality, reduction of biodiversity, increase in the concentration of NO_x, a gas with a powerful greenhouse effect, and contributing to the formation of so-called acid rains, the depletion of the ozone layer and other environmentally unpleasant effects [77]. Thus, it is necessary to develop other alternative fertilizers and technologies that are safer for the environment.

The ion exchange properties of natural clinoptilolites and their affinity for NH_4^+ were used to reduce nitrogen losses by volatilization of ammonia from urea [78][79][80]. Studies with urea/natural clinoptilolite mixtures have shown that such a mixture results in a 53% reduction in volatile ammonia [79]. Natural clinoptilolite from Faku County, Liaoning-Chine, was mixed with soil, and then, the ability of this zeolite for retaining and releasing ammonium was tested by contacting the mixture with an NH_4^+ solution [81]. The authors reported that clinoptilolite enhances the nitrogen-retaining capacity of the soil, where ion exchange processes play a key role, and soil quality is improved due to the co-existence of exchangeable K^+ and Na^+ cations, mainly due to the latter. It was reported that the use of natural clinoptilolite in soils significantly reduces the excretion of ammonium and nitrates from urea compared with the use of urea alone [78]. Furthermore, exchangeable NH_4^+ and the retention of total soil nitrogen as well as available nitrate are improved due to the ability of the zeolite to retain NH_4^+ through cation exchange.

The report of the Commission on Natural Zeolites of the International Zeolite Association [I70] on volcanogenic sedimentary zeolite deposits in Cuba overviews different products and technologies of using Cuban natural zeolites in agricultural development that lead to remarkable results. Among these Cuban products, NEREA@ stands out. NEREA@ products are currently available on the market for use as substrates and fertilizers, and technologies for their production and use have been transferred to Cuban and foreign industries [82]. The properties of natural clinoptilolite, including ion exchange, cause its chemical modification with nitrogen, phosphorous, potassium and others (calcium, minor and trace nutrients) in the quantities required by agricultural crops. NEREA@ is an environmentally friendly technology for both industrial production and use. These products facilitate efficient cultivation, saving up to 90% of chemical fertilizers and water, while significantly increasing crop yields and growth speed. The nutrients available to plants are stored in the zeolite, and crop plants receive them directly from the zeolitic particles. NEREA@ products release nutrients in a slow manner, which limits nutrient loss through leaching and volatilization.

In addition, a controlled release fertilizer was prepared starting from Slovak natural clinoptilolite subjected to ion exchanges processes, first with Na^+ and then with NH_4^+ (ammonium chloride) [83]. The authors reported that this fertilizer is an alternative to reduce losses and increase fertilizer efficiency. Studies of soils with the addition of natural clinoptilolite and vermiculite (in combination with urea or manure), and the associated processes of nitrogen mineralization and nitrification, have shown that these materials affect the availability of NH_4^+ and retard the accumulation of NO^{3-} in the soil [84]. Such an effect on NH_4^+ cation can be associated with the ion exchange property of clinoptilolite and its high affinity for this cation.

Review [85] summarizes recent and innovative applications of zeolites in the wine industry and provides a critical discussion of their ability to prevent protein clouding, tartrate instability, or other certain defects. Heavy metal cations at excessively high concentrations in wine can cause metallic off-flavors, unwanted color changes or cloudiness. Cloudiness in wine caused by heavy metals is a major problem in winemaking. It is usually caused by excessively high iron content in wine. Iron is absorbed through the grape roots in relatively small amounts. The most important source is corrosion of winery equipment. Haze due to copper is based on the formation of insoluble copper sulfide. Some transition metals (such as Fe and Cu) can catalyze oxidation reactions of phenols and other compounds in grape wine. Some metals are also undesirable for toxicological reasons. This is why efforts are being made to reduce the heavy metal content of these drinks. The limits below which clarification is not required are 4 ppm for iron and 0.5 ppm for copper.

6. Zeolites as a Nature-Forming Factor

Discussion of this range of phenomena leads us to the necessity and possibility to assume that, already by their existence on the surface of our planet, zeolite minerals influence the daily life of mankind. If it is possible to move thousands of tons of natural zeolite to create an artificial barrier on the way of spreading certain ions over the surface and in the hydrosphere, then all the same effects exist for geological times in places where they are deposited. Consequently, if comparing and analyzing some data, it becomes possible to discover some global effects that zeolites have on landscapes in which they occur.

Based on these claims, a new interdisciplinary scientific field has been proposed [86][87]. Medical geology is defined as the science that studies the relationship between geological factors and human, animal, and plant health problems. Medical geology can also be recognized as geomedicine; medical geography is developing in parallel, with a somewhat different meaning associated with the broader field of medical geology. Medical geography looks at the geographic distribution of disease without focusing on the underlying geology; this is why there are universally recognized resort centers where medics send the seriously ill to improve their health. This whole body of evolving knowledge examines the causal relationships between specific diseases and the physical and social environment. As the recent example of the discussion of the properties of erionite (see above) demonstrated, the field of study is complex and requires a serious interdisciplinary approach involving a wide range of specialists, from geologists and geochemists to medical scientists, biologists, and geneticists. The unique and exceptional physical and chemical properties of some minerals favor their use in numerous fields of medicine [88]. On the other hand, it is well known that people selfishly use natural resources to satisfy their needs regardless of what happens to the environment; therefore, nature’s “response” and its impact on public health is sometimes unexpected (exposure to toxic levels of trace elements, deficiency of essential trace elements, exposure to mineral dust, radioactivity, industrial disasters, and so on) [86].

The relationship between geology and human health is not unexpected news; it was first noted back in antiquity. During the Renaissance, the Swiss alchemist, physician and philosopher Paracelsus proclaimed the principle: “*Everything is poison, everything is medicine; only the dose differentiates a poison and a remedy*”. The development of atomic emission spectroscopy made it possible to analyze media with extremely low concentrations of elements. The application of this analytical method made it possible to measure the trace element composition of soils, plants, animal tissues, and other substances, leading to important scientific discoveries. Information about the vital necessity of trace elements and their influence on the condition of living organisms was collected [89].

The use of zeolites in the natural environment is important in terms of monitoring the mobilization of toxic metals and trace elements that affect the food chain, and their deficiency as well as excess determine the quality of plants and human and animal health [90]. In addition, zeolites, having certain physical, physico-chemical and chemical properties, interact with physical, physico-chemical, chemical and biological features of the soil, which can lead to changes in their properties. This exchange depends on many factors; however, when natural zeolites are used, one must remember that they are an ecological material and do not have a harmful effect on humans or animals. People suffering from micronutrient deficiencies usually suffer from cumulative element deficiencies, i.e., their diet lacks several vitamins and minerals at the same time. Quality malnutrition is directly or indirectly responsible for half of the deaths among children under five worldwide. Through deliberate intervention in agro-ecosystems, humans can control their productivity and increase the amount of biomass produced, which can be used as food for humans, feed for animals and raw materials for many industries. Therefore, the future of agriculture must be based on a diversity of plant species from which new, more useful and less processed products are produced. This approach contributes not only to security but also to the food sovereignty of society. Zeolites have proven to be promising binding agents for the mobility of toxic metal ions. In addition, their use alters soil pH values, largely determining the forms in which toxic metals exist in the soil [90].

Future research in medical geology should aim to establish a better understanding of the role of minerals in ecosystems. Among the minerals, zeolites interact easily and most importantly friendly with biological organisms (plants, animals, humans). In order to find new applications, one should determine the characteristics of the samples and their influence with regard to human health. It is necessary to consider minerals in relation to human health, to consider sources of toxic elements and possibilities of their removal. Planet Earth contributes to pollution through volcanic eruptions, radiation, toxic elements, dust, etc.; thus, anthropogenic activities should help to reduce pollution.

References

1. Briffa, J.; Sinagra, E.; Blundell, R. Heavy metal pollution in the environment and their toxicological effects on humans. Heliyon 2020, 6, e04691.
2. Suganthi, M.; Ramesh, N. Treatment of water using natural zeolite as membrane filter. J. Environ. Prot. Ecol. 2022, 23, 520–530.
3. Qasem, N.A.A.; Mohammed, R.H.; Lawal, D.U. Removal of heavy metal ions from wastewater: A comprehensive and critical review. npj Clean Water 2021, 4, 36.
4. Baldwin, D.R.; Marshall, W.J. Heavy metal poisoning and its laboratory investigation. Ann. Clin. Biochem. 1999, 36, 267–300.
5. Li, Y.; Li, L.; Yu, J. Applications of zeolites in sustainable chemistry. Chem 2017, 3, 928–949.
6. Yuna, Z. Review of the natural, modified, and synthetic zeolites for heavy metals removal from wastewater. Environ. Eng. Sci. 2016, 33, 443–454.
7. Arancibia-Miranda, N.; Baltazar, S.E.; García, A.; Muñoz-Lira, D.; Sepúlveda, P.; Rubio, M.A.; Altbir, D. Nanoscale zero valent supported by Zeolite and Montmorillonite: Template effect of the removal of lead ion from an aqueous solution. J. Hazard. Mater. 2016, 301, 371–380.
8. Rodríguez-Iznaga, I.; Rodríguez-Fuentes, G.; Petranovskii, V. Ammonium modified natural clinoptilolite to remove manganese, cobalt and nickel ions from wastewater: Favorable conditions to the modification and selectivity to the cations. Microporous Mesoporous Mater. 2018, 255, 200–210.
9. Rodríguez-Iznaga, I.; Petranovskii, V.; Rodríguez-Fuentes, G. Ion-exchange of amino- and aqua-complexes of nickel and cobalt in natural clinoptilolite. J. Environ. Chem. Eng. 2014, 2, 1221–

1227.

10. Rodríguez-Iznaga, I.; Gómez, A.; Rodríguez-Fuentes, G.; Benítez-Aguilar, A.; Serrano-Ballan, J. Natural clinoptilolite as an exchanger of Ni2+ and NH4+ ions under hydrothermal conditions and high ammonia concentration. Microporous Mesoporous Mater. 2002, 53, 71–80.
11. Senila, M.; Neag, E.; Cadar, O.; Kovacs, E.D.; Aschilean, I.; Kovacs, M.H. Simultaneous removal of heavy metals (Cu, Cd, Cr, Ni, Zn and Pb) from aqueous solutions using thermally treated Romanian zeolitic volcanic tuff. Molecules 2022, 27, 3938.
12. Katsou, E.; Malamis, S.; Tzanoudaki, M.; Haralambous, K.J.; Loizidou, M. Regeneration of natural zeolite polluted by lead and zinc in wastewater treatment systems. J. Hazard. Mater. 2011, 189, 773–786.
13. Panayotova, M.; Velikov, B. Influence of zeolite transformation in a homoionic form on the removal of some heavy metal ions from wastewater. J. Environ. Sci. Health-Part A Toxic/Hazard. Subst. Environ. Eng. 2003, 38, 545–554.
14. Vassileva, P.; Voikova, D. Investigation on natural and pretreated Bulgarian clinoptilolite for ammonium ions removal from aqueous solutions. J. Hazard. Mater. 2009, 170, 948–953.
15. Taneva, N. Removal of ammonium and phosphates from aqueous solutions by activated and modified Bulgarian clinoptilolite. J. Chem. Eng. Mater. Sci. 2012, 3, 79–85.
16. Taffarel, S.R.; Rubio, J. On the removal of Mn2+ ions by adsorption onto natural and activated Chilean zeolites. Miner. Eng. 2009, 22, 336–343.
17. Rajic, N.; Stojakovic, D.; Jovanovic, M.; Logar, N.Z.; Mazaj, M.; Kaucic, V. Removal of nickel(II) ions from aqueous solutions using the natural clinoptilolite and preparation of nano-NiO on the exhausted clinoptilolite. Appl. Surf. Sci. 2010, 257, 1524–1532.
18. Figueiredo, H.; Quintelas, C. Tailored zeolites for the removal of metal oxyanions: Overcoming intrinsic limitations of zeolites. J. Hazard. Mater. 2014, 274, 287–299.
19. Elizondo-Villarreal, N.; Obregón-Guerra, R.; García-Méndez, M.; Sánchez-Espinoza, A.P.; Alcorta-García, M.A.; Torres-Barrera, R.O.; Coello, V.; Castaño, V.M. Nanomodification of a natural clinoptilolite zeolite. Rev. Adv. Mater. Sci. 2016, 47, 74–78.
20. Du, G.; Li, Z.; Liao, L.; Hanson, R.; Leick, S.; Hoeppner, N.; Jiang, W.T. Cr(VI) retention and transport through Fe(III)-coated natural zeolite. J. Hazard. Mater. 2012, 221–222, 118–123.
21. Lv, G.; Li, Z.; Jiang, W.T.; Ackley, C.; Fenske, N.; Demarco, N. Removal of Cr(VI) from water using Fe(II)-modified natural zeolite. Chem. Eng. Res. Des. 2014, 92, 384–390.
22. Salgado-Gómez, N.; Macedo-Miranda, M.G.; Olguín, M.T. Chromium VI adsorption from sodium chromate and potassium dichromate aqueous systems by hexadecyltrimethylammonium-modified zeolite-rich tuff. Appl. Clay Sci. 2014, 95, 197–204.

23. Inglezakis, V.J.; Zorpas, A.A.; Loizidou, M.D.; Grigoropoulou, H.P. Simultaneous removal of metals Cu2+, Fe3+ and Cr3+ with anions SO42- and HPO42- using clinoptilolite. Microporous Mesoporous Mater. 2003, 61, 167–171.
24. Rodríguez-Iznaga, I.; Petranovskii, V.; Castillón-Barraza, F.; Concepción-Rosabal, B. Copper-silver bimetallic system on natural clinoptilolite: Thermal reduction of Cu2+ and Ag+ exchanged. J. Nanosci. Nanotechnol. 2011, 11, 5580–5586.
25. Rodríguez-Iznaga, I.; Petranovskii, V.; Chávez-Rivas, F.; Shelyapina, M.G. Bimetallic copper-silver systems supported on natural clinoptilolite: Long-term changes in nanospecies’ composition and stability. Inorganics 2022, 10, 34.
26. European Environment Agency. Available online: https://www.eea.europa.eu/data-and-maps/explore-interactive-maps/wise-soe-ammonium-in-rivers (accessed on 15 November 2022).
27. Molins-Legua, C.; Meseguer-Lloret, S.; Moliner-Martinez, Y.; Campíns-Falcó, P. A guide for selecting the most appropriate method for ammonium determination in water analysis. TrAC—Trends Anal. Chem. 2006, 25, 282–290.
28. Berenzen, N.; Schulz, R.; Liess, M. Effects of chronic ammonium and nitrite contamination on the macroinvertebrate community in running water microcosms. Water Res. 2001, 35, 3478–3482.
29. Saiapina, O.; Vronska, Y.; Dzyadevych, S.; Jaffrezic-Renault, N. Clinoptilolite-based Conductometric Sensors for Detection of Ammonium in Aqueous Solutions. Electroanalysis 2020, 32, 1993–2001.
30. Valdés, M.G.; Pérez-Cordoves, A.I.; Díaz-García, M.E. Zeolites and zeolite-based materials in analytical chemistry. TrAC—Trends Anal. Chem. 2006, 25, 24–30.
31. Walcarius, A. Zeolite-modified electrodes in electroanalytical chemistry. Anal. Chim. Acta 1999, 384, 1–16.
32. Saiapina, O.Y.; Pyeshkova, V.M.; Soldatkin, O.O.; Melnik, V.G.; Kurç, B.A.; Walcarius, A.; Dzyadevych, S.V.; Jaffrezic-Renault, N. Conductometric enzyme biosensors based on natural zeolite clinoptilolite for urea determination. Mater. Sci. Eng. C 2011, 31, 1490–1497.
33. Guida, S.; Potter, C.; Jefferson, B.; Soares, A. Preparation and evaluation of zeolites for ammonium removal from municipal wastewater through ion exchange process. Sci. Rep. 2020, 10, 12426.
34. Inglezakis, V.J.; Loizidou, M.D. Ion exchange of some heavy metal ions from polar organicsolvents into zeolite. Desalination 2007, 211, 238–248.
35. Shelyapina, M.G.; Rodríguez-Iznaga, I.; Petranovskii, V. Materials for CO2, SOx, and NOx emission reduction. In Handbook of Nanomaterials and Nanocomposites for Energy and

Environmental Applications; Kharissova, O.V., Martínez, L.M.T., Kharisov, B.I., Eds.; Springer: Cham, Switzerland, 2020; pp. 1–30. ISBN 978-3-030-11155-7.

36. Ackley, M.W.; Rege, S.U.; Saxena, H. Application of natural zeolites in the purification and separation of gases. Microporous Mesoporous Mater. 2003, 61, 25–42.
37. Bai, R.; Song, X.; Yan, W.; Yu, J. Low-energy adsorptive separation by zeolites. Natl. Sci. Rev. 2022, 9, nwac064.
38. Wang, Q.; Yu, Y.; Li, Y.; Min, X.; Zhang, J.; Sun, T. Methane separation and capture from nitrogen rich gases by selective adsorption in microporous materials: A review. Sep. Purif. Technol. 2022, 283, 120206.
39. Hoang, H.G.; Thuy, B.T.P.; Lin, C.; Vo, D.-V.N.; Tran, H.T.; Bahari, M.B.; Le, V.G.; Vu, C.T. The nitrogen cycle and mitigation strategies for nitrogen loss during organic waste composting: A review. Chemosphere 2022, 300, 134514.
40. Manu, M.K.; Wang, C.; Li, D.; Varjani, S.; Wong, J.W.C. Impact of zeolite amendment on composting of food waste digestate. J. Clean Prod. 2022, 371, 133408.
41. Mehrabadi, Z.; Faghihian, H. Clinoptilolite modified with TiO2 for simultaneous elimination of two herbicides; 2,4-D and MCPA by UV and sunlight-assisted photocatalytic degradation. Mater. Res. Bull. 2019, 119, 110569.
42. Nikazar, M.; Gholivand, K.; Mahanpoor, K. Using TiO2 supported on Clinoptilolite as a catalyst for photocatalytic degradation of azo dye Disperse yellow 23 in water. Kinet. Catal. 2007, 48, 214–220.
43. Sene, R.A.; Sharifnia, S.; Moradi, G.R. On the impact evaluation of various chemical treatments of support on the photocatalytic properties and hydrogen evolution of sonochemically synthesized TiO2/Clinoptilolite. Int. J. Hydrog. Energy 2018, 43, 695–707.
44. Nezamzadeh-Ejhieh, A.; Moazzeni, N. Sunlight photodecolorization of a mixture of Methyl Orange and Bromocresol Green by CuS incorporated in a clinoptilolite zeolite as a heterogeneous catalyst. J. Ind. Eng. Chem. 2013, 19, 1433–1442.
45. Petranovskii, V.; Pestryakov, A.N.; Kazantseva, L.K.; Cruz, J.; Kryazhov, A.N. Formation of catalytically active copper and nickel nanoparticles in natural zeolites. Stud. Surf. Sci. Catal. 2008, 174, 513–516.
46. Petranovskii, V.P.; Pestryakov, A.N.; Kazantseva, L.K.; Castillon Barraza, F.; Farias, M.H. Formation of catalytically active copper nanoparticles in natural zeolites for complete oxidation of hydrocarbons. Int. J. Mod. Phys. B 2005, 19, 2333–2338.
47. Azimi, S.C.; Shirini, F.; Pendashteh, A.R. Advanced oxidation process as a green technology for dyes removal from wastewater: A review. Iran. J. Chem. Chem. Eng. 2021, 40, 1467–1489.

48. Sodha, V.; Shahabuddin, S.; Gaur, R.; Ahmad, I.; Bandyopadhyay, R.; Sridewi, N. Comprehensive review on zeolite-based nanocomposites for treatment of effluents from wastewater. Nanomaterials 2022, 12, 3199.
49. Alvarez-Aguiñaga, E.A.; Elizalde-González, M.P.; Sabinas-Hernández, S.A. Unpredicted photocatalytic activity of clinoptilolite-mordenite natural zeolite. RSC Adv. 2020, 10, 39251–39260.
50. Sydorchuk, V.; Vasylechko, V.; Khyzhun, O.; Gryshchouk, G.; Khalameida, S.; Vasylechko, L. Effect of high-energy milling on the structure, some physicochemical and photocatalytic properties of clinoptilolite. Appl. Catal. A Gen. 2021, 610, 117930.
51. Saramok, M.; Szymaszek, A.; Inger, M.; Antoniak-Jurak, K.; Samojeden, B.; Motak, M. Modified zeolite catalyst for a NOx selective catalytic reduction process in nitric acid plants. Catalysts 2021, 11, 450.
52. Sobuś, N.; Król, M.; Piotrowski, M.; Michorczyk, B.; Czekaj, I.; Kornaus, K.; Trenczek-Zając, A.; Komarek, S. Conversion of dihydroxyacetone to carboxylic acids on pretreated clinoptilolite modified with iron, copper, and cobalt. Catal. Commun. 2022, 171, 106509.
53. Mačala, J.; Pandová, I. Natural zeolite-clinoptilolite—Raw material serviceable in the reduction of toxical components at combustion engines noxious gases. Gospod. Surowcami Miner. 2007, 23, 19–26.
54. Moreno-Tost, R.; Santamaría-González, J.; Rodríguez-Castellón, E.; Jiménez-López, A.; Autié, M.A.; Glacial, M.C.; Castro, G.A.; Guerra, M. Selective catalytic reduction of nitric oxide by ammonia over Ag and Zn-exchanged Cuban natural zeolites. Z. Für Anorg. Und Allg. Chem. 2005, 631, 2253–2257.
55. Ates, A.; Reitzmann, A.; Hardacre, C.; Yalcin, H. Abatement of nitrous oxide over natural and iron modified natural zeolites. Appl. Catal. A Gen. 2011, 407, 67–75.
56. Godelitsas, A.; Armbruster, T. HEU-type zeolites modified by transition elements and lead. Microporous Mesoporous Mater. 2003, 61, 3–24.
57. Shaheen, S.M.; Derbalah, A.S.; Moghanm, F.S. Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. Int. J. Environ. Sci. Dev. 2012, 3, 362–367.
58. Colella, C. A critical reconsideration of biomedical and veterinary applications of natural zeolites. Clay Miner. 2011, 46, 295–309.
59. Pavelić, S.K.; Medica, J.S.; Gumbarević, D.; Filošević, A.; Pržulj, N.; Pavelić, K. Critical review on zeolite clinoptilolite safety and medical applications in vivo. Front. Pharmacol. 2018, 9, 1350.
60. Rodríguez-Fuentes, G.; Rodríguez Iznaga, I.; Boza, A.; Anaisa, P.; Cedré, B.; Bravo-Fariñas, L.; Ruiz, A.; Fernández-Abreu, A.; Sende Odoardo, V. Evaluation of a zinc clinoptilolite (ZZ®) for

drinking water treatment. In Aquananotechnology. Global Prospects; Reisner, D.E., Pradeep, T., Eds.; CRC Press: Boca Raton, FL, USA, 2014; p. 26. ISBN 9780429185632.

61. Cerri, G.; de Gennaro, M.; Bonferoni, M.C.; Caramella, C. Zeolites in biomedical application: Zn-exchanged clinoptilolite-rich rock as active carrier for antibiotics in anti-acne topical therapy. Appl. Clay Sci. 2004, 27, 141–150.
62. Park, H.J.; Lim, H.M. Antimicrobial properties of Ag-exchanged natural and synthetic zeolites: A short review. Curr. Green Chem. 2015, 2, 354–361.
63. Guerra, R.; Lima, E.; Viniegra, M.; Guzmán, A.; Lara, V. Growth of Escherichia coli and Salmonella typhi inhibited by fractal silver nanoparticles supported on zeolites. Microporous Mesoporous Mater. 2012, 147, 267–273.
64. De Gennaro, M.; Cerri, G.; Caramella, C.M.; Bonferoni, M.C. Pharmaceutical Zeolite-Based Compositions Containing Zinc and Erythromycin, to be Used in the Treatment of Acne. International Patent WO2002100420A2, 19 December 2002.
65. Vergara-Figueroa, J.; Alejandro-Martín, S.; Pesenti, H.; Cerda, F.; Fernández-Pérez, A.; Gacitúa, W. Obtaining nanoparticles of chilean natural zeolite and its ion exchange with copper salt (Cu2+) for antibacterial applications. Materials 2019, 12, 2202.
66. Ivankovic, T.; Dikic, J.; Du Roscoat, S.R.; Dekic, S.; Hrenovic, J.; Ganjto, M. Removal of emerging pathogenic bacteria using metal-exchanged natural zeolite bead filter. Water Sci. Technol. 2019, 80, 1085–1098.
67. Guidelines for Drinking-Water Quality: 4th Edition, Incorporating the 1st Addendum; World Health Organization: Geneva, Switzerland, 2017; ISBN 978-92-4-154995-0.
68. Mumpton, F.A. La roca magica: Uses of natural zeolites in agriculture and industry. Proc. Natl. Acad. Sci. USA 1999, 96, 3463–3470.
69. de Campos Bernardi, A.C.; Polidoro, J.C.; de Melo Monte, M.B.; Pereira, E.I.; de Oliveira, C.R.; Ramesh, K. Enhancing nutrient use efficiency using zeolites minerals—A review. Adv. Chem. Eng. Sci. 2016, 6, 295–304.
70. Pal, D.K.; Wani, S.P.; Sahrawat, K.L. Zeolitic soils of the Deccan basalt areas in India: Their pedology and edaphology. Curr. Sci. 2013, 105, 309–318.
71. Brito-Rojas, A.D.; Coutín-Correa, D.P.; Rodríguez-Fuentes, G. Volcanogenic Sedimentary Zeolite Deposits in Cuba. Report to the Commission on Natural Zeolite of the International Zeolite Association (IZA). Available online: http://www.iza-online.org/natural/Catalog/Cuba.pdf (accessed on 19 November 2022).
72. US Geological Survey. Mineral Commodity Summaries; Government Printing Office: Washington, DC, USA, 2009.

73. National Minerals Information Center Zeolites Statistics and Information. Available online: https://www.usgs.gov/centers/national-minerals-information-center/zeolites-statistics-and-information (accessed on 11 November 2022).
74. Fatmah Siregar, A.F.; Sipahutar, I.A.; Masunaga, T. Beneficial effect of silicon application and intermittent irrigation on improving rice productivity in Indonesia. Indones. J. Agron. 2020, 48, 15–21.
75. Alhousari, F.; Greger, M. Silicon and mechanisms of plant resistance to insect pests. Plants 2018, 7, 33.
76. Bakhat, H.F.; Bibi, N.; Zia, Z.; Abbas, S.; Hammad, H.M.; Fahad, S.; Ashraf, M.R.; Shah, G.M.; Rabbani, F.; Saeed, S. Silicon mitigates biotic stresses in crop plants: A review. Crop Prot. 2018, 104, 21–34.
77. Eugercios Silva, A.R.; Álvarez-Cobelas, M.; Montero González, E. Impactos del nitrógeno agrícola en los ecosistemas acuáticos. Ecosistemas 2017, 26, 37–44.
78. Latifah, O.; Ahmed, O.H.; Majid, N.M.A. Enhancing nitrogen availability from urea using clinoptilolite zeolite. Geoderma 2017, 306, 152–159.
79. Souza, I.M.S.; Gurgel, G.C.S.; Medeiros, A.M.; Zonta, E.; Ruiz, J.A.C.; Paskocimas, C.A.; Motta, F.V.; Bomio, M.R.D. The use of clinoptilolite as carrier of nitrogened fertilizer with controlled release. J. Environ. Chem. Eng. 2018, 6, 4171–4177.
80. Omar, L.; Ahmed, O.H.; Jalloh, M.B.; Muhamad, A.M.N. Soil nitrogen fractions, nitrogen use efficiency and yield of Zea mays L. Grown on a tropical acid soil treated with composts and clinoptilolite zeolite. Appl. Sci. 2020, 10, 4139.
81. Wang, Y.; Sun, Y.; Chen, H.; Wu, Q.; Chi, D. Assessing the performance of clinoptilolite for controlling and releasing ammonium in agricultural applications. Energy Rep. 2021, 7, 887–895.
82. International Zeolite. Available online: https://internationalzeolite.com/nerea/ (accessed on 5 November 2022).
83. Mihok, F.; Macko, J.; Oriňak, A.; Oriňaková, R.; Koval', K.; Sisáková, K.; Petruš, O.; Kostecká, Z. Controlled nitrogen release fertilizer based on zeolite clinoptilolite: Study of preparation process and release properties using molecular dynamics. Curr. Res. Green Sustain. Chem. 2020, 3, 100030.
84. Tzanakakis, V.A.; Monokrousos, N.; Chatzistathis, T. Effects of clinoptilolite zeolite and vermiculite on nitrification and nitrogen and phosphorus acquiring enzymes in a nitrogen applied agricultural soil. J. Soil Sci. Plant Nutr. 2021, 21, 2791–2802.
85. Noviello, M.; Gattullo, C.E.; Faccia, M.; Paradiso, V.M.; Gambacorta, G. Application of natural and synthetic zeolites in the oenological field. Food Res. Int. 2021, 150 Pt A, 110737.

86. Ríos Reyes, C.A.; Ríos Gutiéttez, M.P.; Joya Neira, S. The importance of minerals in medical geology: Impacts of the environment on health. Arch. Med. 2020, 21, 182–202.
87. International Medical Geology Association. Available online: https://medicalgeology.org/ (accessed on 15 November 2022).
88. Gomes, C.D.S.F.; Silva, J.B.P. Minerals and clay minerals in medical geology. Appl. Clay Sci. 2007, 36, 4–21.
89. Farkhutdinov, I.; Farkhutdinova, L.; Zlobina, A.; Farkhutdinov, A.; Volfson, I.; Matveenko, I. Historical aspects of medical geology. Earth Sci. Hist. 2020, 39, 172–183.
90. Badora, A. The influence of zeolites on quality indicators of soil-plant connection and food safety. In Zeolites—Useful Minerals; Belviso, C., Ed.; IntechOpen: London, UK, 2016; pp. 203–215.

Retrieved from https://encyclopedia.pub/entry/history/show/88999