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Potential and actual uses of zeolites in crop protection

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Abstract

In this review, it is demonstrated that zeolites have a potential to be used as crop protection agents. Similarly to kaolin, zeolites can be applied as particle films against pests and diseases. Their honeycomb framework, together with their carbon dioxide sorption capacity and their heat stress reduction capacity, makes them suitable as a leaf coating product. Furthermore, their water sorption capacity and their smaller particle sizes make them effective against fungal diseases and insect pests. Finally, these properties also ensure that zeolites can act as carriers of different active substances, which makes it possible to use zeolites for slow-release applications. Based on the literature, a general overview is provided of the different basic properties of zeolites as promising products in crop protection.

Keywords: surface crop protection; zeolites; particle film; photosynthesis; carrier; fungicide/insecticide properties

1 INTRODUCTION

The usage of pesticides to manage diseases, pests, weeds, etc., has become a common practice around the world.[1–3] Environmental pollution and ecological issues, however, make it necessary to look for alternatives, such as other organic agrochemicals or the controlled release of pesticides, including a reduction in the amount of active ingredients.

Current research is based on the use of nanoparticles and their potential role in agriculture to reduce the negative impacts of environmental stresses on crop plants, to suppress diseases and to protect crops from insect pests.[4] This approach has been applied by making use of dust applications. However, such material has some drawbacks – see the discussion of kaolin-based particle films used on plant surfaces in Section 2.

1.1 Basic characteristics of zeolites

Zeolites represent a broad range of microporous, crystalline aluminosilicates of natural or synthetic origin. Generally, their structure can be considered as an inorganic polymer built from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra (primary building units – PBUs) linked by the sharing of all oxygen atoms. A pure silica (SiO_2) solid framework is uncharged. When some of the Si^{4+} in the silica framework is replaced by Al^{3+}, the +3 charge on the aluminium makes the framework negatively charged, which is compensated for by the presence of extra-framework cations (counterions), located together with water, to keep the overall framework neutral.[5]

Connecting small units of several tetrahedra (up to 16) provides the formation of secondary building units (SBUs), i.e. chain- or layer-like units. Subsequently, more complex building units can be formed, i.e. characteristic subunits and cages/cavities that recur in several framework types.

The zeolite structure may be represented by the formula

$$M_{x/n}\left[\left(AlO_2\right)_x\left(SiO_2\right)_y\right].wH_2O$$

where M is an alkali or alkaline-earth cation (Na, K, Li and/or Ca, Mg, Ba, Sr), n is the cation charge, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell and the ratio y/x usually has values ranging from 1 to ∞.[5,6]

Every zeolite material is classified by the framework type to which it belongs. The framework type does not take into account the element in each tetrahedron, just the connectivity (topology) of the framework. It defines the size and shape of the pore openings, the dimensionality of the channel system, the volume and arrangement of the cages and the types of cation site available.[7,8] The chemical formulas and structure types of some important natural and synthetic zeolites are presented in Table 1 and Fig. 1.[9–11]

1.2 Applications of zeolites

Owing to their unique physical and chemical properties, zeolites are used for a great number of applications in different domains. In industry, zeolites are well known and commercially used as separation agents, ion exchangers, adsorbents, as fillers in paints, paper and plastics, etc.[12] Also, the use of zeolites for environmental applications is attracting new research interest, mainly owing to their properties and significant worldwide occurrence. Application of natural zeolites for water and wastewater treatment, focused on ammonium and heavy metal removal, has been realised and is still a promising technique in environmental cleaning processes.[13,14] In addition to these applications, zeolites also have their medical

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Table 1. Chemical formula and structure of some important zeolites[9]

Zeolite	Chemical formula	Structure type	Channel dimensions	Volume (Å^3)	Symmetry
Natural zeolites					
Chabazite[a]	$\|(K,Na,Ca_{0.5})_2(H_2O)_{12}\|$ $[Al_4Si_8O_{24}]$	CHA	3D	2391.59	Rhombohedral
Clinoptilolite	$\|(K,Na,Ca_{0.5})_6(H_2O)_{20}\|$ $[Al_6Si_{30}O_{72}]$	HEU	2D	2054.84	Monoclinic
Mordenite	$\|Na_2,Ca,K_2)4(H_2O)_{28}\|$ $[Al_8Si_{40}O_{96}]$	MOR	1D	2827.26	Orthorhombic
Synthetic zeolites					
Zeolite A[a]	$\|Na_{12}(H_2O)_{27}\|_8$ $[Al_{12}Si_{12}O_{48}]_8$	LTA	3D	1693.24	Cubic
Zeolite L	$\|K_6Na_3(H_2O)_{21}\|$ $[Al_9Si_{27}O_{72}]$	LTL	1D	2153.11	Hexagonal
Zeolite Y	$\|(Ca,MgNa_2)_{29}(H_2O)_{240}\|$ $[Al_{58}Si_{134}O_{384}]$	FAU	3D	14 428.77	Cubic

[a] The scanning electron micrograph and framework are shown in Fig. 1.

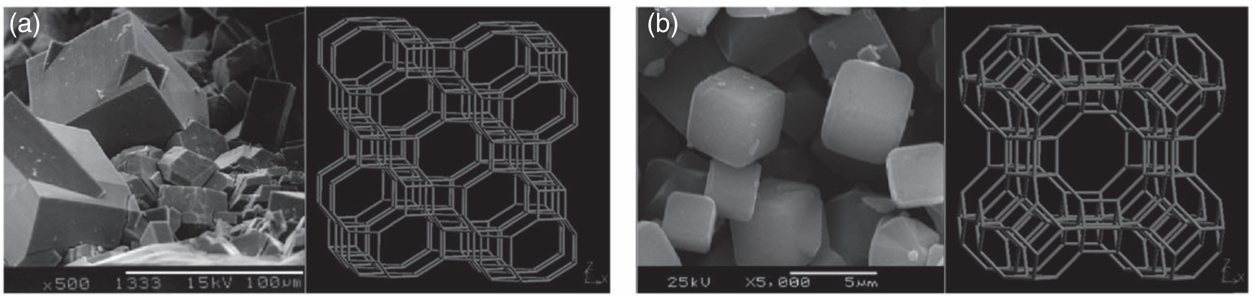

Figure 1. Scanning electron micrographs and frameworks of (a) natural zeolite chabazite and (b) synthetic zeolite Zeolite A.[9–11]

applications, for example as detoxicants, vaccines and agents in haemodialysis, bone formation, etc.[15]

Furthermore, zeolites have been widely used in agriculture for the removal of bad odours in animal stables and for their soil-improving properties (e.g. increase in water-holding capacity and nutrient adsorption, and decrease in levels of heavy metals or radionuclides in contaminated soils). Studies have verified that phytoremediation processes can be performed with the aid of zeolites. In a mixture with compost, zeolites have been shown to promote plant species growth and to increase, at the same time, the accumulation of metals in the aerial part of the plant. When composted together with poultry manure, zeolites become ammoniated and enhance the soil microbial population.[16–19] In combination with fertilisers, zeolites may help to buffer soil pH levels. After a few years of zeolite action in the soil, the zeolite increases crop yields and is used as fertiliser itself.[16]

Natural zeolites can also be added as dietary additives to animal food in order to neutralise the negative effects of mycotoxins. Controlled release of inputs is being employed extensively in agriculture to deliver active substances such as pesticides, herbicides and fertilisers. Zeolites are attractive candidates as carriers to immobilise these crop protection products and nutrients first, before slow release can take place (see Section 2.5).[16,20,21]

Note that the aforementioned list of applications is not exhaustive, and that zeolites can also be used for applications in other domains as well. However, the main emphasis of this review is on the use of zeolites in agriculture, and more specifically on the use of zeolites as plant protection products against pests and diseases.

In the following sections, an overview is presented of the different properties of zeolites for their usage in crop protection. These properties will demonstrate that zeolites are also able to form a good particle film for controlling pests and diseases. The most important characteristics for an effective particle film on plant tissues, summarised in Table 2, are taken into account (Glenn M, private communication).

Table 2. Characteristics of the effectiveness of particle film technology on plant tissues (Glenn M, private communication).

1. The formulation contains chemically inert mineral particles
2. The particle diameter is <2 µm
3. The formulation spreads well and creates a uniform film
4. The porous film does not interfere with gas exchange from the leaf
5. Ultraviolet (UV) and infrared (IF) radiation are excluded, but it transmits photosynthetically active radiation (PAR)
6. The technology alters insect/pathogen behaviour on the plant
7. The particle film is easy removable from harvested commodities

2 ZEOLITES: A GOOD PARTICLE FILM FOR CONTROLLING PESTS AND DISEASES?

Particle film technology may be defined as a synthesis of combined knowledge on mineral technology, insect behaviour and photochemistry. It aims to control pests and diseases of plants. A particle film is a microscopic layer of mineral particles attached to the plant surface. An example of a scanning electron microscope (SEM) image of a particle film is shown in Fig. 2.[22]

This technology has proven to be a viable alternative to synthetic pesticides for managing arthropod pests and diseases of agricultural crops.[23,24] The use of particle films on plant tissues is aimed at preventing most of the negative effects that occur with the current application of pesticides. It might deliver a wide range of beneficial effects in terms of water efficiency, control of pests and diseases, reduction in pesticide use, increase in crop yield and tolerance to abiotic stress (Glenn M, private communication).

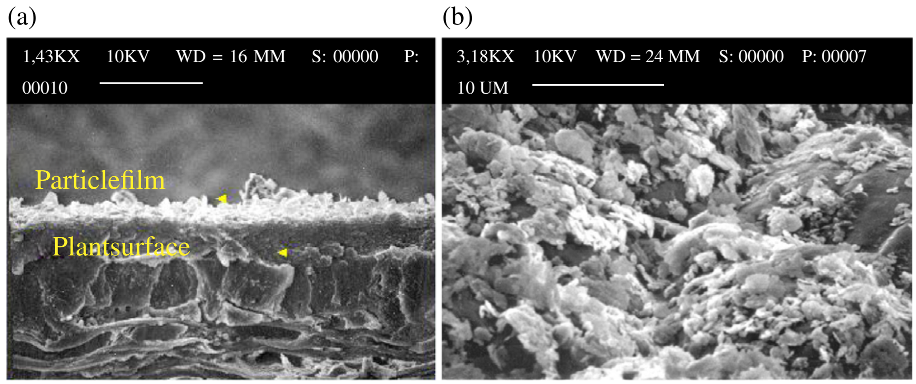

Figure 2. Scanning electron micrographs of (a) a leaf and a particle film and (b) kaolin on the upper surface of an apple leaf.[22]

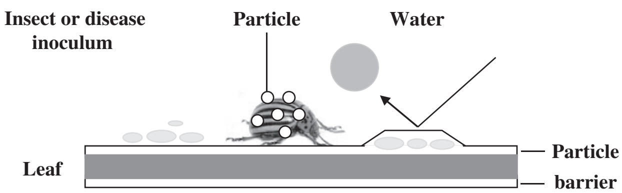

Figure 3. Mechanisms of arthropod pest and disease suppression in plants.[23]

In the 1920s, dusts were increasingly applied and even preferred to liquid sprays (Glenn M, private communication). Current particle film technology is based on kaolin, a white clay mineral $\{[(Al_2O_3)(SiO_2)_2].2H_2O\}$ also called aluminosilicate.[25] The hydrophobic kaolin particle M-96-018 was the first prototype of particle film technology that was applied as a dust on trees in order to make the plant surfaces repellent and to suppress anthropod pests and diseases (Fig. 3).[23]

This dust coating was water repellent, prevented diseases and arthropod infestations, favoured a lower oviposition rate and reduced the survival of insects. Nevertheless, the drift associated with dusting operations and the lack of adhesion to the plant made M-96-018 dust applications impractical. The need for an easier formulation led to the development of M-97-009. A formulation of this hydrophilic kaolin particle combined with a nonionic spreader sticker, M-03, was just as effective as M-96-018 in controlling pests and diseases, with improved formulation properties, i.e. ease of mixing, adhesion, spreading and rainfastness. In 1999 this product became commercially available under the name Surround® WP crop protectant (BASF, Research Triangle Park, NC; previously Engelhard Corp., Iselin, NJ) (Glenn M, private communication). An example of a kaolin-based particle film on crops is illustrated in Fig. 4.[26]

Zeolites are just like clay minerals composed of aluminosilicate $\{M_{x/n}[(AlO_2)_x(SiO_2)_y].wH_2O\}$, but differ in their crystal structure (Table 3).[16,21,27] Therefore, zeolites may also play an increasing role in a wide range of agricultural applications. However, the use of zeolites as a biofilm matrix for controlling various pests and diseases needs further research.

2.1 Chemically inert mineral particles

Unlike typical agricultural chemicals, mineral particle films such as kaolin and zeolite are inert and therefore have no direct biochemical or physiological effect on the plant or pest. Instead, particle films provide activity through their physical properties, such as particle size, shape, surface area, etc.[28,29] The chemical and thermal stability of a zeolite is generally high, but depends on the dealumination of the framework. Zeolites with low Si/Al ratios are the least stable zeolites.[30,31]

2.2 Ideal granulometry of zeolites

Zeolites are commonly fine polycrystalline powders with an average particle size of several micrometres. The different end-uses of silica, for example in the production of paper, paints, etc., depend upon the particle size distribution. A coarse-particle-size silica has very different physical and optical properties compared to a fine-particle silica. Thus, depending on the particular application, it is better to use fine particles instead of coarse particles, and vice versa. The particle size is a critical factor in particle film technology.[32] More than 70% (w/w) of the particles should be smaller than 2 μm. The effectiveness of zeolites against insects generally increases when the particle size decreases to an ideal size of 1–2 μm because of improved adherence to the insect cuticle (see Section 2.4.2).[23]

In recent years, the synthesis of nanocrystalline zeolites has received much attention.[33] The reduction in particle size of zeolites from micrometre to nanometre scale has led to substantial changes in their properties. Previous studies revealed that the particle size and morphology of the zeolite crystals play an important role in their applications in the areas of catalysis and separation.[34] Nanostructured zeolites below 100 nm have a larger external and internal surface, a higher surface energy and a shorter channel in comparison with the conventional microsized zeolites.[35,36] A nanocrystalline zeolite with a crystal size of 50 nm has an external surface area of $>100\ m^2\ g^{-1}$. For comparison, a 500 nm zeolite crystal has less than $10\ m^2\ g^{-1}$ of external surface area. The increased external surface of nanocrystalline zeolites results in enhanced adsorption capacity and additional surface area available for adsorption and reaction of molecules.[37–39]

2.3 Plant-surface-oriented crop protection

In order to understand how crops are grown and protected against pests and diseases, it is important to focus on the general aspects of plant physiology and pesticide application.

2.3.1 *Plant growth*

Plants are essentially autotrophic, photosynthetic organisms, with basic requirements of light, CO_2, water and nutrients (P/K/N/O).[40]

Figure 4. Kaolin sprayed onto crops forms a mineral-based particle film repelling insects and preventing feeding.[26]

Table 3. Mineralogy of kaolin and zeolite[16,21,27]

Kaolin	Zeolite
Aluminosilicate (hydrated)	Aluminosilicate (hydrated)
↓	↓
Phyllosilicates	**Tectosilicates**
(two-dimensional TO_4)	(three-dimensional TO_4)
= parallel sheets	= framework
↓	↓
Clay mineral group	Zeolite family

The three most important physiological phenomena that are basic to plant growth and development are photosynthesis, respiration and transpiration.[41]

2.3.2 *Different steps of pesticide application*

Nowadays, both systemic and non-systemic products are used in agriculture. Systemic products are taken up by the roots and transported throughout the plant, while non-systemic products generally control a pest or disease as a result of direct contact.[42] Just like kaolin, zeolites will be applied as a non-systemic product.[43]

Conventional pesticide application comprises movement of the spray, starting from the spray equipment to the molecular site of action on the target plant. It is a very complex process involving several different steps. The major steps, together with some important influencing factors, are presented in Table 4.[44]

Below, these different steps will be explained using the example of a fungicide application, as this involves the most extended pathway. Insecticide (and herbicide) applications, on the other hand, would not cover all the steps presented in the scheme in Table 4.[44] Given that the use of zeolites will only influence the spraying, it is expected that they will have an impact on steps 1 to 6 of the application process.

Formulation and dispersion stability of the active ingredient(s) in the spray solution (steps 1, 2 and 3). As many active ingredients are hydrophobic and consequently do not easily dissolve in water, pesticide formulations usually contain some specific adjuvants (e.g. dispersion agents) in order to obtain a spray mix suitable for tank mixing.[45] Surfactant impregnation is also commonly employed in order to change the hydrophilic/hydrophobic properties of zeolites.[14]

Spray droplet formation and aerial transport to the target (step 4). Physical properties of the spray liquid, such as viscosity, density, temperature, etc., may affect the droplet size distribution of a spray. The droplet size distribution during atomisation is very important because it affects (1) the biological activity and (2) the spray drift (droplets that are too small are prone to drift away to adjacent fields and non-target areas).[46,47] The optimum droplet size depends on the content of the droplet, the amount of active ingredient in the droplet and the type of application, i.e. as an insecticide, a herbicide, a fertiliser, etc.[48] Studies of Skuterud *et al.*[49] showed that, when applying contact products such as zeolites, it is important to use fine (60 μm) or mediate (60–200 μm) droplets.

Spray deposition: wetting and spreading properties on treated leaf surfaces (step 5). Droplet velocity is known to be a factor affecting impaction; it determines whether a drop is being either retained or reflected. Deposition of droplets on crop canopies is a very complex subject. Generally, the epicuticular wax on a leaf acts as a substantial barrier to wetting.[50] Water alone tends to bead up and roll off the leaf, which can make spray applications ineffective. Because surfactants have the ability to reduce the surface tension of water and to induce a surface tension gradient, they enable spray solutions to wet waxy leaf surfaces more effectively, thereby increasing the amount of spray retained on the leaf. Enhancing droplet spread increases its potential coverage and can result in an increased biological activity.[45] The final coverage is also affected by the spray type. High volume applications can result in product run-off, which leads to considerable losses. On the other hand, low-volume spraying leads to very poor coverage of the leaf surface and results in insufficient biological activity and hence loss of efficacy.[51,52] Adding an appropriate surfactant will reduce the contact angle and enhance the degree of leaf coverage, which will improve crop protection.[50] In general, a good coverage becomes very important when using non-systemic products, such as zeolites.[48] This is because only the parts of the leaf surface covered with the product have a toxic effect. New growth is also unprotected growth, which makes it necessary to reapply the zeolite formulation.[43]

Physical form and adhesion properties of the leaf deposits (step 6). Increased spreading will tend to decrease the dose of active ingredient needed per unit area. According to their concentration and composition, adding adjuvants produces either solid, gel or liquid deposits. Once the droplets on the leaf surface are dry, it is important that the physical form of the deposit is such that the

Table 4. Different steps in the pathway of a fungicidal spray solution from spray nozzle to the aerial part of the plants[44]

1. Active ingredient		
⇓	+ surfactant (emulsifier, ...)	
2. Formulation		
⇓	dispersing agent	
3. Spray solution		
⇓	dynamic surface tension viscosity	
4. Spray droplet formation with transport to target		
⇓	wetting & adhesion, spreading properties, retention or reflection	
5. Impaction and contact on leaf surface		
⇓	sticking properties, rain fastness, evaporation, physical form of deposit, humefactant effects, UV-protection	
6. Formation of deposit		**TOTAL FUNGICIDAL EFFECT**
⇓	transcuticular penetration, stomatal infiltration	
7. Penetration into the leaf	⇒ ⇒ ⇒ ⇒	⇘
⇓	*systemic activity*, translocal activity	***contact activity*** ⇓
8. Translocation in the plant		
⇓	membrane penetration	⇓
9. Penetration into fungal cell	⇐ ⇐ ⇐ ⇐	⇙
⇓	hydrophilic-lipophilic properties	
10. Transport and complexation with site of action		
⇓	reaction with site of action	
11. Fungicidal activity		

active ingredient is (1) uniformly distributed on the leaf and (2) has become rainfast. This phase is greatly affected by the leaf's epicuticular waxy layer, cuticle age and composition, the environmental conditions and the variability in plant species.[53] Areas of low rainfall are most adaptable to this technology, because the applied zeolite, just like kaolin, will eventually get washed off all crops by rain. This will lead to a situation where the plant is unprotected again and the zeolite formulation will have to be reapplied, which causes an increase in costs.[43]

Penetration into and translocation in the leaf (steps 7 and 8). Plant uptake is also affected by the leaf and fruit surface wax, cuticle age and composition and species variability. Transport of the active ingredient through the plant cuticle is determined by three processes: (1) absorption into the cuticle, (2) diffusion through the cuticle and finally (3) desorption from the cuticle.[47] Translocation is the transport of the agrochemical from the initial absorption site to other parts of the plant and can occur either via the phloem or via the xylem or both.[54] However, these steps are mainly of importance when using systemic products, which have some additional barriers to overcome before they reach the pest or the disease. This is not the case when zeolites are used, as contact products will not penetrate into the plant and will not be transported.[48]

Penetration and transport in the fungal cell (steps 9 to 11). Only certain steps mentioned in Table 4 apply to foliar treatments with current pesticide formulations, and some of them are very specific. For fungicides, extra important steps are involved in the process that can influence the final activity dramatically. These extra steps will include possible phytotoxic side effects, specific demands for fungal cell penetration and a range of other interactions that may interfere with these steps, such as the behaviour of infected plants to a treatment, the effect on resistance development of the fungus, the treatment type and the location of the biochemical site of action in the fungal organism.[55,56] The fungus is not actively controlled by the zeolite formulation, because contact products cannot penetrate into the fungal organism. Nevertheless, zeolites can have a reducing effect on spore germination (see Section 2.4.2).[23,25]

2.4 Effects of zeolites that occur after application

Various coating polymers are used to reduce water losses, protect plant surfaces against invading microorganisms and prevent the development of certain plant diseases. These coating polymers used as protective barriers are non-phytotoxic, permeable to gases and resistant to changing environmental conditions and penetration of solar irradiation.[57] The following sections describe whether these effects are also valid when zeolites are used as particle films on plants.

2.4.1 Effects of zeolites on the plant

Photosynthesis enhancement by zeolites on crops. Zeolites are able to adsorb carbon dioxide (CO_2) molecules and release them slowly into the environment.[58,59] When zeolites are spread on plant leaves, they may (this is not yet proven) increase the amount of CO_2 near the stomata, which could induce a higher photosynthesis rate for plants using both C_3 and C_4 carbon fixation. In particular, C_3 plants, such as apple, orange, tomato, grape, etc., take advantage of this increase.[60,61] A higher concentration of CO_2 by applying zeolites may increase the velocity of carboxylation by competitively inhibiting the oxygenation reaction, increasing the efficiency of net carbon CO_2 uptake by decreasing photorespiratory CO_2 loss.[62] Because of the increased CO_2 concentration, the efficiency of light usage increases in net CO_2 uptake, which results in increased growth and an increased rate of production of leaf area. Furthermore, the water usage decreases because of a lower transpiration rate, which further accelerates leaf development (Fig. 5).[62] In the literature, conflicting data have been observed on this subject using kaolin. Grange *et al.*[63] found a reduction in photosynthetic rates of individual leaves owing to a reduction in light because of a 20–40% increase in reflection and decreased absorption. Wünsche *et al.*[64] observed that, in spite of a reduction in photosynthetic rates of individual leaves, there was no decrease in canopy photosynthesis. Glenn *et al.*[65] noted an increase in canopy photosynthesis. Rosati *et al.*[66] conducted a study on this and demonstrated that kaolin application does reduce photosynthesis of individual leaves, but increases the canopy photosynthesis, which explains the increased yield.

Heat stress and sunburn of zeolites on crops. It is known that the affinity of Rubisco (the enzyme responsible for carbon fixation in plants) for CO_2 and the solubility of CO_2 relative to O_2 both decrease with rising temperature. Therefore, the relative ratio of carboxylation to oxygenation is reduced when the temperature increases.[61] By coating the plants with zeolite, the plant leaf temperature can potentially be diminished, caused by increasing

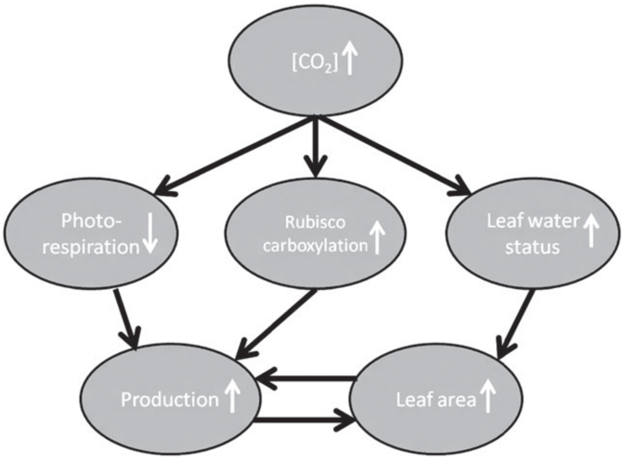

Figure 5. Overview of the direct effects of increasing the CO_2 concentration on C3 plant production.[62]

leaf reflectiveness (whiteness) of infrared radiation. Similar experiments are already executed with kaolin. Tests indicate a higher leaf carbon assimilation rate and a reduced canopy temperature in grapefruit and apples.[24,65,67] That explains why this product is labelled for reduction of heat stress and sunburn on several crops.[4] Kaolin cools tissues and protects plants from extreme heat and ultraviolet radiation by increasing leaf reflectance and reducing transpiration rate.[68] Experiments with kaolin demonstrated that leaf temperature increases linearly with increasing light intensity. This effect was observed with and without the use of a coating, but the leaf temperature was significantly lower ($P < 0.001$) after application of the coating. Abou-Khaled *et al.*[69] have determined that leaves of dwarf orange trees (*Citrus sinensis* cv. Valencia), rubber plants (*Ficus elastica*) and kidney bean plants (*Phaseolus vulgaris*) are cooled approximately 4 °C by the reflecting material (Fig. 6).[69] This effect contrasts with the tendency of antitranspirants to raise leaf temperatures. The lowered temperature results in a 25% reduction in transpiration, which improves water-use efficiency. Subsequently, this effect also has a positive influence on yield and fruit quality. Heat stress is recognised as the main cause of the reduction in tomato yield and fruit quality worldwide. Cantore *et al.*[70] have illustrated that applying kaolin to tomato plants increases the marketable yield by as much as 21% owing to a 96% reduction in sunburned fruit, a 79% reduction in fruit damaged by tomato fruit worm and a 9% increase in fruit mean weight.

Water sorption capacity of zeolites. In addition to the reduction in heat stress, zeolites may also be used to reduce water stress. The adsorption selectivity of zeolites for water (H_2O) is greater than any other molecule.[28] This is shown by an adsorption capacity that may reach up to 30% by weight of the zeolite without any volume modification.[71] These polymers form a film over the stomata, increasing resistance to water vapour loss.[72] By absorbing condensing water and eliminating free water on the plant surface, zeolites will serve as a physical barrier to liquid water. This barrier will prevent the formation of the liquid film of water that is required by many fungal and bacterial pathogens for disease propagule germination.[28] The water sorption behaviour of a sorbent depends on many factors, such as the structure and the chemical composition of the material, the presence of charged species, the type of framework structure and the hydration level. The key physical property of every adsorbent is the surface hydrophobicity.[73]

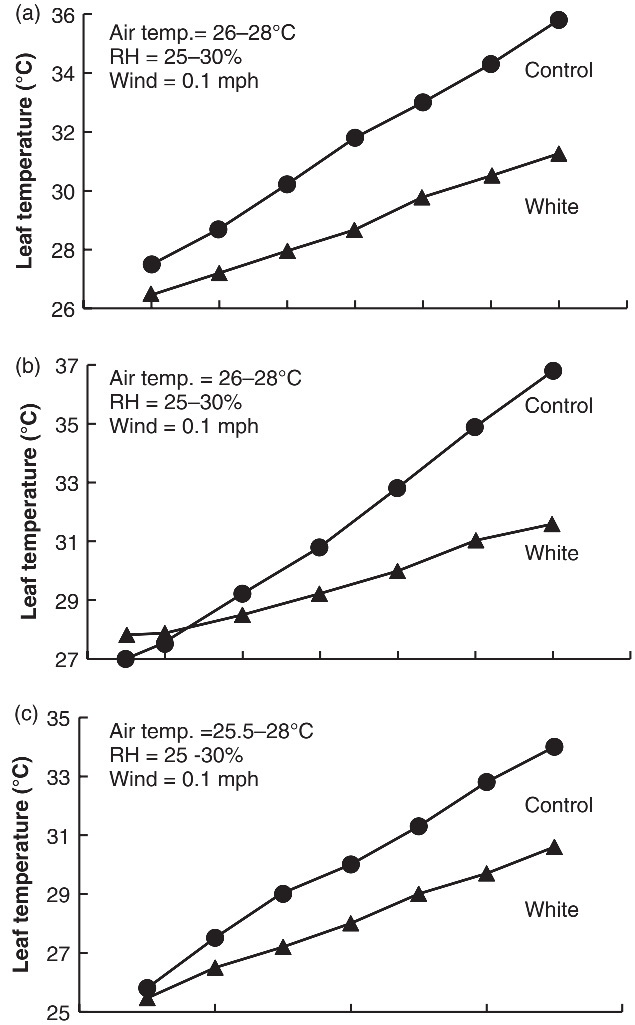

Figure 6. Effect of white reflecting material on the temperature of (a) orange leaves (*Citrus sinensis* cv. Valencia), (b) rubber plant leaves (*Ficus elastica*) and (c) bean leaves (*Phaseolus vulgaris*).[69]

The hydrophobicity of zeolitic adsorbents can be varied by changing the silicon to aluminium ratio. In general, zeolites are highly hydrophilic sorbents owing to their electrostatic charged framework and the abundance of extra-framework cations. Almost all of the zeolites (especially the high-aluminium zeolites) show type I water sorption isotherms (Fig. 7), which indicate a high affinity for water at a low partial pressure.[74] The water sorption capacity generally is also proportional to the size of the pores, because of the highly polar surface within the pores. That is why aluminosilicate zeolites with larger pores have a higher capacity for water. Zeolites can be placed according to pore size into the following categories: extra-large-pore zeolites ($\theta \geq 9$ Å), large-pore zeolites (6 Å $< \theta <$ 9 Å), medium-pore zeolites (5 Å $< \theta <$ 6 Å) and small-pore zeolites (3 Å $< \theta <$ 5 Å), depending on the access to the inner part using 8-, 10- or 12-atom oxygen rings respectively.[75]

2.4.2 *Effects of zeolites on pathogen/insect behaviour*

Fungicide properties of zeolites. Film-coating polymers have been reported to provide additional protection against various foliar pathogens.[57] Aluminium-rich zeolites are often used as desiccants. This is due to their high concentration of hydrophilic active sites, which can enhance the water sorption capacity and

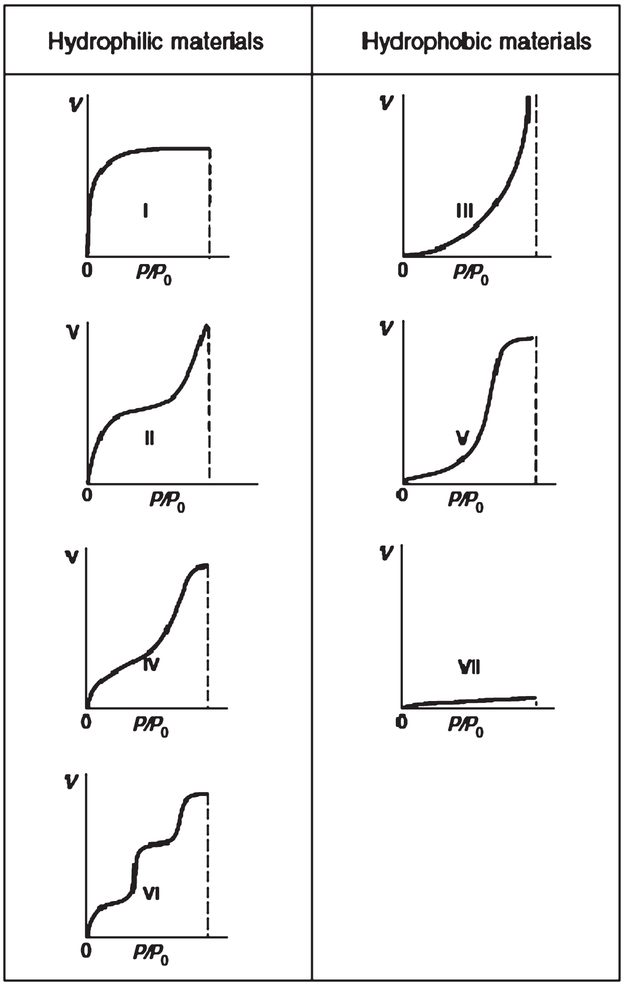

Figure 7. Adsorption isotherms classified according to IUPAC: type I – very hydrophilic material; type II – hydrophilic material; type III – hydrophobic/low-hydrophilic material with weak sorbent–water interactions; type IV – hydrophilic material; type V – hydrophobic/low-hydrophilic material with weak sorbent–water interactions; type VI – hydrophilic material with multiple sorbent–water interactions and stepwise sorption; type VII – very hydrophobic material.[74]

hydrophilicity.[74] Their high affinity for water is another potential advantage of zeolites over kaolin. Just like kaolin, the zeolite coating creates a barrier that prevents disease inoculums from directly contacting the leaf surface (Fig. 8). Each type of microbial organism (bacterium, yeast or fungus) needs water to grow and to develop. The availability, rather than the amount, of moisture is an impediment (such as the pH or the temperature) to avoiding or promoting its development.[76] Scott[77,78] showed that microorganisms have a limiting water activity level below which they will not grow. The water activity, and not the water content, determines the lower limit of available water for microbial growth. Percival and Boyle[79] showed that, just like kaolin, zeolites could provide protection against apple scab (*Venturia inaequalis*) by preventing a liquid film. By absorbing condensing water, the zeolites prevent the formation of the liquid film of water that is required for many fungal and bacterial pathogens for disease propagule germination.[23,25]

Insecticide properties of zeolites. Besides their function as desiccants against microbial organisms,[80] zeolites are also effective against insects.[25] They can partially remove the insect's outer cuticle (epicuticule) through abrasion by hard non-sorptive particles or disrupt the epicuticle by adsorption of epicuticular lipids to sorptive particles. Both processes induce rapid water loss from the insect's body and cause death by desiccation. Consequently, there is an inverse relationship between insect mortality and relative humidity.[23] Tests done with kaolin clay particles showed that pest insects, including psyllids, aphids, fruit flies and thrips, have a lower oviposition rate.[23,81–84] The results also showed that the hatch rate of eggs covered with the particle film decreases, larval development is interrupted and mortality is higher for leaves on which the pest insects are exposed to the particle film. The particles also attach to the insect's body, inducing a tactile deterrence that can lead to disruption of the insect's behaviour to such a degree that it is unable to feed and eventually starves.[23] Moreover, the layer of particle film covering the leaves and fruit reduces the attractiveness of visual cues and prevents insects from recognising and finding plant parts on which they lay eggs.[84] However, particle films also induce negative effects, as some pest insects are able to thrive on leaves sprayed with particle films, while the presence of natural enemies is reduced. Marko *et al.*[85] illustrated that, while a kaolin-based particle film application reduces many insect pests on apple trees, including the codling moth (*Cydia pomonella*), the apple sawfly (*Hoplocampa testudinea*) and several weevils, leafhoppers and scales, the infestation levels of other pest insects increase. Leaves covered with kaolin promote a severe infestation of the woolly apple aphid (*Eriosoma lanigerum*) and reduce the abundance of polyphagous predators and parasitoids. Also it was noted that some weeks after the treatment the number of predaceous coleopterans was low.

2.4.3 *Effects of zeolites on the soil*

Soil water retention of zeolites. When zeolite is lost during application or washed off the leaves by rainfall, it can still have a positive effect on the soil composition. When water is supplied adequately, plants are prodigal in their water usage because only roughly 5% of water uptake is used for their growth and development, while the remaining 95% is lost on transpiration.[86] Actively growing plants transpire each hour a weight of water equal to their fresh leaf weight in arid and semi-arid regions. This makes it necessary to find ways to use the available water economically.[87] Zeolites form a permanent water reservoir and provide prolonged moisture in dry periods, which helps plants to withstand drought. Amendment of sand with zeolite increases available water to the plants by 50%.[16]

Cation exchange capacity of zeolites. Zeolites are also one of the most efficient cationic exchangers. Their cationic interchange capacity is 2–3 times greater than other types of mineral found in soils.[88] That is why zeolites are widely used as slow-release fertilisers that increase nutrient retention capacity. Because zeolites are not acidic but marginally alkaline, their use with fertilisers may also help to increase (buffer) soil pH levels.[89] Zeolites in soils exchange sodium (Na^+) and potassium (K^+) cations for ammonium (NH_4^+).[90] Ammonium and potassium charged zeolites have shown their ability to increase the solubilisation of phosphate (PO_4^{3-}) and the capture of nitrate (NO_3^-). In addition, the inclusion of negatively charged nitrate ions promotes the uptake of positively charged nutrient ions, such as magnesium, calcium and potassium. All of this simultaneously contributes to a reduction in contamination, a reduction in the amount of fertiliser to be applied and an improvement in crop yield.[16,88] A number of examples of zeolites used as fertilisers were given by Mumpton.[21] By using clinoptilolite-rich tuff as a soil conditioner, significant increases in the yields of wheat (13–15%), eggplant (19–55%), apples (13–38%) and carrots (63%) were reported when 1.6–3.2 t zeolite ha^{-1} was used. The addition of NH_4^+-exchanged clinoptilolite in greenhouse experiments resulted in 59 and 53% increases in root weight of radishes in medium- and light-clay soils respectively.

2.5 Carrier effect of zeolites

One of the major concerns in the use of organic compounds, such as herbicides, fungicides and pesticides, in agronomy and horticulture is their leaching into groundwater. As most of these organic compounds are too large to enter the zeolite framework, the high adsorption capacity of zeolites makes it possible to control the rate of diffusion of molecules in and out of the micropores and thus control the release of adsorbed active ingredients.[91] The use of controlled-release formulations can, in many cases, supply the active ingredients at the required rate, thus on the one hand reducing the amount of chemicals needed for pest control and on the other hand decreasing the risk to the environment. Controlled release of pesticides and other organic agrochemicals can, in many cases, permit safer, more efficient and at the same time more economical crop protection.[92]

2.5.1 Pesticide carrier effect of zeolites

Sopkova and Janokova[93] were able to enclose the solid form of the synthetic pyrethroid insecticide supercypermetrine in the natural zeolite clinoptilolite. They used an experimental set-up to indicate the enclosure and stabilisation of the insecticide in the mineral. The pyrethroid was gradually released from the zeolite, demonstrating that the mineral can be used as a reservoir for the insecticide for a longer time. Moreover, the insecticide was better protected against photolysis and early release, which ensured better protection of the environment against an excess of the chemical.

The external surface activity of zeolites can be modified in such way that minerals can be exploited as carriers of different products, including herbicides, fungicides, insecticides and growth regulators.[91] Zhang *et al.*[94] modified the surface of zeolite Y by silylation with 1,1,3,3-tetramethyldisilazane (TMDS). This modification narrowed the pores of the zeolite after the mineral had been loaded with the herbicide paraquat because of ion exchange. Slow release of paraquat in TMDS-modified zeolite Y is obtained by slower diffusion of paraquat through the blocked 'windows' at the zeolite–surface interface, while the pore interior is not modified. This surface alteration is an ideal solution for modifying zeolites to carry products that benefit from slow release.

2.5.2 Semiochemical/plant extract carrier effect of zeolites

Semiochemicals can be defined as chemicals emitted by living organisms (plants, insects, etc.) that induce a behavioural or a physiological response in other individuals. These compounds can be classified into two groups according to whether they act as intraspecific (pheromones) or interspecific (allelochemicals) mediators (see Fig. 9).[95]

Munoz-Pallares *et al.*[96] examined zeolites with different pore diameters for use as dispensers for pheromones. They showed that zeolites are able to decrease initial pheromone emission rates and thus significantly reduce pheromone losses. Zeolites are also used for the controlled emission of semiochemicals in order to contribute to environmental management of agricultural pests and diseases. These active ingredients can play a major role, as they induce interference of the insect's perception: the behaviour of insects towards the plant (depending on the range of colours, odours and textures they can perceive) and the behaviour of insects towards each other (depending on sex pheromones).[95]

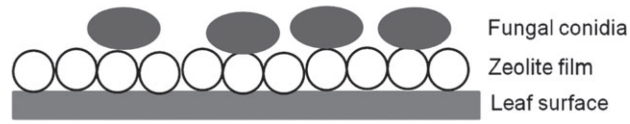

Figure 8. Schematic overview of a zeolite film creating a barrier against fungal germlings.

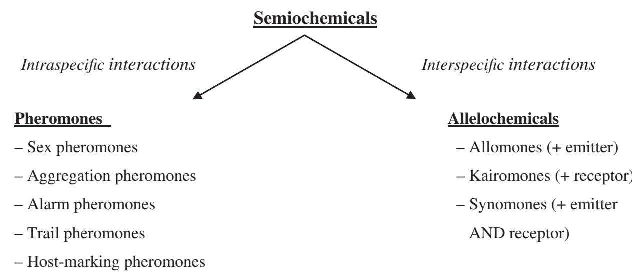

Figure 9. Semiochemicals.[95]

Kvachantiradze *et al.*[97] demonstrated that the natural zeolite clinoptilolite can be used to photostabilise *Bacillus thuringiensis*, a bioinsecticide. Several strains of this environmentally safe entomopathogenic bacterium produce endotoxins that are highly specific against certain insect pests. The main drawback using this pesticide is that its biological activity decreases during exposure to solar irradiation.[98] Kvachantiradze *et al.*[97] and Colella[91] mixed *B. thuringiensis* with the zeolite, demonstrating that the presence of the zeolite can extend the photostability of the complex by deflecting sunlight and allowing a gradual desorption of the endotoxin by this aluminosilicate mineral (Fig. 10).[97]

2.5.3 Microbiological carrier effect of zeolites

In the literature, bacteria, yeasts and fungi are described as promising candidates for development as biopesticide.[99,100] In the past, these microorganisms were mainly characterised as planktonic, free-living cells. However, in nature, most microorganisms are found in association with each other or with solid surfaces and form multicellular aggregates called biofilms.[101,102]

Biofilm formation may facilitate the use of microorganisms as biopesticide. The biofilm serves as support for the formation and functioning of consortia, as it allows stable cell–cell contact. This is necessary because of the high metabolic fluxes between the cells that occur in synergistic interactions.[29] In addition, the biofilm matrix provides additional protection against environmental stress.[103,104] Finally, surfaces and biofilms can also serve as sites for the transfer of genetic material.[105]

In principle, two methods for spore production can be distinguished, i.e. liquid-state fermentation (LSF) and solid-state fermentation (SSF).[106] SSF, defined as the growth of microorganisms on (moist) solid material in the absence or near-absence of free water, is generally the preferred production method, as most fungi sporulate well on solid substrates. In addition, SSF produces biocontrol agents of better quality than liquid fermentation.[107]

Among several other factors that are important for microbial growth and activity in a particular substrate, particle size and moisture level/water activity are the most critical. Generally, smaller

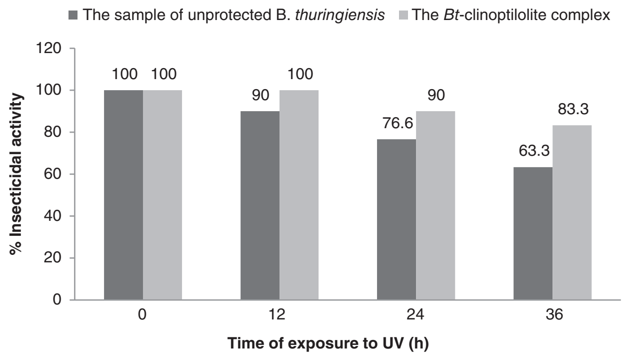

Figure 10. Insecticidal activity of unprotected *B. thuringiensis* affected by solar irradiation and of the *B. thuringiensis*–zeolite complex.[97]

substrate particles would provide a larger surface area for microbial attack and should therefore be considered as a desirable factor. However, excessively small substrate particles may result in substrate agglomeration, which may interfere with microbial respiration/aeration, and may result in poor cellular growth. At the same time, larger particles provide a better respiration/aeration efficiency (owing to increased interparticle space) but provide a limited surface for microbial attack.[107,108]

Zeolite particles represent suitable mineral microhabitats and good carriers for immobilisation of microorganisms.[109–111] SEM micrographs of a zeolite carrier for yeast cells are shown in Fig. 11.[109]

Another example is the use of zeolites as carriers for fungal colonisation. The use of fungal biological control agents to control plant pathogens has been investigated for more than 70 years; however, research in this area has increased dramatically only in the past 20 years. Over 40 biological control products have been introduced into the market within the past 10 years, but these are used on a very small scale as compared with chemical fungicides.[112]

3 RISK OF TOXICITY DUE TO THE COATING

3.1 Plant toxicity

Coating plants with particle films is in general not phytotoxic.[25,113] This particle film can act as an extra barrier against pathogen infections. The coating can also work well as a disguise for both the cues necessary for the development of fungal germlings, as well as for insect pests.

However, a possible disadvantage for plants may be that zeolites used for coating of plants may be washed off by rain showers.[83,114] The Na form of some zeolites in the soil may inhibit growth of some plant species. The zeolitic ion exchange ability and selectivity for certain microelements can result in negative effects for plants, by adsorption of essential trace elements such as manganese, zinc, copper, iron and boron from the soil. Even some of the macroelements, such as potassium or mineral nitrogen (as the ammonium ion), can be made unavailable for plant uptake by counteracting selective uptake on zeolite exchange sites.[91,109]

3.2 Environmental toxicity

Environmental risk assessments performed on zeolite A, a zeolite made from the natural source kaolin, together with the knowledge that zeolites degrade into natural products over time, indicate that the use of zeolites does not pose a risk to the environment.[115,116] Moreover, natural zeolites have the ability to remove soil pollutants and to interact with organic fertilisers (manure) for a modulated transfer of nutrient matter to the soil. Also, the exchangeable cations in zeolites can exert beneficial effects on soil structure stability. Zeolites are able to form aggregate compounds with humic acids, which give stability to the soil structure by avoiding loss by leaching. These humic acid–zeolite aggregates are useful for the reconstruction or remediation of depleted soils.[91]

On the other hand, the Na form of zeolite A exhibited a growth inhibition effect towards the most sensitive plant species, *Raphanus sativus*, at test concentrations higher than 900 mg kg^{-1}. In fact, zeolites are considerably less toxic when charged with Ca^{2+}, as toxicity tests showed a lower toxicity by a factor of 67 compared with the Na form.[115] Therefore, it may be a consideration to exchange the native Na^+ ions with Ca^{2+} ions, but taking into account that, when the Na form of zeolite becomes dispersed in water before application, part of the Na^+ will be exchanged by the soluble Ca^{2+} present in the dispersant (on account of the water hardness).[117]

3.3 Human toxicity

The use of zeolites as feed supplements for animals and their medical applications, as previously stated, indicates that zeolites are not harmful to humans.[15] Material Safety Data Sheets from zeolite products also consider zeolites to be safe.[118] The health hazard induced by prolonged and repeated contact of the zeolite powder and watery suspensions with the human skin of the operators is merely some local irritation, i.e. slight to moderate eye irritation. The raw material may reach the lungs through inhalation and has been shown to induce inflammatory reactions in the lung, alveolar and bronchial tissues. Zeolites are also tested for their carcinogenic effects.[115] Studies on rats, in this case using clinoptilolite, showed no significant increase in incidence of tumours.[119]

In Europe, zeolite is approved as an anticaking and anticoagulant feed additive (Directive 70/524/EC) for all species or categories of animals, for all feeding stuffs. Synthetic sodium aluminium silicate is also used as a food additive (E 554).[120] In the United States, according to the United States Food and Drug Administration (FDA), zeolite A is also approved for use as a food additive. The FDA's GRAS (Generally Recognised As Safe) status is also awarded to pure clinoptilolite (potassium-calcium-sodium-aluminosilicate) zeolite products.[121]

4 CONCLUSION

Once applied on the plant, the zeolite-based product forms a coating that fulfils many functions. The coating will have a double effect regarding water consumption. It may reduce regular evapotranspiration and it may increase photosynthetic efficiency. Particles of zeolite may also protect the surface of the plant from solar UVB/UVC radiation and reduce the superficial temperature. This reduces the risk of 'sunburn' injury (and subsequent crop losses), which also increases CO_2 solubility and RuBisCO yield. All these properties result in an increase in crop yield.

Besides their effects on the plant, these zeolites can also control pests and fungal diseases. The ability of the zeolite to adsorb water molecules from the plant's surface (drying effect) may create a hostile environment for fungi, larvae and eggs, as the coating acts as a desiccant as soon as condensation takes place. On the other hand, active ingredients will endow the coating with persistent effects against pests. In addition, the coating may protect the plant from adult insects and other phytophagous arthropods, as

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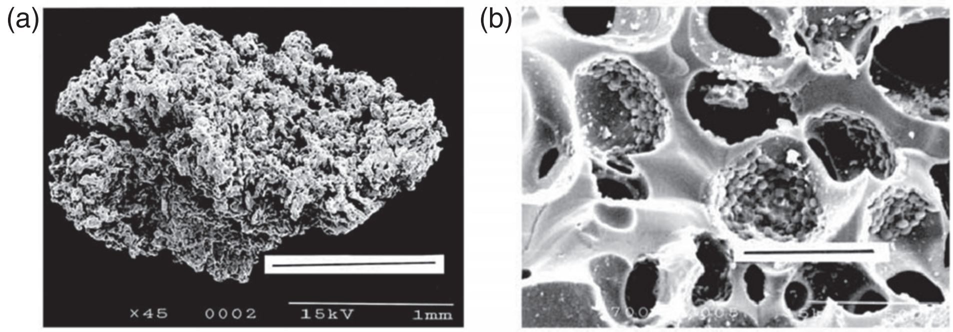

Figure 11. Scanning electron micrograph of (a) a natural zeolite carrier and (b) the same carrier with immobilised yeast cells.[109]

the colouring and microscopic texture of the plant's surface are altered.

Finally, when pesticides are released into the environment, most of their quantity is lost before even reaching the intended target. These pesticides can cause harm to human health and the environment. The high adsorption capacity of zeolites for other molecules besides water makes it possible to use them for controlled release. When zeolites are used as a carrier for pesticides, semiochemicals, plant extracts and microorganisms, this slow-release effect ensures a reduced need for these active substances. Whether or not they are combined with active substances, the use of zeolites for crop protection will reduce the amount of used pesticides, insecticides, etc. This will lead to safer, more efficient and more economical crop protection. In addition to the fact that in this manner zeolites are less harmful to the environment, zeolites are also innocuous substances in terms of human impact and toxicity.

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