Review

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The Contribution of Zeolitites to Current Environmental Problems and Sustainable Applications for Cultivation and Plant Protection

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Abstract: In the light of current justified international concerns about pollution caused by both greenhouse gases and by current agricultural practices, as well as the management of livestock manure, zeolite rocks with a prevalent zeolite content (a mineral endowed with peculiar chemical-physical properties), are widely used worldwide. They have a high extraction potential and represent an effective and scientifically proven means of pollution control. Moreover, based on the results of countless laboratory and field experiments, zeolitites (in particular Italian chabazite) rich in potassium (K) but low in sodium (Na) and with high drainage and water retention properties, have an effective potential for environmental protection, reduction of fertilizers and irrigation water, and increase of agronomic production. In agriculture and horticulture, in particular, the permanent correction of agricultural soils and growing media with appropriate amounts of zeolitites makes it possible to reduce the input of synthetic fertilizers and water as well, in order to substantially increase yields in quantity and quality. However, there are few scientific articles describing the use of zeolite in agriculture and its benefits for farmers. This review is aimed at gaining a better insight into the application of zeolitites in agriculture, particularly in difficult climatic situations, and to provide more information on how these minerals can ensure both the reduction of the use of fertilizers and the increase of plant protection. In addition, details and explanations are provided on the term 'zeolitite' used in order to ensure higher quality agricultural products.

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1. Introduction

In 1909, the German chemist and Nobel Prize winner Fritz Haber transformed nitrogen gas, which is abundant in the atmosphere but not reactive, into reactive nitrogen as it can volatilize as ammonia or oxidize as nitrate. Another German chemist, Carl Bosch, developed a method to exploit Haber's idea industrially [1]. In the decades that followed, many industries began to process tons of industrial ammonia into synthetic fertilizers. Haber-Bosch's invention is now considered one of the most important discoveries for population development [2,3]. Pillar of the Green Revolution, this is how we define the process that affected agricultural practice between the 1940s and 1970s and which, through the use of genetically engineered plant varieties, fertilizers, pesticides, water, and new technical and mechanical means, enabled a significant increase in agricultural production in much of the world [4]. Synthetic fertilizers have enabled farmers to increase production by cultivating poorly fertile soil or relentlessly exploiting soil with the same crop [5]. The advantage of producing crop after crop without waiting for nutrients to regenerate naturally in the soil is one of the main factors that has favoured population growth, with the world population increasing from 1.6 to 6 billion in the 21st century [6]. Current farming practices, which do not naturally require the regeneration of nutrients, come at a high price: the artificially added main elements to the soil (irrigation water, nitrogen (N), potassium (K) and phosphorus (P)), in order to obtain increasingly good harvests, inevitably are a source of environmental issues [7–9]. The widespread use of agro pharmaceuticals (especially highly soluble copper salts) in foliar treatment against phytophagous and

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micropathogenic insects, which are responsible for considerable damage to production, has serious environmental repercussions. Their leaching by rainwater and irrigation water causes pollution of the underlying soils, with relevant loss of their fertility [10,11]. Several papers in the literature describe the structure and application of zeolites in industrial and medicinal sectors [12–14]. On the other hand, few scientific articles describe zeolites' use in agriculture and the benefits farmers can gain from their application [15–17]. The objective of this review work is to highlight the multiple uses of zeolitite in agriculture (Figure 1), in particular the benefits that can be obtained in improving crops in terms of yield, production quality and reducing the use of pesticides. Moreover, this article also better specifies the term 'zeolitite' introduced to provide the consumer with an index of product quality. In fact, zeolitite represents a product that must contain at least 50% or more of the zeolitic mineral indicated on the label. The review of works that are highlighted are the researches that over the years have been most concerned with the practical use of zeolitites in agriculture, to provide farmers with an innovative methodology to make the best use of these minerals in the field and in substrates.

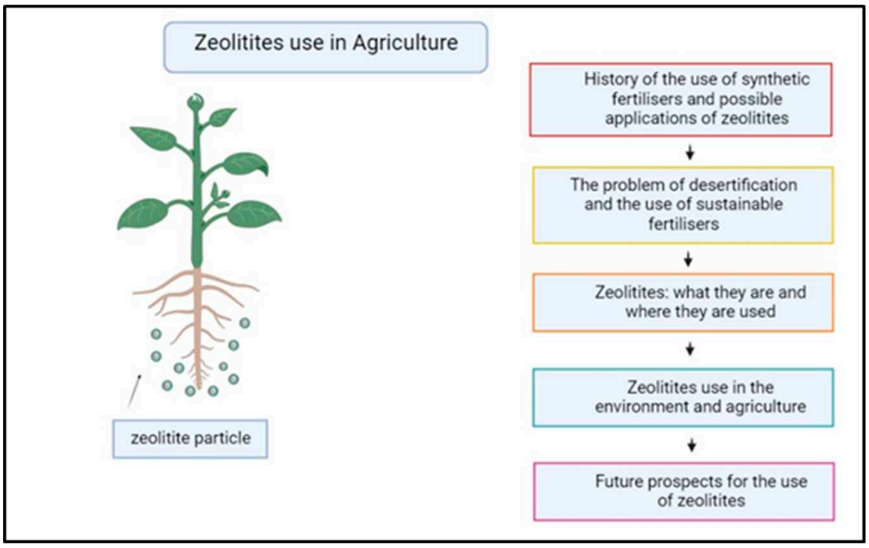

Figure 1. Summary diagram of the topics analysed on the use of zeolitite in the review.

2. Soil desertification and sustainable use of fertilizers

Closely linked to desertification is the increasing practice of deforestation, essentially due to the need to find fertile land to meet growing nutritional needs. As a result, every year, a forest area of 50,000 km^2 disappears from the face of the earth. Thus, since 2010, agriculture has already destroyed or radically transformed 70% of grasslands, 50% of savannas, 45% of temperate deciduous forests and 25% of tropical forests [18]. Against these volumes, the increase in production has been only 20% [19]. With the felling of tropical forests, the exploitation of marginal lands and the use of intensive techniques, agriculture has become the planet's main environmental threat, consuming a large percentage of the earth's surface, destroying habitats, depleting water resources, polluting rivers and oceans and being one of the main (24%) sources of anthropogenic greenhouse gas emissions [20]. Furthermore, with an expected increase of 2-3 billion people by 2050, the demand for food will double for various reasons [19]. Although fertilizer production is the main contributor to the excess nitrogen and phosphorus threatening the planet, stopping it is not a viable option, as these compounds are essential for food production. However, in order to satisfy both future food demand and planet's long-term health, it is necessary to increase yields with drastically reduction of the environmental impact in current agricultural practices [21]. Therefore, it is necessary to use fertilizers in a more efficient and balanced way, promoting their reduction in rich countries. The currently used doses, indeed, are well above the level needed to ensure maximum crop yields and the resulting exaggerated release of nitrogen and phosphorous into the environment [22]. Currently, there is a kind of asymmetry in the distribution of fertilizers, with overuse in some regions of the world. In contrast,

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other countries are caught in the grip of poverty and, therefore, hunger. In wealthier countries, an agricultural production system based on intensive and inefficient nitrogen use has been adopted, with little return on investment. In the US, for example, studies in the Corn Belt and the wheat fields of Mexico have shown that over-fertilization was a mistake, as judicious use of fertilizers does not necessarily mean a lower yield [20]. Tests by the American Farmland Trust have also confirmed that conventionally fertilized crops did not have higher yields than those that were fertilized substantially less. Crops in the US Midwest routinely use an average of 20 to 30% more nitrogen (N) fertilizer than recommended doses [23]; farmers who reduced their fertilizer use did not experience reduced yields and saved money by buying less fertilizer [24]. Problems arising from the nitrogen cycle, where this substance is over-introduced into the environment, can be significantly reduced with current technology and low costs. In this context, the Nitrates Directive (EU Directive 91/676/EEC) limits vulnerable areas to 170 kg N/ha per annum compared with 340 kg N/ha per annum. Recently, the European press has put synthetic fertilizers under the magnifying glass, first acknowledging their merits, then explaining the errors in their use and finally proposing solutions to limit their impact from an economic, environmental and health point of view [25]. The report concludes that about half of the world's population depends on fertilizers for food production. However, measures are needed to reduce the impact of nitrogen pollution, including more effective use of fertilizers [26]. In conclusion, the report encourages science to develop new technologies to improve water purification so that nitrogen (N) and phosphorus (P) can be recycled more efficiently. According to Foley, the combined implementation of the following three points can increase food availability by 100 to 180% by 2050 while reducing the negative effect of agricultural practices on the environment [23]:
1) increase the efficiency of fertilizer and irrigation water use through incentives to farmers to improve the management and recycling of livestock manure;
2) improving the productivity of land that has lower yields, especially in emerging countries, through the use of better seeds and greater availability of synthetic fertilizers;
3) curbing the expansion of agriculture in tropical forests and savannas by saving the most productive land from urban sprawl, degradation and abandonment.

3. Zeolitites

Instead of the generic and improper terms ("natural zeolites", "sedimentary zeolites", "zeolite-rich rocks", and "zeolite-rich tuffs") typically used in the literature, the term zeolitite was introduced to provide a scientifically correct definition of diagenised pyroclastic rocks with a prevalent (> 50%) zeolite content and subordinate quantities of other silicate phases (quartz, cristobalite, feldspar, plagioclase), and volcanic glass [27]. The most common zeolitic species in "zeolitites" are clinoptilolite present in variable quantities (40-60%) in diagenised "acid" tuffs widespread in many European (Slovenia, Czechoslovakia, Hungary, Romania, Bulgaria, Greece) and non-European (Turkey, Iran, Russia, United States, Cuba, Japan, China, Australia) countries [28] (Table 1); chabazite and phillipsite present in variable quantities (30-70%) [29] above all in Italian alkaline-potassium "basic" ignimbrites. Their zeolite content characterizes zeolitites: i) high (140-210 meq/100 g) and selective cation exchange capacity; ii) reversible dehydration; iii) structural cryptoporosity [25]. In addition, given their lithological nature (micro-and macroporosity in texture, lithoid consistency), they are also characterized by: i) water retention; ii) mechanical resistance; iii) permeability; iv) low density [26]. Zeolitic properties depend on zeolite's type and concentration (weight percentage) in the rock. The other properties depend on the nature (tuff, suffice, ignimbrite) and the diagenetic process (hydrological system 'open', 'closed', 'autoclave') undergone by the volcanic rock [30]. As chabazite and phillipsite are zeolitic species with a cation exchange capacity (CSC) of 330-340 meq/100g and occur in micro-and macroporous ignimbrites, clinoptilolite is a zeolitic species with a cation exchange capacity (CSC) of 220-230 meq/100g and occurs in compact tuffs, the chabazite and phillipsite zeolites widespread in Italy show higher cation exchange capacity (CSC) and water retention values and lower density values than the clinoptilolite zeolites widespread abroad (Table 1) [31]. The amount per area of zeolitite used both in the root zone and in the soil surface is crucial for the qualitative result on plant growth. Normally in field situations, a quantity of zeolitite of 2 kg per square metre is

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used, while in pot cultivation the quantity to be included is normally 20% by weight of the substrate mixture [29]. The abilities of zeolitite in terms of cation exchange and water retention are very important in sandy soils and in all the situations where a lack of water resources is observed. Experiments have shown that the quality of zeolitite and the quantities used in various crops can alter plant growth and plant resistance to biotic and abiotic stresses. Table 2 shows the water-holding capacity of zeolitites, as their amount in the soil increases, compared to a corresponding amount of quartz sand [29].

Table 1. Cation exchange capacity (CSC), water retention and density of certain zeolitites [31].

Zeolitites	Origin	Cation exchange capacity meq/100g	Water retention (% p/p)	Density (g/cm³)
Chabazite	Grosseto (Italy	218	43	0,74
Phillipsite-chabazite	Napoli (Italy)	192	38	0,78
Clinoptilolite	Pentalofos (Greece)	131	20	1,04
Clinoptilolite	Nizny Hrabovec (Slovakia)	138	22	0,96
Clinoptilolite	Zlatokop (Serbia)	143	28	0,88
Clinoptilolite	Caimanes (Cuba)	156	20	0,94

Table 2. Comparison of hydrological constants of quartz sand and zeolitite (Italian chabazite) [31].

Zeolitites (t/ha)	Quartz sand (% p/p)	Zeolitites (% p/p)
0	9,6	37,4
28	0,8	14,4
56	8,8	23
112	29	139

4. Utilisation of zeolitites

The chemical and physical properties of zeolites are the basis for their widespread and growing use in the following industrial sectors, as shown by numerous studies published in the 1980s and 1990s [32,33]. Zeolitites, both in their natural state and enriched with heavy metals, are used in the manufacture of hydraulic binders (cement, mortars) and as additives in the base mix for the production of floor tiles. It was observed advantageous effects not only for the technological properties of the products but also for the environmental (reduction of carbon dioxide emissions into the atmosphere) and economic aspects(e.g. possibility of disposing of zeolitites enriched with harmful metals after their previous use in wastewater treatment) [34]. The nonlinearity of water vapour absorption isotherms provides zeolites with the ability to store solar energy and thus their potential use for water heating and thermal conditioning of rooms is relevant [35,36]. As an alternative to talc and kaolin, high whiteness zeolites, used as fillers (20-30%) in papermaking, provide greater firmness, opacity and lower shear and ink-staining resistance as well [29]. Production of oxygen (O_2) and nitrogen (N) in air and construction of portable oxygen-enriched air generators; the drying process of ethanol; removal by adsorption of pollutants such as sulphur oxides (SO2), carbon dioxide (CO2), from industrial and synthetic gas mixtures; removal of ammonia (NH3) and subsequent reduction of odour emission in chicken and turkey farms [37,38]. The possible reduction of 80-85% of nitrogen (N) loss during traditional composting processes of the solid fraction of pig slurry. This increases the fertilizing power (available nitrogen) of the compost. In the dewatering of civil, livestock and industrial wastewater, it is possible:

i) the removal of ammonium (NH_4) from drinking water, urban sewage and sewage from biological treatment plants, leachate from municipal solid waste landfill, pig slurry, effluent from the soap and detergent industry, effluent from the tanning industry, effluent from the slaughterhouse industry, effluent from the fish industry, recirculated water from fish farms [39];

ii) the removal of COD (Chemical oxygen demand), BOD (Biological oxygen demand) and polluting bacteria (total coliforms, faecal coliforms and streptococci) from wastewater;

iii) the removal of methyl-butyl-ether (MtBE) from contaminated groundwater;

iv) the removal of biologically active compounds (PAF inhibitors);

v) the reduction of polyphenols and COD from olive oil mill wastewater;

vi) the removal of aflatoxin B1 and G2 from synthetic solutions simulating gastric fluid (pH 2) and intestinal fluid (pH 7);

vii) the removal of harmful metals: radioactive caesium (Cs) and strontium (Sr) from nuclear power plant generation water; lead (Pb), barium (Ba) and zinc (Zn) from synthetic solutions; Pb, Ba, Zn, copper (Cu), cadmium (Cd) and chromium (Cr) from ceramic sludge eluate;

viii) the removal of sodium (Na) from irrigation water [40].

5. Zeolitites in the environment and in agriculture

Based on the results of countless laboratory and open-field experiments, it was observed that zeolites, especially Italian zeolites with a prevalent chabazite content, are rich in potassium (K) and low in sodium (Na), with high drainage capacity and water retention, and excellent extraction potential. They represent a significant potential for protecting the environment by reducing the use of fertilizers and irrigation water and increasing agronomic production in anticipation of population growth [41]. The use of zeolite allows to reduce the use of water for irrigation as the permeability and high water retention of zeolites minimize, respectively, the loss of irrigation and meteoric water through surface runoff in soils with a high clay component (impermeable) and rapid drainage in soils with a high sandy component (low water retention) (Table 3) [42]. Of secondary but not negligible value is the infinitely reversible property of dehydration (endothermic process) and rehydration (exothermic process) of the zeolitic water, which makes it possible to maintain almost constant humidity and temperature levels at the root level. In order to attenuate the adverse effects caused by peaks in temperature and drought, some experiments were conducted. They have shown on ornamental plants and other species such as vines, that the use of zeolitite in substrate or soil provides more excellent protection for the plant against the cold. In the event of leaf scorch, it was observed a faster restart when temperatures are suitable for cultivation [43]; moreover, the observed decreasing of the excessive levels of salinity of water used for irrigation purposes are relevant [44]. Furthermore, in several research works on *Loropetalum sinensis* in particular, the addition of 20% zeolitite to the growing medium can improve plant growth and leaf quality (Figure 2). In some experiments, Prisa has shown [29] how the use of zeolite in the growing medium can reduce, or eliminate in some cases, the stress effects on plants, that is caused by the presence of excess salts in the irrigation water (Figure 3). The reduction of of fertilizers use as, as an integral part of the soil, increases its cation exchange capacity (CSC) and thus, temporarily remove ammoniacal nitrogen (NH_3) not used by the crop and consequently subject to lose through leaching into the groundwater in the form of nitrates and volatilization into the atmosphere in the form of greenhouse gases. All this contributes to the reduction of the retrogradation process of phosphorus (P) (from soluble monocalcium phosphate ($CaH_4P_2O_8$) supplied by the fertilizer and to the assimilation by the crops of tricalcium phosphate ($Ca_3(PO_4)_2$) through reaction with calcium (Ca) in the soil, insoluble phosphate and therefore not capable of being assimilated by the crops) (Figure 4) [32,45].

The nitrogen in the zeolitite is then released slowly and gradually according to the phenological needs of the crop itself [44]. The possible use of micronized zeolitites for insect and fungal protection on fruit, vegetable and ornamental crops due to mechanical properties of the zeolitic crystal are also relevant for:
(a) the presence of scabrous structures that cause problems of adherence by insects on leaves and fruits [46];
(b) the absorption by zeolite powders of moisture and water veils present on leaves that facilitate the germination of fungal spores [47];
(c) the rapid dehydration of insects with soft exoskeleton and difficulty in the breathing and flying process [46].

Zeolitite is also capable, thanks to its reflective capacity, of creating problems in the localization of target fruits by pathogenic insects and absorbing the ethylene produced by ripe fruits, which carries them to attack plant structures. New experiments have shown that natural zeolitite can act as a magnet for beneficial microbial colonies, which can enter into symbiosis with plants and facilitate their uptake of water and nutrients and stimulate their defence through the production of secondary metabolites [47,48]. It has been demonstrated by Barbarick et al. [49] that zeolite increases dry matter, nutrient content, and nutrient uptake of the crop by providing a sustained and slow release of P. After application of zeolite with ammonium (NH^{4+}) and potassium (K) to spinach plants, a study showed that spinach yields and nutrient uptake increased [50]. A combination of zeolitic tuff and peat moss and perlite produced a more efficient use of N and K fertilizer in croton (*Codiaeum variegatum* L.) [51]. As part of a study in Iran, natural clinoptilolite was used to improve rice grain yield, nitrogen recovery, and nitrogen use efficiency on a coarse-textured paddy field [52]. Results demonstrated that a mixture of zeolite and fertiliser had a significant positive effect on rice grain yield, nitrogen recovery, and nitrogen use efficiency. A significant increase in the uptake of N, P and K and their efficiency in use in root, leaves, and stems was observed by the addition of zeolite to maize tissues (*Zea mays* L.) when inorganic fertilisers are mixed with zeolite [53]. As soil conditioners, zeolites improve the physico-chemical properties of soil by increasing soil moisture, promoting hydraulic conductivity, and increasing yields in acidified soils [54]; they are widely used as soil conditioners. It is possible to increase cation exchange capacity in soil by using zeolites as soil conditioners [55]. As a result of zeolites increasing soil cation exchange capacity, nutrient availability is influenced as well as microbial metabolic activity (increased dehydrogenase activity) and organic matter is altered [56]. Brazilian zeolitic sedimentary rocks are effective soil conditioners for lettuce, tomato, rice, and Andropogon grass [57]. Meanwhile, in Ukrainian sandy soils, clinoptilolite (15 tonnes ha^{-1}) increased yields of potatoes, barley, clover [58] and sugarcane [59]. According to Calzarano et al. [60] on *Vitis Vinifera* L. natural Italian chabazite, sprayed on grapevine, provided simultaneous control of sour rot, gray mold and *Lobesia botrana*, when it was sprayed on grapevines. In several studies it was observed [61,62] that apple trees and grapevines have a lower canopy temperature and a higher rate of leaf carbon assimilation. Using reflective material on rubber plants (*Ficus elastica* L.), dwarf oranges (*Citrus sinensis* L. cv. Valencia) and bean plants (*Phaseolus vulgaris* L.), Abou-Khaled et al. [63] showed a reduction of about 4 °C in temperatures. Studies carried out by Prisa [46] on various types of vegetable, ornamental, succulent and cactaceae plants have shown that chabasite zeolitite has greater functional capabilities, than other types of zeolitites, both for field and pot plant cultivation in order to protect crops against fungi and insects when sprayed on leaves and fruit.

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Table 3. Evaluation of available water in quartz sand and zeolitite (Italian chabazite) [31].

Hydrological constants	Quartz sand (% p/p)	Zeolitites (% p/p)
Field capacity	9,6	37,4
Wilting point	0,8	14,4
Water available	8,8	23

Figure 2. Zeolitite effect on the vegetative growth of *Loropetalum sinensis* (20 per cent zeolitite was added to the treated plants and the experiment was carried out for 12 months).

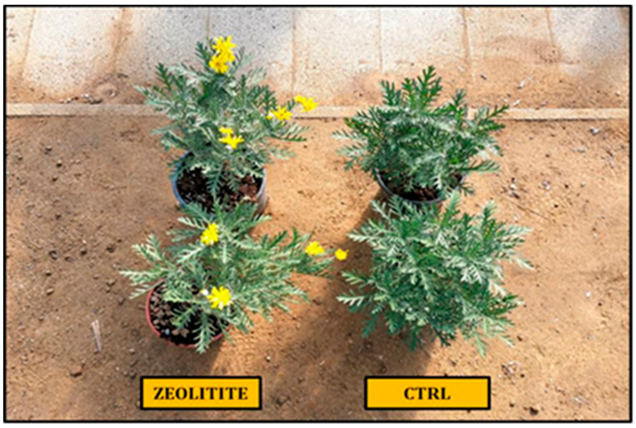

Figure 3. Zeolitite effect on the flowering of *Euryops pectinatus* (10 per cent zeolitite was added to the treated plants and the experiment was carried out for 10 months).

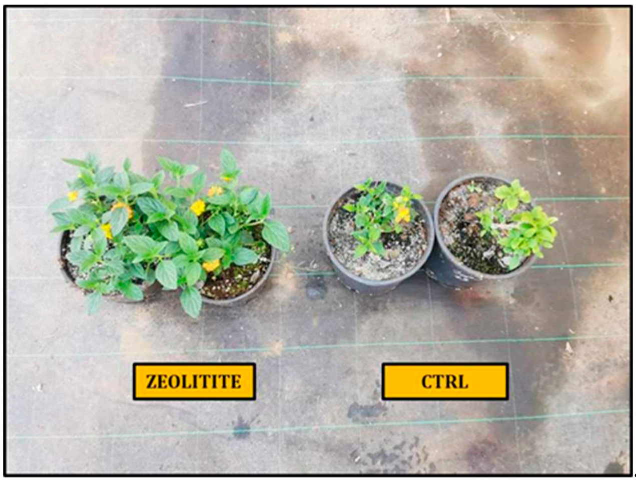

Figure 4. Zeolitite effect on flowering and leaf growth of *Lantana Camara* (20 per cent zeolitite was added to the treated plants and the experiment was carried out for 12 months).

6. Future perspectives on the use of zeolitites

The results presented in this review demonstrate that the correction of soil or substrate with a zeolitite rock with a predominant zeolite content brings undoubted and significant advantages both from an environmental and agronomic production point of view [64,65]. The same results also allow reusing in the agronomic field zootechnical wastes, whose current disposal is a serious and growing environmental problem [66]. Zeolites, due to particular genetic conditions, are not abundant minerals in the earth's crust and usually are absent in soils but are found as fundamental constituents (>50%) in diagenised pyroclastic rocks (tuffs, ignimbrites) [47,67]. These rocks, widespread in many countries, can be advantageous for treating livestock waste and as a soil amendment. Currently, agronomic research aimed at reducing their environmental impact, i.e. pollution of surface and deep water systems; emission of greenhouse gases; pollution of soils by copper salts from foliar treatment and increasing agricultural production in anticipation of the increase in world population, is mainly focused on genetic modifications of the various crop species [68]. The introduction of specific research based on the possible correlations between the mineralogical composition of soils and agricultural production and possible mineralogical modification of soils to improve their production potential could have a significant effect. There are numerous agricultural applications for zeolites, yet their rational and profitable use requires systematic and comprehensive research. Future research must address several important aspects, including:
(a) characterisation of the zeolite deposits available within each country [69];
(b) determining the physical stability of zeolite in different soil environments [70];
(c) developing low-cost methods for organo-zeolite fertilizers [71];
(d) evaluating nutrient release patterns from organo-zeolites [72,73];
(e) assessing the long-term impact of zeolites on soil biological functions [74];
(f) the understanding of zeolite-mediated heavy metal stabilisation mechanisms in contaminated soils [75];
(g) the development of zeolitic herbicides to minimise herbicide residues in soil-plant systems [70].

A further field of research is the application of synthetic zeolites for applications as adsorbents and ion exchangers in numerous areas of agriculture and environmental protection [63,64,76,77]. In agriculture, studies mainly focus on the application of natural zeolites, which can be a useful soil conditioner and fertiliser additive. However, the main focus for environmental remediation is currently on synthesised zeolites. Although numerous articles have been published on the application of zeolites in agriculture and environmental protection [78,79], their great potential has not yet been fully explored.

6. Conclusions

The use of zeolite in agriculture is increasing in popularity today. The application of zeolite has several potential uses in agriculture, particularly in soil management. For example, zeolites can be used as nutrient carriers to promote nutrient efficiency in soil. Due to climate change and rising temperatures, zeolites can serve as a valuable aid to farmers to maintain water content, reduce canopy temperatures and ensure production in greenhouses or soil. As a result of excessive anthropogenic pressure over the years, zeolite is an indispensable tool for reducing pollutant emissions and purifying heavy metals from plant stems. As a result, sustainable agriculture cannot be separated from sustainable products, and zeolites can be an effective tool for reducing fertiliser and water resources waste, as well as decontaminating soil and groundwater. This review aimed to describe and raise awareness of the characteristics of zeolites and zeolitites, their numerous uses in agriculture and environmental remediation, and possible future prospects in the use of this mineral that is interesting in many respects. This paper could be important for all those scientists and farmers who want to start using this mineral on plants and polluted soils.

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