

Review

Application of Zeolites in Agriculture and Other Potential Uses: A Review

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Abstract: Excessive use of nitrogen fertilizer and inappropriate fertilization designs have negative results in agricultural ecosystems, such as considerable nitrogen losses through nitrogen dioxide (NO₂) soil leaching and ammonia NH₃ volatilization. In addition, climate change, with rising summer temperatures and reduced precipitation, leads to production declines and water shortages in the soil. This review aims to highlight the characteristics of natural zeolite and focus on their multiple uses in agriculture. These minerals are tectosilicates showing an open three-dimensional structure involving the cations required to balance the framework electrostatic charge of aluminum and silicon tetrahedral units. Different research groups reported more than fifty natural zeolites; chabazite, clinoptilolite, phillipsite, erionite, stilbite, heulandite, and mordenite are the most well-known. Zeolites are great tools to help the farmer and agronomist cope with several issues, such as soil or water pollution, contamination by heavy metals, loss of nutrients, and loss of water-use efficiency (WUE) of drylands. These natural crystalline aluminosilicates are considered soil conditioners to improve soil chemical and physical properties, such as saturated hydraulic conductivity (K_s), infiltration rate, cation exchange capacity (CEC), and water-holding capacity (WHC). Owing to their properties, these materials are able to reduce nitrate leaching and ammonia volatilization. Zeolites are also known for their carrying capacity of slow-release macronutrients, micronutrients, and fertilizers. However, the potential of these materials in agricultural areas is apparent, and zeolites show the promise of contributing directly to improve agricultural ecosystems as a sustainable product.

Keywords: zeolite; agriculture; global warming; compost; synthetic fertilizers; water stress; ammonia



Citation: Cataldo, E.; Salvi, L.; Paoli, F.; Fucile, M.; Masciandaro, G.; Manzi, D.; Masini, C.M.; Mattii, G.B.

Application of Zeolites in Agriculture and Other Potential Uses: A Review.

Agronomy **2021**, *11*, 1547. <https://doi.org/10.3390/agronomy11081547>

Academic Editor: Frédéric Marsolais

Received: 21 June 2021

Accepted: 28 July 2021

Published: 31 July 2021

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1. Introduction

The widespread use of synthetic fertilizers in current agricultural practices has disrupted the planet's chemistry by doubling the flow of nitrogen and phosphorus into ecosystems to levels of around 121 million tons of nitrogen (N) and 9 million tons of phosphorus (P) per year [1,2]. In addition, ammonia (NH₃) volatilization is the leading cause of nitrogen loss in agricultural systems worldwide [3], and, consequently, it is conducive to low fertilizer nitrogen use efficiency with health and environmental damages and leads to indirect nitrous oxide (N₂O) emission [4]. The growing intake of synthetic fertilizers, associated with the use of brackish irrigation water, especially in coastal areas, represents a serious threat to the environment, as it alters the humic-mineral and microbiological context of the soil with consequent progressive loss of fertility until sterility is reached, i.e., desertification (degradation of land resources) [5,6].

On the other hand, the fertilizer industry is considered a source of heavy metals and natural radionuclides [7]. Synthetic fertilizers contain a large majority of the heavy metals, notably mercury (Hg), cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), and nickel

(Ni), and natural radionuclides, such as uranium (U-238), thorium (Th-232), and polonium (Po-210) [8–10]. Hence, fertilization may affect the accumulation of several heavy metals in plant systems and soil [11,12]. As a result, most agricultural soils are intrinsically low in fertility or made less fertile due to inadequate or incorrect replenishment due to low efficiency of input use (fertilizers and water) owing to nutrient losses through various loss mechanisms: non-absorption, runoff, volatilization, water deficit, etc. [13].

In addition to the scenario of soil resources' depletion, the situation regarding climate change is added and has caused diverse ecological responses in crops [14,15]. Global warming increases the frequency of exposure to extreme temperatures in crops, increasing the risk of a water deficit, and therefore, can cause damage to production and quality [16,17]; higher temperatures also affect plants' ability to obtain and use moisture (increased evapotranspiration) [18].

It is in this context that the zeolites' use in agriculture/water stress/heavy metals/soil-fertility management assumes greater significance [19]. The present paper reviews the critical properties of natural zeolites and their important uses in agriculture and other sectors. This work also calls for greater involvement of scientists in biochemical investigations essential for the future development of zeolite and its applications.

2. History and Origin of Zeolites

The discovery of natural zeolites has opened an important chapter in the mineralogy sector owing to their exciting surface and structural properties that have been exploited in many areas: agriculture, industrial technology, animal husbandry, cosmetics and biotechnology industry.

Firstly, natural zeolites were found in vugs in basalt rocks and in cavities. Afterwards, they were also discovered in sedimentary rocks (19th century). In 1756, Alex Fredrik Crönstedt, a Swedish mineralist, first identified natural zeolite as a mineral after he sampled crystals from a copper mine in Sweden. The mineralist discovered that the new mineral, when heated quickly after absorbing water, produced large amounts of water vapor [20]. Based on this phenomenon (ability to froth when heated to about 200 °C), he called the material zeolite, "boiling stones", from the Greek words ζέω, "boil" and λίθος, "stone" [21]. For many years, the discovery remained unapplied, but fortunately in the 1950s, they were rediscovered and detected on many continents. After several geological explorations, geologists included the following genetic types in zeolite formation:

- Crystals found from hot-spring or hydrothermal activity (reaction with basaltic lava flows);
- Sediments originating from volcanic deposits in saline and alkaline lake systems;
- Deposits originating in alkaline soil from volcanic sediments;
- Deposits formed from marine sediments' low-temperature or hydrothermal alteration;
- Formations resulting from low-grade burial metamorphism [22].

The golden age period for the zeolites' development was from 1954 to 1980. Their commercial production and their use began in the 1960s, in most countries, while in Turkey they were first discovered in 1971 [23,24]. To date, more than 50 types of natural zeolites have been reported by several research groups: clinoptilolite, chabazite, erionite, phillipsite, mordenite, analcite, etc. [25]. Rarely are natural zeolites present in nature in sediments pure; in fact, they are often contaminated with other minerals, quartz, metals, etc. [26]. In the 1960s, most research on the use of zeolites in agriculture began in Japan. Japanese farmers, over the years, used zeolites to control soil moisture and to increase the pH of acidic volcanic soils [27,28]. Even though there are no affordable data on the total amount of these minerals in the world, some countries, for instance Japan, South Africa, Cuba, USA, Italy, Bulgaria, Hungary, Germany, and Russia, have important reserves and production potentials [29]; nonetheless more than 300,000 tons of zeolite-rich tuff is mined each year in these countries [27]. Besides, over the years, more than one hundred and fifty zeolites have been synthesized. Synthetic zeolites are useful because of their controlled and known chemical-physic properties [30]. By the 1980s, over 100 zeolites had been synthesized.

While synthetic zeolites have been used extensively in commercial application, demand for natural zeolite has been limited. Their primary use is in areas where the use of synthetic zeolites would be uneconomical [31]. Annual data of the United States Geological Survey (USGS) released zeolite production estimates as 4 million tons per year; US consumption is around 0.5 million tons, while China uses around 2.5 million tons per year, firstly as an additive to pozzolan cement [32].

3. Classification and Structure of Zeolites

Zeolites are a large family of minerals and are among the most important in microporous materials. The word “zeolite” indicates a silica polymorph or crystalline aluminosilicate based on several corner-sharing TO_4 tetrahedrals (T = usually silicon and aluminum) forming a three-dimensional four-connected framework with regularly sized pores of molecular dimension [33].

Nowadays, the “zeolite framework” term, in general, indicates a corner-sharing network of tetrahedrally organized atoms [34]. Zeolites are tectosilicates, hydrated crystalline aluminosilicates of alkaline and alkali earth element (cations) [35]. In nature, when volcanic ash interacts with the high-pH water and high-salt content, zeolites are normally formed, causing a rapid crystal formation [36]. These volcanogenic sedimentary mineral, found in volcanic rocks for a period of 250 years, are joined into three dimensional frameworks and composed by pores and corner-sharing tetrahedrons of alumina (AlO_4) and silica (SiO_4) [37]. The “roca magica” has an infinite, open, three-dimensional structure [38]. Briefly, they are solids with an open, three-dimensional crystal structure composed of several elements, such as silicon (Si), aluminum (Al), and oxygen (O), with alkaline or alkali metals (for example magnesium (Mg), sodium (Na), and potassium (K)) and trapped water molecules in the pores between them [39]. The pores’ diameters are around 12 ångström (Å); the pores are interlinked with channels about 8 Å in diameter; rings of approximately 12 linked tetrahedrons compose these cages [40,41].

The ratio of Si/Al is a zeolites’ important characteristic; in fact, it determines the ion exchange characteristics of the mineral. Until 1977, zeolite minerals were distinguished based on the Si/Al ratio, except for clinoptilolite (Si/Al \geq 4.0) and heulandite (Si/Al < 4.0). Zeolite minerals are classified on the basis of silica/alumina ratio in the following way [42]:

- (a) Zeolites erionite and mordenite—high Si/Al ratio (from 10 to several thousands);
- (b) Zeolites Y—intermediate Si/Al ratio (2 to 5);
- (c) Zeolites A—low Si/Al ratio (between 1.0 and 1.5).

The siliceous zeolites are organophilic non-polar sorbents, while the aluminous ones are strong desiccants [43].

After the report of the International Mineralogical Association Commission on New Minerals and Mineral Names there was a suggested nomenclature for zeolite species. Partial hydration, dehydration, and over-hydration were not sufficient points for the recognition of several zeolites [44]. In 2001, Jacobs et al. [45] introduced a new classification of zeolites based on the size of their pores (pore diameter):

- (1) 14 member rings; extra-large-pore zeolites with free pore diameter of 0.8–1.0 nm;
- (2) 12 member rings; large-pore zeolites with free pore diameter of 0.6–0.8 nm;
- (3) 10 member rings; medium-pore zeolites with free pore diameter of 0.45–0.6 nm;
- (4) 8 member rings; small-pore zeolites with free pore diameter of 0.3–0.45 nm [46].

4. Properties of Zeolites

The empirical formula of a zeolite is of the type: $\text{M}_{2/n}\text{O Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where n is the valence charge on that element; M is an alkali or alkaline earth element, and y is a number from 2 to 7. The empirical and unit-cell formulas of some of the most common natural zeolites are reported in Table 1. In the formula, exchangeable cations are contained in the first set of parentheses; structural cations are contained in the second set of parentheses instead (with the oxygen they make up the tetrahedral framework of

the structure). Loosely bound molecular water is normally present in the structures of all-natural zeolites [27].

Table 1. Representative formulae and selected physical properties of important zeolites. Reproduced from [38], with permission from “Copyright (1999) National Academy of Sciences, U.S.A.”. * Calculated from unit-cell formula.

Zeolite	Representative Unit-Cell Formula	Void Volume, %	Channel Dimensions, Å	Thermal Stability (Relative)	CEC, meq/g *
Analcime	$\text{Na}_{10}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \bullet 16\text{H}_2\text{O}$	18	2.6	High	4.54
Chabazite	$(\text{Na}_2\text{Ca})_6(\text{Al}_{12}\text{Si}_{24}\text{O}_72) \bullet 40\text{H}_2\text{O}$	47	3.7×4.2	High	3.84
Clinoptilolite	$(\text{Na}_3\text{K}_3)(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \bullet 24\text{H}_2\text{O}$	34	3.9×5.4	High	2.16
Erionite	$(\text{NaCa}_{0.5}\text{K})_9(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \bullet 27\text{H}_2\text{O}$	35	3.6×5.2	High	3.12
Faujasite	$(\text{Na}_{58})(\text{Al}_{58}\text{Si}_{134}\text{O}_{384}) \bullet 240\text{H}_2\text{O}$	47	7.4	High	3.39
Ferrierite	$(\text{Na}_2\text{Mg}_2)(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \bullet 18\text{H}_2\text{O}$	28	4.3×5.5	High	2.33
Heulandite	$(\text{Ca}_4)(\text{Al}_8\text{Si}_{28}\text{O}_{72}) \bullet 24\text{H}_2\text{O}$	39	$4.0 \times 5.544 \times 7.241 \times 4.7$	Low	2.91
Laumonite	$(\text{Ca}_4)(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \bullet 16\text{H}_2\text{O}$	34	4.6×6.3	Low	4.25
Mordenite	$(\text{Na}_8)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \bullet 24\text{H}_2\text{O}$	28	$2.9 \times 5.767 \times 7.0$	High	2.29
Phillipsite	$(\text{NaK})_5(\text{Al}_5\text{Si}_{11}\text{O}_{32}) \bullet 20\text{H}_2\text{O}$	31	$4.2 \times 4.428 \times 4.833$	Medium	3.31
Linde A	$(\text{Na}_{12})(\text{Al}_{12}\text{Si}_{12}\text{O}_{48}) \bullet 27\text{H}_2\text{O}$	47	4.2	High	5.48
Linde X	$(\text{Na}_{86})(\text{Al}_{86}\text{Si}_{106}\text{O}_{384}) \bullet 264\text{H}_2\text{O}$	50	7.4	High	4.73

The chemical composition of zeolites varies widely depending on their area of origin, especially as regards the content of Na_2O , K_2O , CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 . For example, zeolite originated from Naples: 52.15% SiO_2 , 2.35% CaO , 7.54% K_2O , 18.56% AlO_3 , 3.30% Na_2O , 0.20% FeO_3 , 0.20% MgO , 212 CEC (cation-exchange capacity ($\text{cmol}(\text{p}+) \text{kg}^{-1}$)), 2.18 $\text{SiO}_2/\text{Al}_2\text{O}_3$; zeolite originated from Argentina: 62.70% SiO_2 , 0.40% CaO , 1.20% K_2O , 12.50% AlO_3 , 6.40% Na_2O , 0.60% FeO_3 , 0.60% MgO , 175 CEC (cation-exchange capacity ($\text{cmol}(\text{p}+) \text{kg}^{-1}$)), 5.02 $\text{SiO}_2/\text{Al}_2\text{O}_3$ [19].

Chemical and physical properties of these minerals include their thermal expansion, morphology, color, density, particle size, uniformity of composition, hardness, optical properties, dielectric properties, electrical conductivity, thermochemistry, zeolitic water, pore-volume, the structure of external and internal tetrahedral linkages, and framework density [47]. Dimension, shape, high purity, and linkage of their pores and their voids are the key characteristics of zeolite properties [48,49]. Zeolites have three main properties that are of interest for agricultural purposes: high water-holding capacity in the free channels both in soil and pots, high cation-exchange capacity, and high adsorption capacity [50]. Water molecules and cations occupy interconnected voids and pores. The mineral structure is very complex, but zeolite has large-open ‘channels’ in its crystal structure, which provide void space for cation exchange and adsorption [51]. Zeolites are extremely effective ion exchangers due to the internal surface area of channels. Zeolites, without a change of their crystal structure, are able to gain and lose water reversibly and to exchange extra-framework cations. The entry channels and large structural cavities into them contain molecules of water that construct hydration spheres around exchangeable cations. With heating at 350–400 °C and water removal, small molecules (larger molecules are excluded) can pass through entry channels, the “molecular sieve” zeolite property [52]. Other useful properties include: cation selectivity, specifically for such cations as potassium, cesium, and ammonium; low density (2.1–2.2 g/cm^3); high void volume (50%); and high cation-exchange capacity of 150–250 cmol/kg (CEC) [53,54]. Some physical properties among the most well-known zeolites are [21]:

- Analcite: high heat stability, 18% porosity, 2.24–2.29 g/cm^3 specific gravity, 1.85 g/cm^3 bulk density, 4.54 meq/g ion exchange capacity;
- Chabazite: high heat stability, 47% porosity, 2.05–2.10 g/cm^3 specific gravity, 1.45 g/cm^3 bulk density, 3.84 meq/g ion exchange capacity;

- Clinoptilolite: high heat stability, 34% porosity, 2.15–2.25 g/cm³ specific gravity, 1.15 g/cm³ bulk density, 2.16 meq/g ion exchange capacity;
- Erionite: high heat stability, 35% porosity, 2.02–2.08 g/cm³ specific gravity, 1.51 g/cm³ bulk density, 3.12 meq/g ion exchange capacity;
- Heulandite: low heat stability, 39% porosity, 2.18–2.20 g/cm³ specific gravity, 1.69 g/cm³ bulk density, 2.91 meq/g ion exchange capacity;
- Mordenite: high heat stability, 28% porosity, 2.12–2.15 g/cm³ specific gravity, 1.70 g/cm³ bulk density, 4.29 meq/g ion exchange capacity;
- Phillipsite: moderate heat stability, 31% porosity, 2.15–2.20 g/cm³ specific gravity, 1.58 g/cm³ bulk density, 3.31 meq/g ion exchange capacity.

To summarize, zeolites' properties that are structure-related are as follows:

- The behavior of 'zeolitic' water: high potency of hydration and dehydration [55];
- Extensive void volume and low density when dehydrated [56];
- Molecular sieve property [57];
- Stability of the crystal structure of many dehydrated zeolites when 50% volumes of the dehydrated crystals are void [58];
- In the dehydrated crystals, homogenous molecular-sized channels [32];
- Cation exchange features [59] and the removal of heavy metals [60];
- Several physical properties, such as electrical conductivity [61];
- Gases and vapors adsorption [62];
- Catalytic properties [63].

5. Application of Zeolites in Agriculture

Due to the International Agency for Research on Cancer (IARC) classification of zeolites as 'non-toxic' and due to the Food and Drug Administration (FDA) classification as "safe" for human consumption, zeolites are extensively used for agricultural uses [64]. Clinoptilolite, a member of the natural zeolite heulandite group, is the most abundant in sediments and soils and is the most common zeolite used in agricultural practices (for instance, for promoting nitrogen retention in soils and as a soil amendment) [65].

5.1. Fertilizer Efficiency

The enormous use of chemical fertilizers causes serious environmental hazards as only a fraction is really absorbed by the soil. The extra fertilizer is washed off, and this phenomenon leads to high concentrations of potassium, nitrogen, and phosphorus in surface water bodies (eutrophication) or of groundwater nitrates [66]. These problems can be resolved using slow-release fertilizers (SRFs) [67]; the elevated selectivity of clinoptilolite for cations, such as potassium and ammonium, has been taken advantage of in the preparation of chemical fertilizers [68]. Zeolites promote the nutrient-retention capacity of the soils by improving the slower release of these elements for uptake by crops [69]. By using a cationic surfactant, hexadecyltrimethylammonium bromide, the zeolite-A surface was positively modified to increase its capacity to retain anion phosphate (PO₄³⁻) [70]. Barbarick et al. (1990) [71] demonstrated on *Sorghum bicolor* L. that zeolite with slightly soluble phosphate rock provides a sustained and slow release of P by increasing dry matter, nutrient content, and nutrient uptake of the crop. An increase in spinach yield and in spinach plants' assimilation of nutrients, in a greenhouse test, were found after the application of zeolite with ammonium (NH₄⁺) and potassium [72]. In croton plants (*Codiaeum variegatum* L.), zeolitic tuff added to peat moss and perlite retained nutrients in the root zone, leading to the more efficient use of N and K fertilizers [73]. The use of a natural clinoptilolite to enhance rice grain yield, nitrogen recovery, and nitrogen-use efficiency, was tested in a coarse-textured rice field in Iran; results indicated a significant positive effect of the mixture of zeolite and fertilizer [74]. In addition, nutrient concentrations determined in maize (*Zea mays* L.) tissues were clearly affected by the addition of zeolite; the use of inorganic fertilizers mixed with zeolites remarkably increased N, P, and K uptake and their use efficiency in roots, leaves, and stem [75]. It was found that the nitrogen adsorption

by radish tops increased with a zeolite treatment compared with an ammonium sulfate control. Also, they found that clinoptilolite added to soil with urea reduced the growth suppression that normally occurs when urea is added alone in soil [27].

5.2. Soil Amendment

Zeolites have several positive effects on soil properties, such as increasing soil moisture, promoting hydraulic conductivity, and increasing yields in acidified soils; they are widely used as soil conditioners to improve soil physio-chemical properties [76]. Soil-cationic exchange capacity can be increased using zeolites as soil amendment [77]. Zeolite is not acidic but is marginally alkaline, and its use with fertilizers can help buffer soil pH levels, thus reducing the need for lime application [21]. In Japan, natural zeolites were used as amendments for sandy soils and were exported to Taiwan for this purpose. Zeolitic amendment is an effective way to improve soil conditions in semi-arid and arid environments [78]. Zeolite increased the cation-exchange capacity of vineyard soils, thus affecting nutrient availability and triggering microbial metabolic activity stimulation (increase in dehydrogenase activity) and soil organic matter alteration [79]. The application of the Brazilian zeolitic sedimentary rocks as a soil conditioner significantly increases the yields of lettuce, tomato, rice, and *Andropogon* grass [80]. On the other hand, in Ukrainian sandy soils, clinoptilolite (15 tonnes ha⁻¹) boosted the yields of potatoes, barley, clover [81], and sugar cane with utilization of 6 tonnes ha⁻¹ [82]. In a study by Chander and Joergensen (2002) [83], zeolite, as a soil amendment, increased the soil microbial biomass and the incorporation of added ¹⁴C into microbial biomass.

5.3. Slow Release of Herbicides

Increasing safety for the farmer and savings in energy are some other advantages of slow-release formulation (SRF) application. SRFs have been shown to supply the active ingredient of herbicides for a longer duration of efficacy at the required rate for weed control and reduce leaching potential and environmental pollution of herbicides by decreasing the total amount of the chemical required [84]. Due to their ion-exchange capacities, many natural zeolites are effective carriers of herbicides, fungicides, and pesticides. 'ZSM 5' zeolite (or MFI type, a synthesized zeolite), a hydrophobic solid, was found to adsorb atrazine better when organics were present in the zeolite's compartmentalized intra-crystalline void space [85,86]. ZSM-5 was found to accommodate paraquat herbicide in its microstructure with restricted mobility [87]; after this, Zhang et al. (2006) [88] studied the release of paraquat from zeolites by ion exchange with 1.0 M Na⁺, and it was estimated to be 0.75 mmol g⁻¹ of zeolite (14% by weight). Zeolites were also found to be slow-release carriers for 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide [89,90].

5.4. Heavy Metal Traps

Soil pollution by heavy metals, such as lead, cadmium, zinc, nickel, manganese, chrome, copper, and iron, is one of the preeminent issues of modern agriculture; its increase is highly influenced by industry development and the abuse of fertilizers. The main factor determining the solubility of heavy metals in soil is low pH, which is associated with the risk of their inclusion in a trophic chain [91]. The phytoavailability of heavy metals is correlated with their concentrations in soil solution [92]. Zeolites, in general, have a high cation-exchange capacity, and they attract positive-charged ions; therefore, zeolites are widely used for cationic pollutants' sequestration, such as heavy metals: Cd, Pb, Cr, Zn, Cu, etc. [93]. Many authors demonstrated the high affinity of natural zeolites to heavy metals [94]; for instance, 1% added zeolite could retain 3.6 mmol Pb kg⁻¹ or 750 mg kg⁻¹ soil [95]. Nishita and Haug (1972) [96] showed that, in contaminated soil with radioactive strontium (Sr90), the addition of clinoptilolite resulted in a significant decrease in the uptake of Sr90 by plants. In addition, clinoptilolite can remove heavy metals from sewage sludge compost with a particle size of 3.3–4.0 mm [97]. In some cultivation, the use of heavy metals is a common practice (i.e., copper in viticulture), resulting in an increase of

metal pollution in the soil. Zeolites can mitigate this pollution by adsorbing Cu^+ ions and storing them in its reticle.

5.5. Water Absorption

Due to the high porosity of their crystalline structure, zeolites can retain molecules of water up to 60% of their weight. Water, in their pores, could be steadily evaporated or reabsorbed without damaging the crystalline structures; moreover, adsorption on zeolites is characterized by Langmuir-type isotherms [27]. Zeolites can modify soil water content by reshaping the bulk density and aeration porosity. Bulk density is a physical property of soils that can have an effect on the total porosity and topsoil stability [19]. In sandy soils, zeolites can lead to higher water-holding capacities; the treated soil capacity with natural zeolite in holding water in drought and general conditions increased 0.4–1.8 and 5–15%, respectively, compared to non-treated soil [98,99]. Huang and Petrovic (1994) [100] showed that, at soil matric potentials from -3 kPa to -10 kPa, the water content of zeolite-sand mixtures increased with decreasing zeolite particle size, for instance >1 mm, 1 to 0.5 mm, 0.5 to 0.25 mm, 0.25 to 0.105 mm, 0.105 to 0.047 mm, and <0.047 mm. Briefly, zeolites can increase total porosity and decrease bulk density, and, consequently, increase soil water content [35]. For instance, Bigelow et al. (2001) [101] showed that the porosity, bulk density, and cation-exchange capacity (CEC) of sandy soil were 0.413 , 1.66 Mg m^{-3} , and $0.8 \text{ cmol}(+) \text{ kg}^{-1}$, respectively, while the same parameters for zeolite-treated soil were 0.437 , 1.60 Mg m^{-3} , and $1.6 \text{ cmol}(+) \text{ kg}^{-1}$, respectively.

Zeolites improve water-use efficiency (WUE) by increasing the soil water-holding capacity and its availability to crops due to their extraordinarily porous structure [98,102]. Zeolites also help rapid re-wetting and enhance the lateral flow of water toward the root zone during irrigation. This leads to the preservation of the water needed for irrigation [21].

Hydraulic conductivity is a soil physical property that shows the ease of water movements in the soil; saturated hydraulic conductivity (Ks) is the soil skill to conduct H_2O when water fills the whole pores, and it is used for modeling water and solute movements in soil [103]. Many authors showed that zeolite applications increased hydraulic conductivity [104]; clinoptilolite Ks was 1.42 m h^{-1} and erionite Ks was 1.29 m h^{-1} , which was higher than sand Ks (0.41 m h^{-1}) [105]. Soil-hydraulic properties improvement can lead to increased water-use efficiency (WUE) and to increased crop production [106]. Under arid conditions in Karapinar Konya, Turkey, the water-use efficiency of the common bean (*Phaseolus vulgaris* L.) was positively affected by zeolite and irrigation treatments [107]. The addition of zeolite to soils and the alternate wetting and drying irrigation (AWD) of rice crops (*Oryza sativa* L.) required 27.8% and 8.1% less water, 33.3% less N fertilizer, and increased yields by 10.6% and 0.6%, respectively, without measurably affecting rice grain quality [108]. In another study, as compared to conventional continuous flooding irrigation (CF), AWD with zeolite reduced water consumption by 15–30% and improved the aeration of a paddy field while meeting the physiological requirements of plant growth for water [109]. The application of zeolite on the soil of barley (*Hordeum vulgare* L.), irrigated with diluted seawater, also enhanced the water- and salt-holding capacity of the soil [110]. Taking into account climate change, especially the reduction and concentration of precipitation, with the consequent increase in water deficit, zeolites can be of great importance in reducing water stress in agriculture.

5.6. Gas Absorption

All zeolites materials, natural and synthesized zeolites, can absorb methanol (CH_3OH), formaldehyde (HCHO), sulfur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen sulfide (H_2S), water (H_2O), ammonia (NH_3), molecular hydrogen (H_2), argon (Ar), oxygen (O_2), nitrogen (N_2), xenon (Xe), helium (He), krypton (Kr), and many other gases and can thus be used to collect them or control odors. For these reasons, zeolite is being used in intensive animal husbandry livestock, to reduce undesirable odors caused by the content of H_2S and NH_3 . Ammonium-adsorption capacities of the zeolites ranged

from 8.149 mg N g⁻¹ to 15.169 mg N g⁻¹ [111]. The clinoptilolite ammonium-adsorption capacity increased linearly with pH and was estimated to be 9.660 mg N kg⁻¹ at pH 4, 11.220 mg N kg⁻¹ at pH 5, 12.720 mg N kg⁻¹ at pH 6, and 13.830 mg N kg⁻¹ at pH 7 [112].

In addition, zeolite, combined with other additives, can be widely used to reduce gas emissions, salinity, and nutrient loss during the composting process [113,114]. In fact, wood vinegar mixed with zeolite and biochar to compost pig manure decreased methane, carbon dioxide, and nitrous oxide emissions by 50.39–61.15%, 33.90–46.98%, and 79.51–81.10%, respectively, and reduced ammonia loss by 64.45–74.32% [115].

5.7. Antifungal Activity and Crop Protection

Ecological issues and environmental pollution make it necessary to look for alternatives to synthetic pesticides, such as controlled release or organic agrochemicals. It has been demonstrated that zeolites have the potential to reduce the environmental impacts caused by the control of plant diseases. Several authors investigated these materials for the control of harmful insects [116,117]. Their particular framework, their smaller particle sizes, carbon dioxide (CO₂) sorption capacity, and heat-stress reduction skill make zeolites satisfactory as a leaf-coating product against fungal diseases and insect pests [41]. In this context, the material's micronization degree to avoid nozzle occlusion for its distribution becomes very important; moreover, the ability of zeolite to interact with the external environment intensifies as the size dwindles when the specific contact surface increases, i.e., 0–50, 0–150, and 0–500 µm [116].

In a study carried out by Calzarano et al. (2019) [118] on *Vitis Vinifera* L. it was shown that natural Italian chabazite, sprayed on grapevines, provided simultaneous control of sour rot, grey mold, and *L. botrana*.

Due to their non-toxicity, zeolites can be applied against a large range of insect species in the stored product, such as the confused flour beetle, *Tribolium confusum* Jacquelin du Val (Coleoptera: Tenebrionidae); the maize weevil, *Sitophilus zeamais* Motschulsky (Coleoptera: Curculionidae); the red flour beetle, *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae); the rice weevil, *Sitophilus oryzae* L., and the lesser grain borer, *Rhyzopertha dominica* F. (Coleoptera: Bostrychidae) [119].

5.8. Photosynthesis Enhancement on Crops

Zeolites can absorb carbon dioxide molecules and release them gradually into the ecosystem [120].

Spraying zeolites on plant leaves may raise the amount of carbon dioxide near the stomata. This phenomenon could lead to a higher photosynthesis rate for C3 plants, such as vines, tomato plants, apple trees, and orange trees, with an increase in the efficiency of net carbon CO₂ (velocity of carboxylation) uptake and a decrease in carbon dioxide loss by the photorespiratory system. This leads to higher growth, an increase in the rate of production of the leaf surface, and a decrease in transpiration rate [121].

5.9. Heat Stress and Sunburn of Zeolites on Crops

With the rising temperature, Rubisco's affinity (the enzyme responsible for C fixation in plants) for CO₂ and the solubility of CO₂ relative to O₂ both decrease. Hence, the carboxylation to oxygenation ratio is reduced when the temperature increases [122]. Owing to the increasing leaf reflectiveness (whiteness) of infrared radiation, the leaf temperature can be significantly diminished by coating the plant with zeolites. Several studies indicated a reduced canopy temperature and a higher leaf carbon assimilation rate in apple tree and vines [123,124]. Abou-Khaled et al. (1970) [125] showed a reduction of approximately 4 °C for leaves of rubber plants (*Ficus elastica* L.), dwarf orange trees (*Citrus sinensis* L. cv. Valencia), and kidney bean plants (*Phaseolus vulgaris* L.), caused by the reflecting material.

5.10. Aquaculture

In modern intensive fish farms or closed-system fish cultures with high densities, ammonia nitrogen is the major nitrogenous waste of aquatic animals; NH_3 is produced by protein de-amination in aquaculture feeds and is excreted mainly through fishes' gills [126]. The concentration of ammonia such as to achieve toxicity to fish fauna is >0.02 ppm [33]. Most of the applications of zeolitic minerals in aquaculture and water quality processes are based on their high selectivity for ammonia [127]. In shrimp-culture tanks, phillipsite from Neapolitan Yellow Tuff was used to remove ammonia from the effluent from saline water. In addition, zeolites can play other two roles in aquaculture: to generate oxygen for aeration systems in aquaria or transport and to supplement fish rations [38].

5.11. Animal Feed Additive

Zeolites dietary supplementation is a cooperative and efficacious strategy in the prevention of several diseases and in the advancement of animal health. Many authors in several species, such as swine [128], calves [129], and lambs [130], have documented the benefits of their dietary inclusion. Briefly, below some mechanisms by which zeolite minerals may exert their performance-promoting properties in the diet of livestock husbandry [131]:

- Aflatoxin-sequestering effect: elimination of mycotoxin growth inhibitory effects;
- Ammonia-binding effect: elimination of ammonia toxic effects produced by intestinal microbial activity;
- Enhanced pancreatic enzymes activity: favorable effect on feed components hydrolysis over a wider range of pH, improved energy and protein retention;
- Fecal elimination of p-cresol: reduction of the absorption of toxic products of intestinal microbial degradation, such as p-cresol;
- Retarding effect on digesta transit: slower passage rate of digesta through the intestines and more efficient use of nutrients.

6. Conclusions

Nowadays there is an increasing interest in zeolite utilization in agriculture. Zeolite application finds several potential uses in agriculture, particularly in soil management. For example, zeolites can be used as carriers of nutrients to promote nutrient use efficiency. On the one hand, considering climate change and rising temperatures, the application of zeolites to the soil or in greenhouses can be a valuable aid for farmers to preserve water content, reduce canopy temperature, and ensure production. On the other hand, zeolites can be an indispensable tool for reducing polluting emissions and for purifying heavy metals from plant stems, as a result of excessive anthropic pressure over the years. Nowadays, the approach to sustainable agriculture cannot be separated from the use of sustainable products, and it is precisely in this perspective that zeolites will be able to help farms achieve fertilizer savings, better management of water resources, soil decontamination, and groundwater. The goal of an agricultural ecosystem is, in fact, resilience, that is, that property present in natural ecosystems that guarantees the renewability of resources. A great leap in quality in soil management is characterized by sustainable agriculture, which represents that form of production that responds to the needs of the present without compromising the ability of future generations to respond to theirs. These minerals are therefore a valuable aid in the search for balance in the agricultural ecosystem.

Author Contributions: E.C. wrote the original draft manuscript, which was edited and improved by G.B.M. and D.M. Investigation, L.S., F.P., M.F., G.M., C.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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