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# On the potential effect of micronized zeolites on seed germination: a prospective study

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**ABSTRACT**

It is well known that zeolite yields positive effects to seed germination. However, any previous study has so far highlighted how the zeolite interacts with the seeds. The goal of this paper is to assess the effect of zeolite on radish seed germination by means of standard analytical methods.
As starting assumption, we hypothesize that the micronized zeolite mixed with water may try to break the seed's husk and allow the water to enter the seed. X-Ray diffraction is used to characterize the structural properties of the zeolite employed in this work, while Energy Dispersive X-Ray Spectroscopy coupled with Scanning Electron Microscope is employed to investigate seeds of radish that were previously treated with or without micronized natural zeolite. The present results confirm the positive effects of the zeolites on seed germination. In addition, it is found that zeolite grains on the surface of the seeds cannot penetrate its husk, implying that there is no risk of zeolite accumulation within the tissues of the plant's embryo.

Keywords: XRD; SEM-EDX; zeolite; seed.

## INTRODUCTION

Among the inorganic soil conditioners used in agriculture, natural zeolites are the most commonly used (Mumpton, 1981; Kesraoui-Ouki et al., 1994; Perrin et al., 1998; Ma et al., 2000; Polat et al., 2004; Reháková et al., 2004; Passaglia, 2008; Misaelides, 2011; Palanivell et al., 2016; Campisi et al., 2016; Ferretti et al., 2017). Natural zeolites are pioneering "mineral fertilizers" with high and selective cation exchange capacity (CEC), molecular sieving and reversible dehydration (Bish and Ming, 2001). Zeolites have a complex three-dimensional, negatively charged, tecto-silicatic structure with large cage-like cavities interconnected through channels that are able to accommodate $K^+$, $Na^+$, $Ca^{2+}$ or other cations, water and even small organic molecules (Passaglia, 2008; Bish and Ming, 2001). Cations are only weakly bounded to the mineral framework and this allows them to migrate in and out of the structure of the zeolite. When cations are partly or totally released and the mineral comes in contact with a solution, the zeolite extracts an equivalent amount of other cations (Passaglia, 2008; Bish and Ming, 2001).

The use of natural zeolites in environmental protection has progressively increased. In particular, they have been used for the treatment of sewage waters, to remove ammonium and to amend substrates for greenhouse and agricultural soils (Palanivell et al., 2016; Ming and Allen, 2001; Faccini et al., 2015; Di Giuseppe et al., 2015; Di Giuseppe et al., 2016a). Moreover, zeolites maintain soil buffering, improve water retention (Durukan et al., 2014; Di Giuseppe et al., 2015) and, indirectly, regulate soil pH (Polat et al., 2004).

Colombani et al. (2014) showed a decreasing loss in nitrogen and water contents in soils amended with natural zeolites with respect to those treated with chemical fertilizer. Conditioning soils with zeolites favors the development of helpful microorganisms (Yang, 1997; Andronikashvili et al., 2007) and allows the dissolution of phosphates (Pickering et al., 2002; Lancellotti et al., 2014).

Another important aspect of the use of the zeolites is that they promote seeds germination (Khan et al., 2009; Palanivell et al., 2016). In this sense, research is focusing on a way to accelerate or make more effective the germination of plants by spreading micronized zeolite on seeds. The effectiveness of micronized zeolite application (often clinoptilolite) has been discovered working on the stimulations of roots during seedlings, desiccation tolerance, vigor of the seed, germination and physiological maturity time (Khan et al., 2009; Palanivell et al., 2015). However, the process involved in the improvement of seed germination through the zeolite is still a matter of debate.

The use of healthy seed is essential for satisfactory crop yields and quality (Khan et al., 2009). Environment at seed planting and during harvest is a key component of sustainable agriculture. Good germinations of seed improve fertilization and water efficiency and optimize of plant growth (Khan et al., 2009).

A key issue to understand the relationship between inorganic fine particles (e.g. micronized zeolite) and seed was proposed by Zang et al. (2015). They found that very fine material, such as graphene, is able to penetrate and break the husks of tomato seed. This process facilitates water uptake for the plant embryo, resulting in faster germination and higher germination rate. Zang et al. (2015) highlighted also that after penetration in the seed, graphene accumulated in the vacuoles and then in the roots, causing reduced biomass production of plant at the stage of seedling growth.

Since the mechanism by which zeolite affects seed germination is not yet known, the purpose of this study is to check whether the micronized zeolite mixed with water and spread on the seeds is able to perforate their husk and accumulate inside them (similarly to graphene). Since zeolites are aluminosilicates consisting of $SiO_4$ and $AlO_4$ tetrahedra, X-ray spectroscopy techniques can be considered as highly suited for the study of this kind of minerals (Galván et al., 2009; Di Giuseppe et al., 2016b).

In the present work, we employ different X-ray based techniques, such as X-ray diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDX) coupled with Scanning Electron Microscope (SEM), in order to characterize the zeolite samples and to investigate the interaction between natural zeolites and radish seeds. These were chosen for the present study due to their short germination times. The main goal of this paper is to verify if the micronized zeolite is able to pierce the husks of the seeds and accumulate inside them. The potential benefits and drawbacks of the micronized zeolites are discussed in comparison with those of graphene.

## MATERIALS AND METHODS

### Micronized zeolite characterization

In this study, a commercially available powder of natural zeolite was used. This material is easy to find in the on-line commerce and is commonly used in farming as soil amendment and biological insect repellent.

The selected natural zeolite is a byproduct of a quarry situated near Sorano village (Grosseto, central Italy), which is mainly exploited to obtain blocks and bricks for construction and gardening. The quarry is located in a zeolitized pyroclastic deposit belonging to the Lithic Yellow Tuff body of the Sorano formation (Faccini et al., 2015). This Formation is part of phonolitic-tephritic ignimbrite with black pumices deposits, erupted during Quaternary by the volcanic complexes of Bolsena, Vico and Bracciano lakes (Passaglia, 2008). These rocks underwent extensive zeolitization in response to the activity of pore fluids heated by the thermal energy of the pyroclastic deposit itself, resulting in a sort of "geoautoclave"(Passaglia, 2008). As a consequence of this process, the mineral composition reflects the low Na/K and Si/Al ratios of the original volcanic glass and the pH of the circulating pore waters (Passaglia and Vezzalini, 1990; Passaglia et al., 1990).

The main zeolite species found are chabazite (~68%), phillipsite (~1.8%), analcime (~0.6%) (Malferrari et al., 2013).

In order to have the material as fine as possible, the zeolite powder was milled 10 times with an agate mill during 30 minutes grinding cycles. The powder was characterized using Wavelength dispersive X-ray fluorescence (WD-XRF) for the total chemical compositions, by XRD for mineralogical composition, and by X-ray Sedigraph for granulometric class determination (Di Giuseppe et al., 2016b).

For chemical and mineralogical analyses, zeolite was quartered and two sub-samples were dried at 60 °C for 24 hours to eliminate the hygroscopic water.

For the WD-XRF analysis, one dried sample (4 g of powder) was pressed with the addition of ~13.5 g boric acid by hydraulic press applying a pressure of 101.81 kg/cm$^2$ to obtain powder pellets. Meanwhile 0.5-0.6 g of powder was heated for about 12 hours in a furnace at 1000 °C in order to determine the loss on ignition (LOI). The WD-XRF analysis of the powder pellets was carried out using an ARL Advant-XP spectrometer Thermo Scientific. Calibrations were obtained analyzing certified reference materials (Di Giuseppe et al., 2014) and matrix correction was performed according to the method proposed by Lachance and Trail (1966).

One zeolite sub-sample was analyzed by Micromeritics Sedigraph 5100 Particle Size Analysis System in order to obtain grain size distribution. This instrument measures the size distribution of settling fine particles assuming that X-ray absorption is directly proportional to the particle mass. The radiation from an X-ray tube (with a tungsten target inclined at about 55° with respect to a thin beryllium window) is collimated and passes through the sample cell. The primary radiation has a wavelength of 0.125 nm.

The mineralogical characterization was carried out on dried-samples by using a Bruker D8-A25 powder diffractometer equipped with a 2.2 kW sealed Cu X-ray source and a Lynxeye position sensitive detector (PSD). The scans were acquired between 4° and 60° 2θ with a 0.035° step size and an equivalent counting time of 192 s per step. Phase identification was performed with the DIFFRAC.EVA software together with the Powder Diffraction File PDF-2.

### Germination and seedling growth of radish seeds

In order to test the effect of micronized zeolite on seeds germination, radish seeds were chosen because of their fast germination.

Twelve sterilized radish seeds were placed on cotton-cushioned, six of which treated with 5 mL of zeolite-water solution at 1 g/l of concentration and left to germinate for three day at 25 °C in dark conditions (Figure 1). Deionized water (DI water) at resistivity >18 MOhm/cm was used as water source. Cotton-cushioned were saturated with water for the duration of the test. The seeds without zeolite treatment were used for control experiments. All the seeds

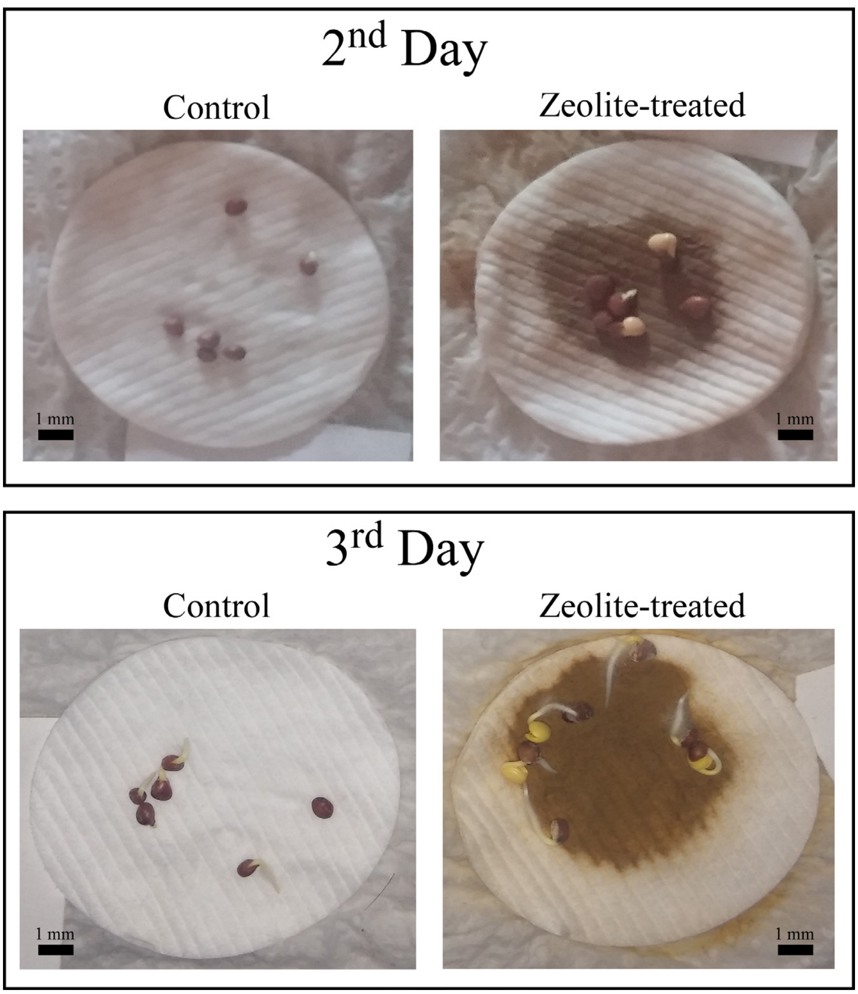



Figure 1. Two-day and three-day incubation of the seeds with MZ treatment and without MZ treatment.

were subsequently washed with DI water and then dried in an oven at 35 °C for 1 day in order to stop the growth. This procedure was repeated three times for a total of 36 seeds used, 18 of which treated with micronized zeolite (MZ) and the remaining 18 seeds used as control.

### XRD and SEM-EDX seeds analysis

For XRD analysis, ten seeds (five MZ five control seeds) were washed with DI water and heated at 500 °C for one night in order to remove their organic matter and concentrate the hypothetical zeolite inside them. Then all the samples were pulverized (<5 μm), carefully homogenized and analyzed in the same way as the micronized zeolite powder.

SEM Quanta 200 FEI was used to investigate the presence of particle material (such us zeolite grains) inside the seeds treated with MZ. This instrument can operate in regular high-vacuum, low-vacuum and ESEM modes and has 3.0 nm resolution at 30 kV and 10 nm resolution at 3 kV.

The SEM instrument was equipped with the standard secondary electrons (SE) and backscattered (BSE) detectors as well as an Electron backscatter diffraction (EBSD) orientation mapping system. Moreover, it was coupled with EDX and internal TV camera (Charge Coupled Device, CCD).

Dried seeds were opened by longitudinal cut, stuck with bio-adhesive to the sampler holder and then graphite coated. The use of the SEM optical options allowed investigating internal surface of the husk and radish embryo. In addition, zeolite was searched within the husk, exploiting the internal parts exposed after cutting. Any detected material not related to the seed was analyzed with EDX to investigate if it could be attributed to MZ. For comparison purposes, the as-purchased zeolite powder was also analyzed with the EDX.

## RESULTS AND DISCUSSION

As shown in Figure 1, after the 2$^{nd}$ day seeds treated with MZ already started to germinate. The 3$^{rd}$ day MZ treated seeds showed roots of almost 2 mm. At the end of the experiment, all the seeds treated with MZ were germinated one day before the controls, thus confirming the beneficial effect of the zeolites on seed germination

A typical diffraction pattern produced through XRD analysis of MZ is reported in Figure 2a. The XRD analysis confirms that the sample is mainly constituted by chabazite. Small amounts of illite/muscovite and orthoclase are also found in the sample (see Figure2a, which includes patterns from the PDF-2 database for the identified phase). The XRD scan suggests that the crystal structure of the zeolite is close to that of Ca-chabazite (sg. R-3m), as can be seen in Figure 2. Full-pattern matching of the diffraction pattern using the Pawley method allowed us to extract the following lattice spacings for the zeolite phase (hexagonal setting): a=13.792 Å and c=14.981 Å. These values are in good agreement with those obtained in previous structure refinements of Ca-chabazite (Smith et al., 1963; Gualtieri, 2000).

In turn, the XRF major element composition (Figure 2b) suggests that the principal cations of the zeolite are K and Ca. Most of K probably arises from the mica and K-feldspar detected in the sample. Indeed, these results are in agreement with previous Rietveld-RIR (Reference Intensity Ratio) studies on the zeolitized material (Sorano formation) of the same origin (Malferrari et al., 2013). Such analyses revealed an average mineralogical composition of chabazite 68.5%, phillipsite 1.8%, analcime 0.6%, mica 5.3%, K-feldspar 9.7%, pyroxene 2.9% and volcanic glass 11.2%.

In turn, results of granulometric analyses through the sedigraph highlight a grain size range of MZ from 0.2 to 30 μm (Figure 2c). The 50% of MZ grains have size of 2 μm and 90% of grains were below of 9 μm.

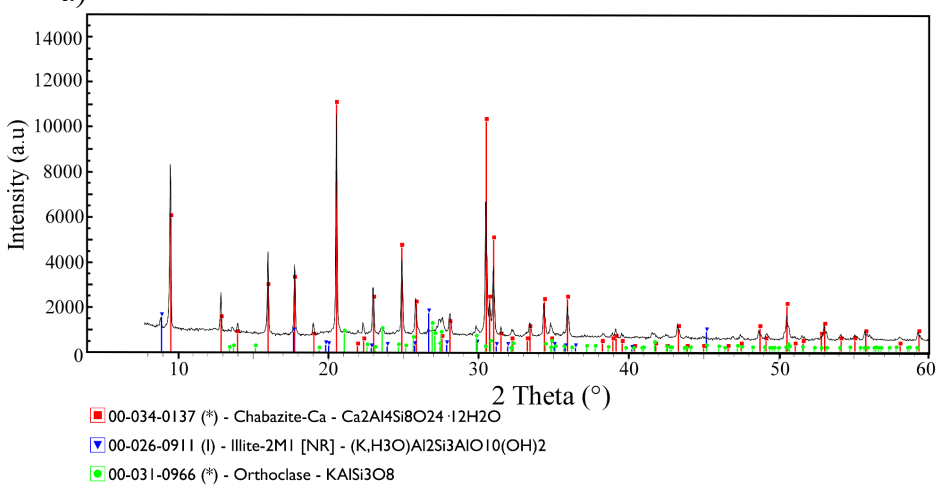
Several analytical tools were employed to investigate the interaction between natural zeolites and the germinated radish seeds. First, XRD analyses involving very-long integration times on germinated seeds that were calcined in order to remove the organic matter (XRD diffraction pattern not shown) did not allow us to detect the presence of zeolite in the MZ seeds. This is probably a consequence of the very small amounts of zeolite (if any) that might be incorporated into the seeds during growth.

Figure 3 shows a SEM image of a single MZ grain. The figure also shows the characteristic Si, Al, K and Ca peaks of a typical EDX spectrum of zeolite powder. Figure 4a shows a half part of a radish husk and Figure 4b shows its 294X magnification. As can be seen in the figure, the husk is intact and no opening or cracks are detected (Figure 4b). To test the presence of zeolites at the intracellular level, a cut on the husk was performed (Figure 4 a,c). The inside of the husk exposed by the cut was observed with magnification 2346X (Figure 4c) and no zeolite granules were found (Figure 4d).

Some zeolite granules were however found on the surface of the husk. None of them had a size smaller than 5 μm and none of them seemed to have modified the surface structure of the husk (Figure 5).Most probably MZ was not completely removed during washing, so that some of the larger grains remained on the surface of the seeds.

Figure 6a shows the digital image of a leaf of a radish embryo, with no zeolite on it. The grain highlighted in the 500X and 3683X magnification (Figure 6b and 6c) was analyzed with EDX and can be attributed to a crystal of sodium chloride (Figure 6d).

The SEM images clearly show that when zeolite comes a)




b)

Major elements composition expressed in percent by weight

| $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | MnO | CaO | $Na_2O$ | $K_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|
| 30.5 | 0.01 | 29.3 | 0.38 | <0.01 | <0.05 | 0.13 | 19.5 | <0.01 | 20.7 |

c)

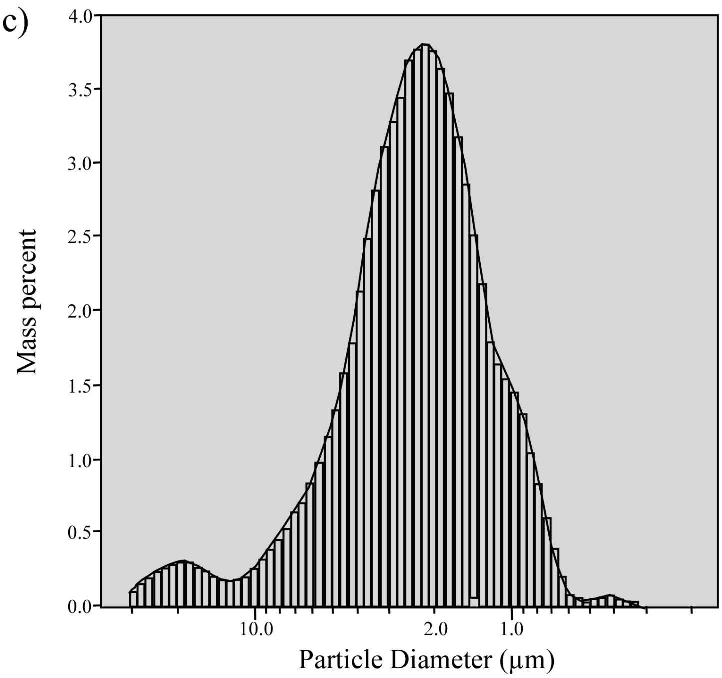



Figure 2. (a) Diffraction pattern produced through XRD analysis of MZ and patterns from the PDF-2 database for the identified phase. A.u. stands for arbitrary units; (b) XRF MZ major element composition; (c) MZ granulometric curve.

into contact with the surface of the seed it cannot pierce its husk, thus suggesting that the risk of an accumulation of the zeolite within the tissues of plant's embryo (as is the case for graphene) does not exist.

Since germination of a seed is triggered by the supply of water in the embryo of the plant, it can be concluded that the zeolite affects seed germination differently from graphene.

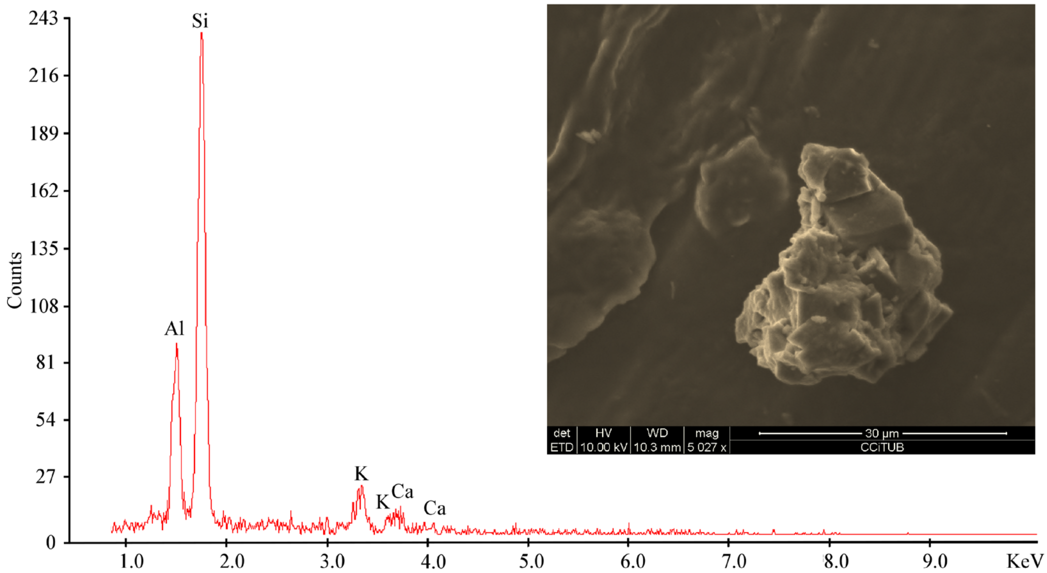



Figure 3. EDX spectrum of zeolite (in red) and digital SEM image of a MZ grain.

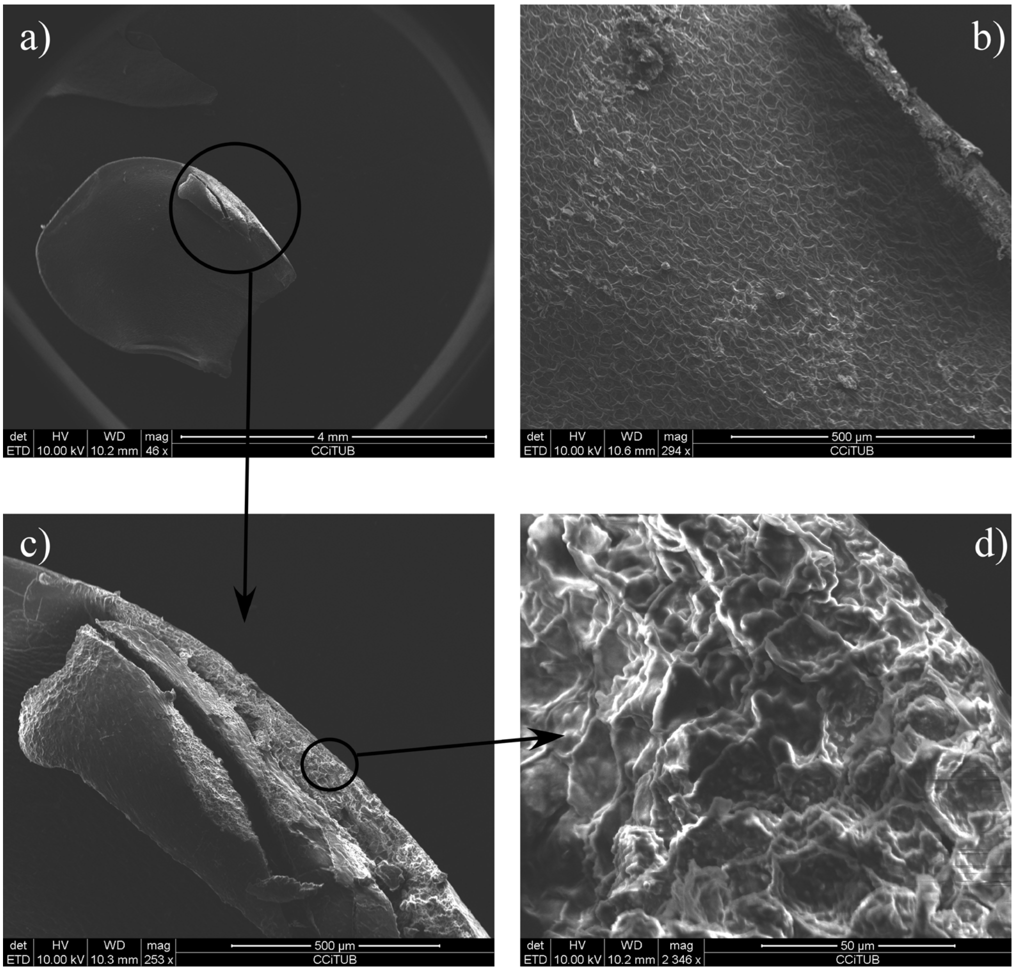



Figure 4. SEM digital image of radish husk (a); 294X magnification of husk surface (b); 500X and 2348X magnification inside the seed, respectively (c,d).

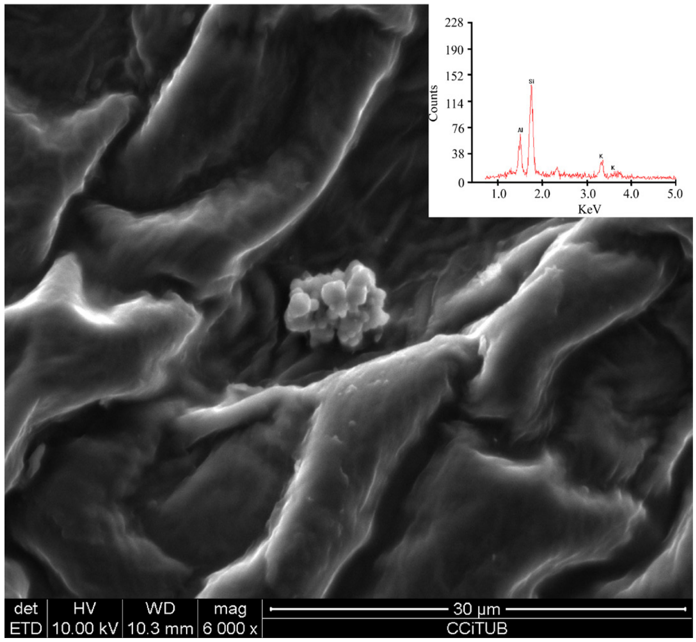



Figure 5. SEM digital image and EDX spectrum of MZ granules found on the surface of the husk.

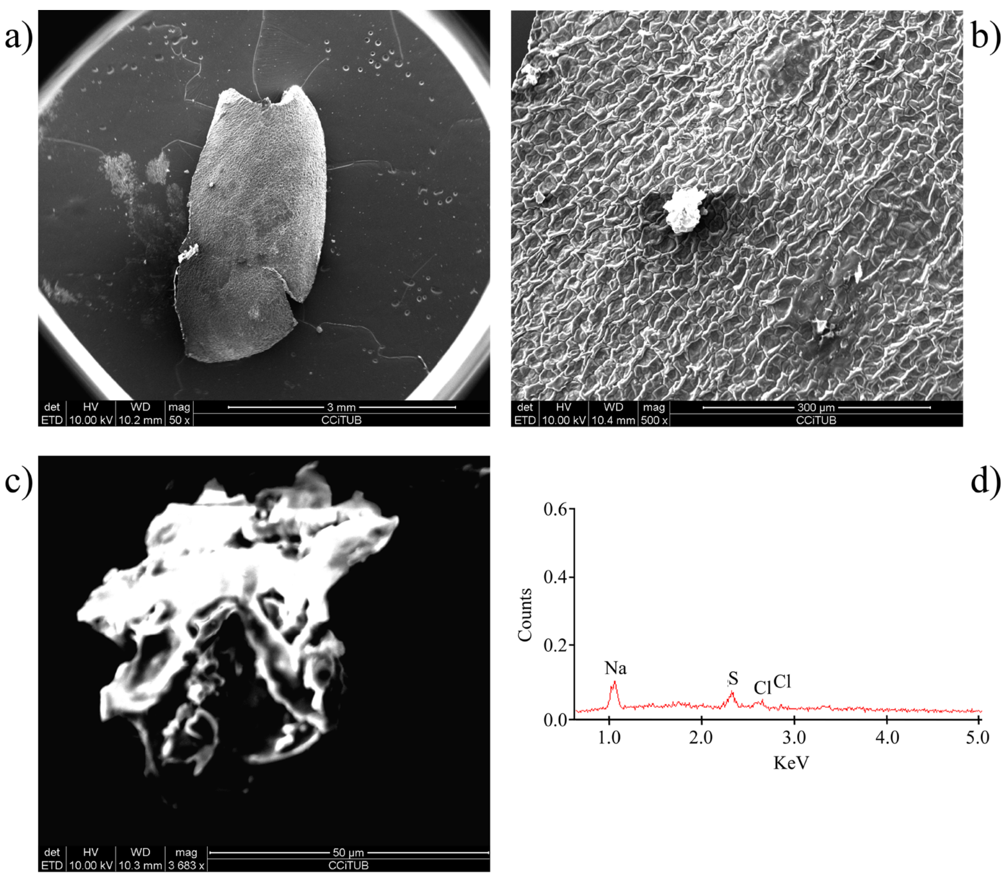



Figure 6. Digital image of a leaf of a radish embryo (a); 500X (b) and 3683X (c) magnification of a crystal of superficial grain; EDX spectrum of the grain (d).

Zeolites are crystalline hydrated aluminosilicates (Reháková et al., 2004) and have been recognized to improve the water holding capacity of soil or plant growing substrates (Colombani et al., 2014; Huang and Petrovic, 1994; Xiunin and Zhanbin, 2001). Probably, the water retention capacity of MZ allows the treated seeds to have more water available than in the case of control seeds. Both treated seeds and control samples have suffered the same loss of evaporation water, but those treated with MZ have been able to count on the zeolite water tank. It cannot be ruled out that part of the zeolite is also acting as a fertilizer, yielding a larger amount of cations to the plant. More work is thus required to understand the actual interaction mechanisms between the seeds and the zeolites.

In the field of seed treatment, some important factors may be in favor of zeolite in comparison to graphene. The latter, which is currently more expensive than zeolite, can cause reduced plant biomass production. In contrast, zeolite is a natural and non-toxic material that does not have this problem and whose positive effects on plant growth after germination have already been brought into attention in the literature.

## CONCLUSIONS

Although the positive effects of zeolite as a seed germination improver had already been highlighted in the literature, there were no previous studies dealing with the interactions between zeolite and the seeds. The research proposed in this manuscript is the first step towards the understanding of this phenomenon. Growth tests realized on radish seeds confirmed rapid germination when treated with MZ in comparison to the control (untreated) seeds. Our results suggest that zeolite does not affect seed development in the same way as graphene. When the zeolite comes into contact with the surface of the seed, no evidence is found that the zeolite is able to pierce its husk. Therefore, the risk of an accumulation of the zeolite within the tissues of plant's embryo (as is the case for graphene) does not exist.

The application of the SEM-EDX technique allowed us to verify that zeolite aggregates, even in the case of very low grain sizes (~2 μm), are too large to overcome the outer barrier of the seeds.

Thus, the positive impacts on the germination of radish seeds can be probably attributed to the fact that MZ was able to improve the water holding capacity of growing substrates and consequently facilitate water uptake.

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