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(Research Article)

Chabazitic zeolitite in cultivation and spray protection against *Phytophthora infestans* and *Tuta absoluta* in *Solanum lycopersicum*

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Abstract

Research objective: This article aims to highlight how chabazite zeolitite can lead to better growth and protection of tomato plants, in particular the benefits it can bring to crops both when buried in the soil, in terms of plant growth and fruit production, and as a reduction in the incidence of fungal diseases and insect attack when used as a spray in water.

Materials and Methods: The experiments, which began in March 2024, were conducted in the CREA-OF greenhouses in Pescia (Pt), Tuscany, Italy (43°54′N 10°41′E) on tomato cv 'Ciliegino' plants. The plants were placed in pots with a diameter of 14, 20 plants for 3 replications, for a total of 60 seedlings per experimental thesis. The first trial on *Solanum lycopersicum* involved the following theses (irrigated and fertilised): i) peat 70% + pumice 30%; ii) peat 70% + pumice 20% + zeolitite chabazite 10%; iii) peat 70% + pumice 10% + zeolitite chabazite 20%. The second trial on *Solanum lycopersicum* included spray treatments with micronised zeolitite on the leaves to evaluate the control of diseases such as *Phytophthora infestans* and *Tuta absoluta*. The trial included the following theses (irrigated and fertilised): i) control with treatment with water sprayed on the leaves every 10 days; ii) control with treatment with Flipper 1 L/hl + Ranman Top 0.5L/hl, every 7 days; iii) treatment with zeolitite chabazite 5 kg/hl, every 7 days. On 19 September 2024, plant height (measured at 70 days after transplanting), plant nodes (measured at 70 days after transplanting), leaf area index, total dry biomass, fresh fruit weight and number of total fruits were determined. In addition, the number of plants affected by *Phytophthora infestans* and *Tuta absoluta* was evaluated.

Results and Discussion: The experiment showed that the use of zeolitite and chabazite added to the growing medium to the extent of 10-20% can effectively improve the vegetative and root growth of *Solanum lycopersicum*. Furthermore, when micronised zeolitite is micronised on leaves, it can contain diseases such as *Phytophtora infestans* and *Tuta absoluta*, the same as using conventional products. This experiment conducted on *Solanum lycopersicum* shows an improvement in plant growth in the theses treated with zeolite added to the substrate, due to increased water and nutrient uptake and increased microbiological interactions in the plant, as well as a significant improvement in protection against plant diseases when micronised zeolite is sprayed on the leaves. In addition to having an insect repellent effect, zeolite has a disintegrating and dehydrating effect. The product causes respiratory problems, burns the exoskeleton, creates flight problems and reflects light. In addition, zeolitite chabazite, having a rough structure, causes problems of adherence to the leaf. As for fungi, on the other hand, it reduces moisture on the leaf and inhibits spore germination, as demonstrated in other scientific works by the same author.

Conclusions: Zeolites have the potential to affect soil physical properties. In addition to reducing soil bulk density and increasing soil porosity, these factors can improve water retention, as well as their high internal pore volume. Also, due to the open network of the zeolite structure, new routes for water movement can be formed, resulting in improved infiltration rates and saturated hydraulic conductivity. Due to their outstanding chemical and physical properties, natural zeolites can be utilized in agricultural applications, such as their affinity for K+ and NH4+ and ability to exchange

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cations. Before any commercial applications can be made, it is necessary to evaluate the risk of leaching toxic surfactants loosely attached to zeolite surfaces. Using their ion exchange properties, natural, synthetic, and modified zeolite can be used to make slow-release nitrogen, potassium, and sulfur fertilizers. To control and release phosphorous slowly, zeolite ion exchange and mineral dissolution (similar to phosphate rock) can also be used. It is generally determined by a variety of experimental conditions how zeolite application impacts soil physical and chemical properties, including the type and rate of zeolite applied, the method of application, the texture and structure of the soil, the size of the zeolite particles, and the salinity of the water. Soils with coarse textures may benefit from zeolite amendments more than those with fine textures.

Keywords: Corroborant; Zeolitites; Spray treatment; Tomato; Soil improvement

1. Introduction

The tomato, which, like other solanaceous plants, originates from certain regions of South America, was introduced to Europe as early as the second half of the 16th century and was soon appreciated as a tasty, aromatic and nutritious vegetable; although mainly composed of water, the fruits are very rich in sugars, organic acids, mineral salts, vitamins and other substances useful for the body [1,2]. It should not be forgotten that the green parts of the plant, especially the leaves, contain poisonous substances and are also rich in glands that produce a yellowish secretion with an unpleasant odour [3]. It is an annual herbaceous plant of rapid growth and remarkable vegetative development, at least in the most common varieties, whose sarmentose stems up to 3 m long. must be suitably supported with stakes or other fairly robust supports, given the considerable weight of the vegetation and the fruits; there are also varieties of much smaller size and with shorter stems, which, at least in areas with a very hot and dry climate, can be left to crawl freely on the ground; other varieties are still smaller in size and the plants look like small, erect, branched trees, similar to those of peppers [4]. Numerous horticultural varieties are cultivated that differ in plant habit, leaf size, shape, size and other characteristics of the fruits, which when ripe have a deep red skin and flesh; The fruits are fleshy berries with a very variable shape (globular and perfectly rounded or flattened, pear-shaped, bottle-shaped, heart-shaped), smooth or ribbed, and very variable in size (the smallest tomatoes resemble a cherry and the largest ones can weigh more than 500-600 g.). Tomatoes can be eaten in a variety of ways, mostly fresh, but can also be preserved by simply hanging them up or drying them in the sun; some varieties are excellent for making preserves or other jams; among the most suitable varieties for direct consumption, which have large, rounded and fleshy fruits, the 'Cuore di Bue' variety is particularly popular; however, at least in the south, rather small tomatoes are often preferred, as they are undoubtedly tastier and more aromatic [5,6]. Tomatoes hybridise easily and recently, excellent hybrid varieties have been selected that are very productive, disease resistant and have excellent quality characteristics [7]. For open field production, whose product is largely destined for industry, dwarf-sized varieties are preferred, which do not require supports and can be harvested easily even using special machines [8].

1.1. Tomato cultivation

The tomato grows well and fructifies abundantly when cultivated in areas with a very warm or at least warm-temperate climate; in fact, it should not be forgotten that it is a plant native to subtropical regions. In southern regions, along the coasts or in any case in areas with a very mild winter climate, i.e. in the citrus region, it can be cultivated without difficulty and with possible protection or by having special greenhouses it is possible to obtain fructification in any month of the year [9]. However, it can also be cultivated elsewhere and practically anywhere in Italy, in the plains or even in well-exposed and sunny hilly areas; if the climate is cold, transplanting is done in May so that the fruit ripens in midsummer or early autumn, i.e. in the warmer months [10].

Normally, sowing is carried out in seedbeds on warm boxes or in greenhouses, from February to March, depending on the climate, in order to anticipate the crop and transplant the seedlings to the ground as soon as the weather conditions are favourable; as mentioned above, sowing can be further anticipated if the climate is exceptionally favourable or if the crop is carried out, at least during the first few months, in greenhouses [11,12]. In larger, open-field crops, sowing can also be done directly in the ground, but only if the spring climate is very mild, in which case the seed is sown around mid-April. The distance between rows can vary from 40 to 90 cm, depending on the vegetative vigour of the plants and the form of cultivation; similarly, the distance between plants along the rows can vary from 40 to 70 cm [13,14].

It has already been mentioned that some small-fruited varieties are dwarf in size and form 35-40 cm high, branched bushes with erect vegetation; therefore, in this case, no supports of any kind are needed. Other tomatoes such as the concentrate or peeled varieties, which are quite small in size, are allowed to grow with the shoots crawling on the ground [15]. On the other hand, the best varieties of table tomatoes, whose fruits are intended for direct consumption, are much more vigorous and therefore the plants need to be supported with appropriate supports; this is also useful because the plants are better exposed to the sun in this way; it also prevents the spread of cryptogamic diseases, which easily undermine this crop. As soon as the plants are 25 cm in height, they are tamped down and then, if necessary, the relevant stake is placed next to each plant, to which the shoots are gradually tied [16]. For plants grown in the open field, no special care is required other than some spraying with fungicides or, if necessary, specific insecticides. In vegetable gardens, repeated treatments against cryptogams must also be carried out; in addition, the femminella, i.e. the axillary shoots, must be removed to prevent the vegetation from becoming excessively thick. Tomatoes should be cultivated on well-tilled soils fertilised with mature manure that should be supplemented with complete chemical fertilisers; during the summer season it is advisable to irrigate, if it does not rain, by running water along the furrows dug between the rows [17]. Tomatoes destined for direct consumption, i.e. for canteens, are usually harvested as soon as they change colour and become a little reddish; in fact, at least in the summer season when the temperature remains very high, the ripening process is regularly completed even after harvesting and in 3-4 days at the most the fruit takes on a beautiful deep red colour [18]. This custom is justified by commercial requirements and primarily by the fact that fruit picked while still quite unripe is harder and withstands transport better. In the case of family crops, it is certainly better to leave the tomatoes on the plants to ripen better, even if they are intended for direct consumption, and to pick them only when they are well coloured, as they are then more tasty and aromatic [19].

1.2. Agronomic uses of zeolite and zeolitite

A German chemist named Fritz Haber won the Nobel Prize for converting nitrogen gas from the atmosphere, which was abundant but non-reactive, into reactive nitrogen that could be oxidized or volatilized during the 1909 season [20]. During the following decades, a German chemist, Carl Bosch, developed a method for exploiting Haber's idea industrially, leading to the production of tons of synthetic fertilizers [21]. One of the most important discoveries in the field of population development was the invention of Haber-Bosch. According to the Green Revolution definition, it refers to the process that influenced agricultural practices between 1940 and 1970, which, as a result of genetically engineered plant varieties, fertilizers, pesticides, water, and new technological and mechanical methods, increased agricultural production worldwide [22,23]. Farmers have been able to cultivate poor soils with synthetic fertilizers or increase their production by continuously utilizing the same soil with the same crop [24]. By the end of the 21st century, the world's population will increase from 1.6 to 6 billion thanks to the ability to produce crop after crop without allowing nutrients to regenerate naturally in the soil. Currently used farming practices, which do not naturally regenerate nutrients, are expensive: fertilisers, potassium, nitrogen, and phosphorus are added to the soil artificially to increase yields, but they inevitably lead to environmental problems [25-27]. Using agropharmaceuticals as foliar treatments against phytophagous and micropathogenic insects that severely damage crops (particularly highly soluble copper salts) has serious environmental consequences [28]. This problem is described in several papers in the literature as the result of their leaching by rainwater and irrigation water, which pollutes the soils, resulting in a loss of fertility [29-32]. Zeolites have been used in agriculture for a long time, but very few scientific papers explain how farming can benefit from their use [33-35].

This article aims to highlight how chabazite zeolitite can lead to better growth and protection of tomato plants (**Figure 1**), in particular the benefits it can bring to crops both when buried in the soil, in terms of plant growth and fruit production, and as a reduction in the incidence of fungal diseases and insect attack when used as a spray in water.

Figure 1 Details of the plants used in the experiment at CREA-OF

2. Materials and methods

The experiments, which began in March 2024, were conducted in the CREA-OF greenhouses in Pescia (Pt), Tuscany, Italy (43°54′N 10°41′E) on tomato cv 'Ciliegino' plants.

The plants were placed in pots with a diameter of 14, 20 plants for 3 replications, for a total of 60 seedlings per experimental thesis.

All plants were fertilised with a controlled-release fertiliser (2 kg m-3 Osmocote Pro®, 9-12 months with 190 g/kg N, 39 g/kg P, 83 g/kg K) mixed with the growing medium before transplanting. The trial was divided into two parallel trials. The first trial on *Solanum lycopersicum* involved the following theses (irrigated and fertilised):

- Peat 70% + pumice 30% (CTRL);
- Peat 70% + pumice 20% + zeolitite chabazite 10% (ZEO10);
- Peat 70% + pumice 10% + zeolitite chabazite 20% (ZEO20).

The second trial on *Solanum lycopersicum* included spray treatments with micronised zeolitite on the leaves to evaluate the control of diseases such as *Phytophthora infestans* and *Tuta absoluta*. The trial included the following theses (irrigated and fertilised):

- Control with treatment with water sprayed on the leaves (CTRL) every 10 days;
- Control with treatment with Flipper 1 L/hl + Ranman Top 0.5L/hl (CTRL2), every 7 days;
- Treatment with zeolitite chabazite 5 kg/hl (ZEOCHAB), every 7 days.

The plants were watered once a day and grew for seven months. The plants were drip-irrigated. Irrigation was activated by a timer whose schedule was adjusted weekly according to weather conditions and leaching fraction.

On 19 September 2024, plant height (measured at 70 days after transplanting), plant nodes (measured at 70 days after transplanting), leaf area index, total dry biomass, fresh fruit weight and number of total fruits were determined. In addition, the number of plants affected by Phytophthora infestans and Tuta absoluta was evaluated.

2.1. Statistics

The experiment was carried out in a randomized complete block design. Collected data were analyzed by one-way ANOVA, using GLM univariate procedure, to assess significant ($P \leq 0.05$, 0.01 and 0.001) differences among treatments. Mean values were then separated by the LSD multiple-range tests ($P = 0.05$). Statistics and graphics were supported by the programs Costat (version 6.451) and Excel (Office 2010).

3. Results

The experiment showed that the use of zeolitite and chabazite added to the growing medium to the extent of 10-20% can effectively improve the vegetative and root growth of *Solanum lycopersicum* (Table 1). Furthermore, when micronised zeolitite is micronised on leaves, it can contain diseases such as *Phytophtora infestans* and *Tuta absoluta*, the same as using conventional products (Table 2). In general, in the first experiment with the addition of zeolitite to the growth medium on *Solanum lycopersicum*, a significant increase in all observed agronomic parameters was observed, particularly with the use of 20% zeolitite (ZEO20), followed by 10% (ZEO10) and the untreated control (CTRL) (Figure 2). All the theses were significantly better than the control (CTRL) with peat and pumice. The same trend was observed with regard to vegetative growth, root growth (Figure 3), leaf area and fruits weight and number (Figure 4).

In the second trial concerning the use of micronised zeolitite spray for plant protection, the application of zeolitite chabasite (ZEOCHAB) led to a significant improvement in plant protection against *Phytophtora infestans* and *Tuta absoluta*, equal to that of the use of conventional chemicals, demonstrating that the use of a natural mineral can be equally effective in the control of plant disease (Table 2).

Table 1 Evaluation of the use of different substrates on *Solanum lycopersicum*

Groups	Plant height70 (cm/plant)	Plant nodes70 (n°/plant)	LAI tot (m^2 m^{-2})	DW Tot (g m^{-2})	FW (Kg m^{-2})	FN (n°)
CTRL	131.67 c	23.59 c	2.26 c	421.74 c	8.16 c	35.68 c
ZEO10	136.48 b	25.87 b	2.58 b	432.69 b	8.85 b	38.81 b
ZEO20	138.71 a	26.64 a	2.79 a	437.55 a	8.93 a	40.94 a
ANOVA	***	***	***	***	***	***

One-way ANOVA; n.s. – non significant; *,**,*** – significant at P ≤ 0.05, 0.01 and 0.001, respectively; different letters for the same element indicate significant differences according to Tukey's (HSD) multiple-range test (P = 0.05).Legend: (CTRL) peat 70% + pumice 30%; (ZEO10) peat 70% + pumice 20% + zeolitite chabasite 10%; (ZEO20) peat 70% + pumice 10% + chabasite zeolitite 20%

Figure 2 Comparison of the thesis with peat 70% + pumice 30% (CTRL) and peat 70% + pumice 10% + zeolitite chabasite 20% (ZEO 20) on the vegetative growth of the tomato plants

Figure 3 Comparison of the thesis with peat 70% + pumice 30% (CTRL) and peat 70% + pumice 10% + zeolitite chabasite 20% (ZEO 20) on root growth of the tomato plants

Table 2 Evaluation (number of plants with disease symptoms) of the use of different spraying treatments with micronised chabasite zeolitite on the control of certain fungal and insect diseases

Groups	***Phytophtora infestans* (n°)**	***Tuta absoluta* (n°)**
CTRL	5.26 a	13.24 a
CTRL2	1.47 b	3.22 b
ZEOCHAB	1.44 b	3.44 b
ANOVA	**	**

One-way ANOVA; n.s. – non significant; *,**,*** – significant at P ≤ 0.05, 0.01 and 0.001, respectively; different letters for the same element indicate significant differences according to Tukey's (HSD) multiple-range test (P = 0.05).Legend: (CTRL) treatment with water sprayed on the leaves; (CTRL2) control with Flipper 1 L/hl + Ranman Top 0.5L/hl; (ZEOCHAB) chabasite zeolitite 5 kg/hl

Figure 4 Comparison of the thesis with peat 70% + pumice 30% (CTRL) and peat 70% + pumice 10% + zeolitite chabasite 20% (ZEO 20) in the fruit production of tomato plants

4. Discussion

As a natural mineral, zeolite is composed of more than 50 different minerals with different physical and chemical properties [36]. Zeolites are typically found in unmetamorphosed sedimentary rocks, particularly volcanic rocks covered in white material [37]. They are mined and synthesized around the world. Zeolites, in essence, are hydrated aluminosilicates made from sodium, potassium, calcium, and magnesium cations [38]. The manufacturing and/or synthesis of synthetic zeolite involves one or more chemical reactions that break and/or make chemical bonds. With a three-dimensional structure framework of SiO_4 and AlO_4 tetrahedra, these compounds are described as hydrated aluminum-silate complexes of alkali and alkaline earth cations [39,40]. They are rare, beautiful, complex, and have unique crystal habits. Zeolite's unique physical and chemical properties are essential to environmental, agricultural, and health applications [41-44]. Water and wastewater treatment, pollution control, ammonium ion removal, and air and gas purification are some of the environmental applications for zeolite [45-48]. A wide range of agricultural applications exist, including fungicides and herbicides, aquaculture, soil conditioning, feed supplements, and slow-release insecticide carriers [49-51]. A large number of fungicides are not satisfactory due to their limited effectiveness against a narrow range of diseases and phytotoxicity. In light of this, it has been desirable to develop high-performance chemicals that are effective at low doses and have little phytotoxicity. As a result of their extensive research, the researchers were able to develop chemicals that can effectively treat fruit and vegetable diseases, while also being safe for application to crops [52]. This has led them to discover that copper-containing zeolites exhibit excellent fungicidal activity while exhibiting no problematic phytotoxicity. In agriculture and horticulture, crystalline zeolite (chabazite, clinoptilolite, phillipsite, and faujasite) is used as a fungicide to control pathogenic fungi [53]. An example of an inert carrier is kaoline clay, attapulgite clay, bentonite, terra alba, pyrophillite, talc, diatomaceous earth, calcite, corn stalk powder, walnut shell powder, urea, ammonium sulfate, synthetic hydrated silicon dioxide, calcium lignosulfonate, sodium laury sulfate, polyoxyethylene sorbitan monooleate, and water. Aluminum silicate can be used to produce agricultural and horticultural fungicides [54]. In reality, the copper-containing aluminosilicate does not have a strong fungicidal activity per copper content and cannot compensate for the defect of conventional inorganic copper-containing chemicals. It has been developed to be highly effective at a very low dose rate of copper by developing a chemical whose copper content results in extremely high fungicidal activity. As a general rule, the present fungicide may be applied by any method or combination of methods, including foliage application, soil treatment, seed disinfection, etc, by those skilled in the field. It is an active ingredient in agricultural and horticultural fungicides, and dosage rates vary according to the crop, disease to be controlled, intensity of disease outbreaks, preparation methods, application time, weather conditions, and copper content [55,56]. The unique characteristics of zeolites allow their application to increase soil water content, increasing water use efficiency (WUE). Infiltration and hydraulic conductivity are the two most important soil physical properties improved by zeolites. In agricultural applications, zeolitic soil amendments reduce water use by increasing water holding and preventing deep percolation. Many studies have investigated their impact on soil hydraulic properties. Zeolite can improve the WHC of light-textured soils [57,58]. Natural zeolites show a cation exchange capacity (CEC) of between 100 and 200 cmol (+) kg^{-1}. Zeolite is a silicate mineral whose characteristics differ from other silicate minerals such that it has spacious pores and channels within its structure. Natural zeolites are loaded with cations such as sodium (Na^+), potassium (K^+), and calcium ($Ca2^+$). These compounds possess a number of significant and well-known properties. The first one is a high CEC, which is much greater than that of soils, the second one is a large amount of free water within their structural channels, and the third one is a high surface area for adsorption [53].

This experiment conducted on *Solanum lycopersicum* shows an improvement in plant growth in the theses treated with zeolite added to the substrate, due to increased water and nutrient uptake and increased microbiological interactions in the plant, as well as a significant improvement in protection against plant diseases when micronised zeolite is sprayed on the leaves. In addition to having an insect repellent effect, zeolite has a disintegrating and dehydrating effect. The product causes respiratory problems, burns the exoskeleton, creates flight problems and reflects light. In addition, zeolitite chabazite, having a rough structure, causes problems of adherence to the leaf. As for fungi, on the other hand, it reduces moisture on the leaf and inhibits spore germination, as demonstrated in other scientific works by the same author [40-48].

5. Conclusion

Recent population growth and urbanization have limited agricultural production in recent years. In order to perform more efficient agricultural activities, nutrient application rates must be increased and irrigation systems must be more efficient. If high rates of fertilizers are applied to soils, however, a substantial amount of nutrients might be washed out, polluting water resources and reducing yields. To increase crop yields, a cost-effective, pervasive, and green solution is crucial. Zeolites have been extensively studied for improving agricultural productivity. Zeolites have the potential to affect soil physical properties. In addition to reducing soil bulk density and increasing soil porosity, these factors can improve water retention, as well as their high internal pore volume. Also, due to the open network of the zeolite structure, new routes for water movement can be formed, resulting in improved infiltration rates and saturated hydraulic conductivity. Due to their outstanding chemical and physical properties, natural zeolites can be utilized in agricultural applications, such as their affinity for K^+ and $NH4^+$ and ability to exchange cations. Before any commercial applications can be made, it is necessary to evaluate the risk of leaching toxic surfactants loosely attached to zeolite surfaces. Using their ion exchange properties, natural, synthetic, and modified zeolite can be used to make slow-release nitrogen, potassium, and sulfur fertilizers. To control and release phosphorous slowly, zeolite ion exchange and mineral dissolution (similar to phosphate rock) can also be used. It is generally determined by a variety of experimental conditions how zeolite application impacts soil physical and chemical properties, including the type and rate of zeolite applied, the method of application, the texture and structure of the soil, the size of the zeolite particles, and the salinity of the water. Soils with coarse textures may benefit from zeolite amendments more than those with fine textures.

Compliance with ethical standards

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Disclosure of conflict of interest

The author declares no conflict of interest.

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