Review

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Applications of natural zeolites on agriculture and food production

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Abstract

Zeolites are crystalline hydrated aluminosilicates with remarkable physical and chemical properties, which include losing and receiving water in a reverse way, adsorbing molecules that act as molecular sieves, and replacing their constituent cations without structural change. The commercial production of natural zeolites has accelerated during the last 50 years. The Structure Commission of the International Zeolite Association recorded more than 200 zeolites, which currently include more than 40 naturally occurring zeolites. Recent findings have supported their role in stored-pest management as inert dust applications, pesticide and fertilizer carriers, soil amendments, animal feed additives, mycotoxin binders and food packaging materials. There are many advantages of inert dust application, including low cost, non-neurotoxic action, low mammalian toxicity and safety for human consumption. The latest consumer trends and government protocols have shifted toward organic origin materials to replace synthetic chemical products. In the present review, we summarize most of the main uses of zeolites in food and agruculture, along with the with specific paradigms that illustrate their important role.

Keywords: zeolites; food production; mycotoxin control; stored-pest management

INTRODUCTION

Natural zeolites are referred to as 'the magic rock' by researchers and mineralogists[1] as a result of their widespread application, including their use as soil enhancers in agronomy, dietary supplements in animal diets, insecticide and pesticides in plant protection, and hydroponic (zeoponic) substrates for growing plants on space missions, extending even to their successful use with respect to healing cuts and wounds, as well as acting as anticarcinogenic compounds. Similar to other clay minerals, zeolite minerals have attractive physical and chemical properties that enable them to play a critical role as dust applications against stored product pests in integrated pest management (IPM) protocols and organic agriculture. Their adsorption capacity, cation-exchange, dehydration-rehydration and catalysis features establish their direct use in chemistry, biotechnology, environmental pollution control, and pesticide and medical industry.[1] Zeolites have been utilized as a corrector of soil acidity, as a donor of macro and microelements, as a source for the preservation of the quality and germinability of seeds, as carriers of active substances of pesticides, as biologically active substances, as reaction filters, and as filtered and rheological additives.[2] In this way, they contribute to agricultural productivity and directly affect the quality of food products.

Zeolites are crystalline hydrated aluminasilicates of alkali and alkaline earth cations. Zeolites have an infinite and three-dimensional structure identified by interconnected cavities or cages. They are classified as 'molecular sieves' as a result of their structure and the fact that zeolites are members of the family of microporous solids.[3] To date, 232 zeolites have been described, which include more than 40 zeolites, as classified by the Structure Commission of the International Zeolite Association.[4] The common zeolite types are referred to be clinoptilolite, analcime, chabazite, laumontite, mordenite and philipsite.[5] Moreover, in 2015, the European Patent Office declared almost 47 000 patents in a worldwide database including or related to zeolites.[6]

Here, we review the most important properties of natural zeolites regarding their use in agriculture, as well as their current uses and potentials in different areas, with the intent of increasing the involvement of scientists with varied backgrounds in future studies of zeolite applications.

Zeolites have a broad variety of commercial uses cited by various sources:[7]

- Agriculture: odor control, storage pest management, environmental control, livestock feed additives, fertilizer and soil management, mycotoxin control.
- Horticulture: nurseries, greenhouses, grass soil amendment,[8] reclamation, revegetation, medium for hydroponic growing.
- Household products: household-pet odor control.
- Industrial products: absorbents for oil and spills, catalysis (shape selective, acid catalyst, environmental catalyst), ion exchange

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Table 1. Estimated world mine production by US Geological Survey, Mineral Commodity Summaries (Virta 2010, 2014)

	Annual production			
Countries	2009	2010	2012	2013
China[a]	2 000 000	2 000 000	2 000 000	2 000 000
United States	59 500	59 000	74 000	75 000
Jordan	425 000	140 000	15 000	13 000
Korea, Republic of	165 000	210 000	230 000	230 000
Turkey	100 000	100 000	150 000	50 000
Other countries[a]	5500	5500	350 000	350 000
Japan	155 000	150 000	–	–
Slovakia	90 000	85 000	–	–
World total (rounded)	3 000 000	2 750 000	2 800 000	2 700 000

Estimates are for countries that do not report production represent a range with possibly 15–20% variability, rather than an absolute value. [a] Includes materials appropriate for pozzolan applications.

(water softeners in powdered laundry detergents), Adsorption (drying purification, separation, removal of volatile organics from air streams).

- Environmental applications: radioactive waste site remediation and decontamination, radionuclide applications,[9] water and soil and wastewater treatment (water filtration, heavy metal removal, ammonia removal in municipal sludge/wastewater, septic leach fields).
- Aquaculture: ammonia filtration in fish hatcheries, biofilter media.
- Medical uses: healing of wounds, studies for use against cancer.

Although there was no certainty about the gross quantity of zeolites in the world, all continents report varying zeolite mineral contents and reserves.[10] The world production of zeolites is estimated as approximately 4×10^6 metric tons (Mt).[11] United States Geological Survey (USGS) annual data released similar worldwide production estimates that placed zeolite production at 4 million tons per year, with China producing and using approximately 2.5 million tons primarily as a low-grade additive to pozzolan cement, whereas US consumption is approximately 0.5 million tons.[12,13] Currently, the primary industrial use of zeolites is as a petrochemical catalyst, with detergent builder being the second most important use. Yet, commercial applications with zeolites have gradually increased with respect to other uses, such as in the filter industry.

Estimated world mine production by the US Geological Survey, Mineral Commodity Summaries, is shown in Table 1.[12,13]

CHARACTERISTICS OF ZEOLITES

Zeolites are extensively used for agricultural uses, especially after their classification as 'non-toxic' by International Agency for Research on Cancer (IARC)[14,15] and 'safe for human consumption' by the Food and Drug Administration (FDA).[16] Furthermore, the Codex Alimentarius Commission[17] acknowledged pest control agents in food commodities and listed zeolite as an approved substance in organic food production and plant protection. The European Food Safety Authority (EFSA) Panel on Food Contact Materials, Enzymes, Flavorings and Processing Aids (CEF) approved zeolites (clinoptilolite type) as one of the safe substances in food and feed additives.[18] Moreover, the EFSA Panel of Additives and Products or Substances used in Animal Feed (FEEDAP) declared that the use of zeolite additives in feed was safe for all animal species and does not pose a risk to the environment.[19] The use of clinoptilolite as a mycotoxin binder and also as an anti-caking agent and coagulant has been recognized and suggested by the Europea Union for use in swine, rabbit and poultry breeding (Directive 70/524/EEC, Commission Regulation No. 1245/1999 of 16 June 1999). The FDA, in contrast, allowed the use of zeolite in animal feeds only as an anti-caking agent (CFR 582–2727).[4] According to US Government Printing Office, if used in accordance with good agricultural practices, zeolite minerals noted under the heading of 'hydrated silica, silicon dioxide, fumed, amorphous' are exempted from tolerance as solid diluents or as a carrier to encapsulate chemicals such as pesticide or herbicides. Almost all zeolite types, especially those with current widerange uses, are regarded as safe and they are currently being marketed as a health food, with references to their medicinal use dating back thousands of years.[20] However, one zeolite type, erionite, is considered as a carcinogen because of its fibrous nature and high iron content, mostly based on long-term studies in the Cappadocia region of Turkey and studies in North Dakota and Oregon in the USA, as well as Mexico.[21–23] Because of inhalation toxicity and airborne zeolite dust in these areas, it has been associated with the incidence of mesothelioma, and workers may have potential for exposure to erionite-related lung disease, such as parenchymal and pleural fibrosis.[24]

PHYSICAL AND CHEMICAL PROPERTIES

Hydrated aluminosilicates of group I and group II (natural or synthesized), which contain high concentrations of sodium, potassium, magnesium, calcium, strontium and barium, form the zeolite family. The fundamental building unit for natural zeolites is the tetrahedron and the secondary building units are the geometric arrangements of tetrahedra of SiO_4 and AlO_4. The zeolites are 'framework' aluminosilicates structurally based on a three-dimensional anionic network of SiO_4 and AlO_4 tetrahedra linked to each other by sharing all the oxygen.[25] This situation of no unshared oxygen in the frameworks means that, in all tectosilicates such as zeolites, the Al and Si ratio is: $(Al + Si)/O = 1/2$.[5] Zeolites display large external surfaces that are negatively charged by hydrated inorganic cations, leading to interactions with other cations or polar molecules.[4] The external surface area, which is an indirect measure of the external adsorption capacity, and the external cation exchange capacity are important characteristics for evaluating zeolites.[4]

Table 2. Characteristic formulae and premium physical properties of important zeolites (Mumpton[1])

Zeolite	Representative unit-cell formulae	Void volume (%)	Channel dimensions (Å)[a]	Thermal stability (relative)	Cation exchange capacity (meq g^{-2})
Analcime	$Na_{10}(Al_{16}Si_{32}O_{96}).16H_2O$	18	2.6	High	4.54
Chabazite	$(Na_2Ca)_6(Al_{12}Si_{24}O_{72}).40H_2O$	47	3.7 × 4.2	High	3.84
Clinoptilolite	$(Na_3K_3)(Al_6Si_{30}O_{72}).24H_2O$	34	3.9 × 5.4	High	2.16
Faujasite	$(Na_{58})(Al_{58}Si_{134}O_{384}).240H_2O$	47	7.4	High	3.39
Ferrierite	$(Na_2Mg_2)(Al_6Si_{30}O_{72}).18H_2O$	28	4.3 × 5.5	High	2.33
Heulandite	$(Ca_4)(Al_8Si_{28}O_{72}).24H_2O$	39	4.0 × 5.5 4.4 × 7.2 4.1 × 4.7	Low	2.91
Laumonitte	$(Ca_4)(Al_8Si_{16}O_{48}).16H_2O$	34	4.6 × 6.3	Low	4.25
Mordenite	$(Na_8)(Al_8Si_{40}O_{96}).24H_2O$	28	2.9 × 5.7 6.7 × 7.0	High	2.29
Philipsite	$(NaK)_5(Al_5Si_{11}O_{32}).20H_2O$	31	4.2 × 4.4 2.8 × 4.8 3.3	Medium	3.31
Linde A	$(Na_{12})(Al_{12}Si_{12}O_{48}).27H_2O$	47	4.2	High	5.48
Linde X	$(Na_{86})(Al_{86}Si_{106}O_{384}).264H_2O$	50	7.4	High	4.73

[a] In some cases, only one dimension is given (one-dimensional).

Physical and chemical properties of zeolites include their morphology, particle size, thermal expansion, density, hardness, uniformity of composition, optical properties, color, dielectric properties, electrical conductivity, thermochemistry, zeolitic water, structure of internal tetrahedra and external linkages, pore volume, and framework density.[25] Applications based on external surface activity are noted by Colella[4] and include sorption of large organic molecules (mycotoxins; herbicides, fungicides and pesticides; drugs and molecules of biological relevance), interaction with humic substances and surface modification by interaction with surfactant cations (preparation of zeolite-surfactant complexes, anion exchange and sorption of hydrophobic organic molecules).

The properties that are structure-related include:[25]

- High potency of hydration and the behavior of 'zeolitic' water.
- Extensive void volume and low density when dehydrated.
- Stability of the crystal structure of many zeolites when dehydrated and when as much as 50% volumes of the dehydrated crystals are void.
- Cation exchange features.
- Homogenous molecular-sized channels in the dehydrated crystals.
- Various physical properties such as electrical conductivity.
- Adsorption of gases and vapors.
- Catalytic properties.

The characteristic formulae and premium physical properties of important zeolites are shown in Table 2.[1]

The description of the void spaces and the interconnecting channels in dehydrated zeolites are essential for determining the physical and chemical features. Three types of channel systems are identified: one-dimensional system, two-dimensional system and two types of three-dimensional systems with intersecting channels. The zeolite structure contains (–Si-O-Al-) linkages that comprise pores of uniform diameter within 2–12 Å pore size ranges running through the material. As a result of these channels and pores uniformly penetrating the entire volume of the solid, the zeolite family has a high internal surface area available for adsorption. The dimensions of pore apertures are another important criterion for dividing zeolites into categories: small pore system (eight-membered rings, diameters of approximately 4 Å), medium-pore system (10-membered rings, approximately 5–6 Å), dual pore system (eight- to 10-membered rings, approximately 7 Å), large pore system (12-membered rings, approximately 7 Å) and mesopore system (12-membered rings, > 12 Å)[26]. Concerning their 'high Si' content, zeolites can be classified as 'high silica' with Si/Al atomic ratio > 10, intermediate silica (1.5 < Si/Al atomic ratio < 10) and 'low silica' with a Si/Al ratio of approximately 1.[27] The highly porous structure of zeolites catches particles of < 4 μm. The ion exchange capability catched heavy metal cations such as Pb, Cu, Cd, Zn, Co, Cr, Mn, Fe, Pb and Hg selectively.

CLASSIFICATION

There are more than one mineral arrangement systems. Currently, three classification schemes are used for zeolite structures circumglobally. Two of these are contingent on their crystal structures structures (secondary building unit by Breck;[25] framework topology by Meier *et al.*[28]), whereas the third (secondary building unit by Armbruster and Gunter[29] underwent further historical groundwork and places zeolites with similar properties such as morphology into the same group, as described by Gottardi and Galli.[30] Moreover, the mineralogist E. S. Dana, employed a classification of Zeolites under the main group of VIII-Silicates, under the subgroup of Tectosilicates and Class 77-Tectosilicate Zeolite minority group.[31] Nickel-Strunz classification (version 10) has arranged Zeolites under the Silicates group, 09-G-Tectosilicates subgroup with zeolitic H_2O.[32] Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, philipsite and stilbite.

The pore structure of some zeolites is shown in Table 3.[26,33]

FORMATION

Natural zeolites formed in the areas of volcanic rocks and ash layers react with alkaline groundwater. The mineral formation of zeolite

Table 3. Pore structure of some zeolites (Chen[26] and Alp[33])

IUPAC Code	Pore system	Number of rings	Pore size (Å)[a]	Description
Eight-membered pore system				
CHA	Chabazite	8	3.8 × 3.8	Intersecting
LTA	Linde Type A	8	4.1	Intersecting
Medium pore system				
PAR	Partheite	10	3.5 × 6.9	One-dimensional
MFI	ZSM-5	10	5.1 × 5.5	Intersecting
			5.3 × 5.6	
Dual pore system				
FER	Ferrierite (ZSM-35, FU-9)	10	4.2 × 5.4	One-dimensional
		8	3.5 × 4.8	10:8 intersecting
HEU	Heulandite	10,8	3.0 × 7.6	One-dimensional
			3.3 × 4.6	
		8	2.6 × 4.7	10:8 intersecting
KLI	Clinoptilolite	10	4.4 × 7.2	One-dimensional
		8	4.1 × 4.7	10:8 intersecting
STI	Stilbite	10	4.9 × 6.1	One-dimensional
		8	2.7 × 5.6	10:8 intersecting
MOR	Mordenite	12	6.5 × 7.0	One-dimensional
		8	2.6 × 5.7	10:8 intersecting
Large pore system				
LTL	Linde Type L	12	7.1	One-dimensional
FAU	Faujasite (X,Y)	12	7.4	Intersecting
			7.4 × 6.5	12:12 intersecting
Mesopore system				
VFI	VPI-5	18	12.1	One-dimensional
	M41-S		16–100	One-dimensional

[a] In some cases, only one dimension is given (one-dimensional).

sedimentary rocks has been correlated with the chemical composition of the host rock (high or low silica), the water chemistry (pH, salinity, dissolved ions) of the depositional and post-depositional environment, as well as the age and burial depth.[25] The salt content of water also favors the conversion of volcanic glass to form zeolites.[25] The formation of natural zeolite, especially Clinoptilolite reserves, is categorized by Eyde and Holmes[34] into six groups:

1. Closed and salty lake waters react with volcanic material.
2. Open system, salty and sweet lake waters with volcanic ash residues react with sea water.
3. Volcanic ashes accumulated in shores and deep sea sediments react with sea water (the most homogeneous mineral reserves up to 95%).
4. Low burial temperature metamorphosis of volcanic ashes and thick sediments layers
5. The decomposition of Al-Si material by the effect of hydrothermal reserves and hot springs.
6. Lack of evidence that original volcanic residues react of lake or sea waters.

APPLICATION OF INSECTICIDE AND HERBICIDE, CARRIERS AND PESTICIDES

Environmental conditions, species of insects or plants as a commodity, and the structure of the dust are three principal characteristics that affect the efficacy of zeolites and other inert dusts with regard to insecticide and herbicide applications. Temperature, relative humidity, method of treatment, insect species (the developmental stage, size of which greater surface area to volume ratio, softness of wax layers, hairiness, susceptibility and physical mobility) and plant species (plant biology) assess the potential of the product.[35–42] Furthermore, some dust properties, such as molecular structure, content of silicon dioxide, shape and size of particles, Al/Si ratios, sorption ability and geographical origin, also affect the insecticidal potential directly.[35,37,43,44] Inert dust access to the insect body, although not certain, is suggested to follow these paths: (i) spiracle blocking and asphyxiation; (ii) abrasion of cuticle that causes water loss; (iii) ingestion of the dust particles; and (iv) absorption of epicuticular lipids that leads to dessication.[37,45,46] With what is available so far in the literature, the main mode of action is the last one (dessication).

Dry air conditions resulting from the use of adsorbents, silica gel and alumina silicate crystals of the zeolite group, noted as molecular sieves, have been tested with success against some stored-product beetle species, including the lesser grain borer *Rhyzopertha dominica* (F.) (Coleoptera: Bostrychidae) on wheat, the rice weevil *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae) and the saw toothed grain beetle *Oryzaephilus surinamensis* (L.) (Coleoptera: Silvanidae).[25,47,48] Natural zeolite applications were also found to be effective in controlling the maize weevil *Sitophilus zeamais* Motschulsky (Coleoptera: Curculionidae) by Haryadi *et al.*[49] with high rates of $\geq 50\,g\,kg^{-1}$ on maize. In a more recent study, natural zeolite formulations originating from Serbia (Minazel Plus and Minazel) and diatemaceous earth (DE) (Protect-It™) were found to be effective on wheat against *S.*

oryzae, *R. dominica* and the red flour beetle *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae).[42] Another experiment on zeolites (Minazel) from Serbia revealed the higher efficacy of this compound in controlling *S. oryzae*, *R. dominica* and *T. castaneum*, at doses that did not exceed 1000 ppm.[41] Bentonite (Bosnia and Herzegovina), natural zeolite (Serbia) and DE (Belgrade, Serbia) formulations were found, under laboratory conditions, to be effective against *S. oryzae* and *T. castaneum* adults.[41] Zeolites and modified zeolits originating from Serbia were also studied to test progeny reduction rates and the insecticidal effect of stored product insects, with good results being reported.[50]

South American native flowering plants that release peppery odor 'Matico' (*Piper aduncum* subsp. *ossanum*) as PAO-1, PAO-2 and zeolite (Heulandite type Zeolite which Clinoptilolite + Mordenite Type I, purity is above 70%) were studied to control the cigarette beetle, *Lasioderma serricorne* (F.) (Coleoptera: Anobiidae) in chickpea, showing the highest mortality rates of adults with PAO-2 and the best repellent effect with PAO-1.[51] Mortality rates of zeolites rose higher in the first 6 days, exceeding 90% and then with not much efficacy being observed compared to other characters during the 15-day study, which may related to the chemical properties of the source.

Soil applications are important treatments in organic agriculture. Clinoptilolite was investigated for its effectiveness on organic oilseed rape fields in Switzerland against the pollen beetle *Meligethes* spp. (Coleoptera: Nitidulidae).[52] Dust and spray applications of the same Clinoptilolite in several large-scale fields between 2008 and 2011 were evaluated.[52] Under the dry and sunny years of 2009 and 2010, pollen beetles were significantly reduced by 50% to 80%, whereas there was no reduction observed for rainy weather occurring in 2008. The yield was reported to be increased significantly (23%) under IPM conditions in 2010.[52] A Turkish Clinoptilolite that was studied for the control of the confused flour beetle *Tribolium confusum* Jacquelin du Val (Coleoptera: Tenebrionidae) on barley at different temperature levels (18, 24 and 30 °C) was found very effective at dose rates that exceeded 2000 ppm.

Insecticidal efficacy of natural zeolites on stored-product pests is shown in Table 4.

Other than stored product pest control, zeolites are also used for the physical control of pests as well as pesticide carriers. Furthermore, a zeolite-based granular formulation of the organophosphorous compound temephos was evaluated with success for the control of larvae of the yellow fever mosquito *Aedes aegyptii* (L.) (Diptera: Culicidae).[53]

Natural zeolites, especially clinoptilolite, have been considered as possible sorbents because they are slow-release carriers and retard water contamination.[4] Almost all of these organic compounds are too large to penetrate the zeolite framework; sorption is a result of polar chemical bonds with the external surface of the microporous mineral.[54] Fungicide application of clinoptilolite to control *Phythium* spp. on turfgrass was also found to be moderately active in preventing the migration of the fungicide metalaxyl to groundwater.[55] Clinoptilolite was found to protect *Bacillus thuringiensis* from ultraviolet radiation and, although this mode of action is not clear, it is suggested that zeolite adsorption of bacterial endotoxins is directly related to photostability as a result of sunlight deflection.[56]

Heulandite-clinoptilolite-rich tuffs and mordenite-rich tuffs have been used in Cuba as a substrate for the synthesis of the herbicide 2,4-dichlorophenoxyacetic acid.[57] Phillipsite-rich tuff from the Canary Islands (Spain) showed remarkable selectivity for oxamyl and demonstrated good features as a potential slow-release pesticide carrier agent.[58] Similar results have been reported for cypermethrin, a second-generation pyrethroid, with clinoptilolite from Slovakia.[59,60] The formation of a stable complex was indicated by thermal and infrared spectrocopy analyses, which gave results different from those of the parent components.[60] Although the exact mechanism is not clear, natural zeolites have been applied as dusting agents to control aphids infesting fruit orchards in Italy.[1]

Nanoporous zeolites for nanocapsules have been used as carriers in herbicide delivery, pest management, and as nanosensors for pest detection.[61–66] Stadler *et al.*[67] examined the insecticidal effect of nanostructured alumina on two stored-grain insect species, *S. oryzae* and *R. dominica*, and found that mortality reached 80–100% after 14 days of exposure to treated wheat. After 9 days of application, the median lethal doses (LD_{50}) detected ranged from 127 to 235 mg kg^{-1}. In this regard, inorganic nanostructured alumina may provide a cheap and reliable alternative for commercial insecticidal dusts for the control of insect pests. Additional research is needed regarding its mode of action, non-target toxicity and the potential for use in pest control strategies for insects.

MYCOTOXIN CONTROL

The use of aluminasilicates such as zeolites, montmorillonite and bentonite clays has grown to be common practice with respect to combining mycotoxin binding agents in the feed and food industry with the aim of effectively adsorbing mycotoxin.[68] The ability of clinoptilolite and other zeolites to absorb aflatoxins that contaminate animal feeds has resulted in measurable improvements in the health of different farm animals. These specific silicate minerals have been indicated to bind with aflatoxin as consequence of chelating the β-dicarbonylmoiety in aflatoxin with uncoordinated metal ions in the clay materials.[69] There are some established criteria to evaluate the functionality of any binding additive, such as a supremely low inclusion rate, stability over a wide pH range, huge capacity and an affinity to absorb various concentrations of mycotoxins.[68] The supplementation of mycotoxin binders to contaminated diets has been suggested as the most advantageous dietary approach for decreasing the effects of mycotoxins.[70] Hydrated sodium calcium aluminosilicates-zeolite powder (HSCAS) was found to be effective for this purpose. Phillips *et al.*,[71] after screening a large number of silicates, found that HSCAS was more effective. HSCAS possesses calcium ions and protons that replace the naturally occurring sodium ions belonging to phyllosilicates (possessed of layers of aluminum and silicon connected in a 1:1 or 2:1 arrangement). The suitability and convenience of aluminosilicates for the adsorption of mycotoxins has been investigated for more than 20 years (zeolites: Mumpton and Fishman;[72] clays: Masimango *et al.*;[73] HSCAS: Davidson *et al.*;[74] Ramos and Hernandez[75]). HSCAS at a level of 0.5–2.0% in the diet prevented aflatoxicosis in species such as chickens,[76–78] turkeys,[79] lambs and dairy cows,[80] and dairy goats.[81] HSCAS is identified as'aflatoxin-selective clay', although it is not a good adsorbent of other mycotoxins such as cyclopiazonic acid, which may coexist with aflatoxin,[82] and the responses appear to be dose-dependent.[81–83] Parlat *et al.*[84] reported that clinoptilolite was successful in minimizing the effects of aflatoxin in quail. Various clay products along with a calcium bentonite formulation were similar in effectiveness to HSCAS with respect to reinforcing performance in pigs consuming aflatoxin.[85] Natural zeolites with a high content of clinoptilolite (over 80%) effectively adsorbed aflotoxin

Table 4. Insecticidal efficacy of natural zeolites (NZ) on stored-product pests

Zeolite type	Laboratory conditions	Substrate	Dosage (g kg^{-1})	Test insects	Efficacy (%)	Inhibition rate in F1 (%)	Reference (Year)
Zeolites to dry air		Wheat		*Rhyzopertha dominica*	+		Pezzutti *et al.*[47] (1979)
		Maize		*Sitophilus oryzae*	+		
		Rice		*Oryzaephilus surinamensis*	100		
NZ	27–30 °C 75–85%	Maize	50	*Sitophilus zeamais*	100	–	Haryadi *et al.*[49] (1994)
			40		–	70.1	
NZ (Minazel SP)	24 + 1 °C 50–55%	Wheat	1.00	*Sitophilus oryzae*	96–98	51–85	Kljajic *et al.*[41] (2010)
				Rhyzopertha dominica	70–82	80–96	
				Tribolium castaneum	100	87–99	
NZ (Minazel)	24 + 1 °C 45–5%	Wheat	0.75	*Sitophilus oryzae*	100	95.0	Kljajic *et al.*[42] (2010b)
				Rhyzopertha dominica	73.7	88.8	
				Tribolium castaneum	100	90.3	
NZ (Minazel Plus)				*Sitophilus oryzae*	98.9	80.0	
				Rhyzopertha dominica	43.7	76.6	
				Tribolium castaneum	100	80.6	
				Tribolium castaneum			
NZ (Minazel Plus)	24 + 1 °C 60–5%	Wheat	0.75	*Sitophilus oryzae*	53		
				Tribolium castaneum			
NZ (Minazel)	24 + 1 °C 50–55%	Wheat	1.00	*Sitophilus oryzae*	96.0	81.8	Andric *et al.*[50] (2012)
				Tribolium castaneum	100	96.5	
NZ (Minazel Plus)	24 + 1 °C 50–55%	Wheat	1.00	*Sitophilus oryzae*	45.0	62.0	
				Tribolium castaneum	28.0	71.3	
NZ		chickpea		*Lasioderma serricorne*	50–21.46	15.97	Perez *et al.*[51] (2012)
Clinoptilolite (Klinofeed, dust)		Oilseed rape field	300–750 kg ha^{-1}	*Meligethes* ssp.	50–80% reduced pop.		Daniel *et al.*[52] (2013)
Clinoptilolite (Heliosol, spray)		Oilseed rape field	600 l water ha^{-1}	*Meligethes* ssp.	50–80% reduced pop.		

B_1, aflatoxin B_2 and aflatoxin G_2.[86] By contrast, zeolite with a surface modified with ammonium ions, displays very good adsorption features for ochratoxin A, T-2 toxin, zearalenone and aflatoxin B_1.[87] Modified zeolite, also applied at 2 g kg^{-1} enhanced silage fermentation and reduced mould, zearalenone and T-2 toxin.[88]

There are numerous reviews of mycotoxin binders that acknowledge the concentration and adsorption capacity of specific inert materials.[75,89,90] In the case of mycotoxicoses, zeolites are able to bind polar toxins such as aflatoxins, a characteristic that has been confirmed in many studies, despite the fact that the results are often contradictory. The application of aluminosilicates for mycotoxin binding is impressive with respect to preventing aflatoxicosis; however, their efficacy against zearalenone, ochratoxin, and trichothecenes is regarded as limited. At the same time, these compounds show high inclusion rates for vitamins and minerals, which is one of the major disadvantages.[89,91]

APPLICATION AS SOIL AMMENDMENT

As a result of their physical and chemical characteristics, natural zeolites can be highly effective adsorbents of toxic metals, radionuclide, ammonia and other unacceptable matters. Naturally occurring crystalline aluminum silicates accomodate water infiltration and retention in the soil because they have porous properties and capillary suction. Furthermore, zeolites as natural wetting agents can improve the water retention of sandy soils and expand porosity in clay soils, retain nutrients and increase yields.[66] At the same time, as in the case of insecticides, zeolites can be good carriers of nutrients and control their slow release after application, although there are additional chemical and physical benefits, such as their utilization as artificial soil and nitrate leaching reducers.[4,8,66]

Zeolites have some positive effects on soil properties, such as raising the soil cation-exchange capacity and soil moisture, promoting hydraulic conductivity, increasing yields in acidified soils, and reducing plant uptake of metal contaminants.[8] They are used extensively as soil amendments and slow-release fertilizers.[92] Clinoptilolite-rich tuff as a soil conditioner significantly increases the yields of wheat (13–15%), eggplant (19–55%), apples (13–38%) and carrots (63%) with the use of 4–8 tonnes of zeolite/acre. The supplementation of clinoptilolite boosted the yields of potatoes, barley, clover and wheat, when applied at 15 tonnes ha^{-1} to Ukrainian sandy loams.[93] The use of zeolites, especially clinoptilolite, as the primary component of artificial soil was formulated in Bulgaria in the late 1970s.[1] Zeolite mixed with phosphate rock application performs as a controlled delivery system and a renewable source of nutrients for plants.[94] Brazilian sedimentary zeolite fortified with N, P and K was found to be a sufficient slow-release source of nutrients to plants, whereas it was able to increase water retention and availability to sandy soils.[95]

The growth of plants in synthetic soils providing zeolites with or without peat, vermiculite, and related substances is termed zeoponics. A zeoponic substrate improves root systems and produces more yields of strawberries, cucumbers, tomatoes and peppers, without further fertilization.[96] Bulgarian clinoptilolite was used successfully for the growth of cabbage and radishes in the Russian space station Mir.[97] The National Aeronautics and Space Administration (NASA) investigated zeoponic mixtures of 'zeolite–apatite' and developed a special cation-exchanged clinoptilolite and apatite composed of essential trace nutrients for plant-growth media in shuttle flights. This formulation may be utilized for vegetable production in the case of space missions.[98]

Natural and modified zeolite increased the yield and improved some qualitative characteristics of mycelium mushroom (*Agaricus blazei, Ganoderma lucidum*, *Lentinula edodus* and *Pleurotus ostreatus*).[99] Moreover, the addition of natural and modified zeolite for mushroom growing (*Agaricus biosporus*) increased the final product by 10%.[99]

The feasibility of surfactant-modified zeolite and clinoptilolite was used by Malekian *et al.*[100] to decrease nitrate leaching and to enhance crop growth. The effect of size (mm and nm) and an application rate of 20 and 60 g kg^{-1} was tested for this purpose, and the results indicated that maize plants had a better response to zeolite use as a fertilizer carrier at a rate of 60 g kg^{-1}.[100] In another study, zeolite and diatomaceous earth (originating from Bigadic, Turkey; OR-TAR Organic Tarim Ur. Lmt.) were applied to acidic soils of Black Sea region in Turkey to evaluate the development of two maize varieties, soil pH and mineral substrate. Both applications were successful; diatomaceous earth application affected the content of dry matter on Mg, S, Cu and Fe levels, whereas zeolite application affected N, P, K, Ca, Na, B, Mn and Zn levels.[101] Moreover, aluminosilicate minerals in natural and modified form can be good adsorbents of toxins and toxic metals (Pb, Cu, Cd, Mn, Zn, Cr, Ni).[102] Clinoptilolite, as a soil amendment, effectively reduced heavy metals and metalloids, including Cd, Pb and Zn.[103,104] Zeolites and apatites were found to reduce the accumulation of Cd, Pb and Zn by up to 72%, 81% and 41%, respectively, at a dose of 0.25% and 0.50% on maize leaves.[105]

APPLICATION AS ANIMAL FEED ADDITIVE

One of the earliest reviews on the use of zeolites associated with animal science and aquaculture was provided by Mumpton and Fishman.[72] Dietary supplementation of zeolites is an efficacious and cooperative strategy in the prevention of certain diseases and the advancement of animal health. The purity and physicochemical properties of natural zeolites, such as particle size, crystallite size and the degree of aggregation, as well as the porosity of individual particles, may influence efficacy. These features indicate the access of ingested fluids to the zeolitic surface as a result of the time passage across the gastrointestinal tract and strongly affect its ion exchange, adsorption and catalytic properties.[106] Poultry performances of zeolite applications were reviewed by Shariatmadari,[107] who cited some controversial studies regarding impurity levels of raw materials. However, there are clear indications of certain benefits resulting from the addition of natural zeolite with respect to feed intake, weight gain and growth rate, bone performance, feed efficiency ratio, nutrient utilization, egg production and weight, shell thickness, water consumption, manure, and litter condition.[107]

The benefits by dietary inclusion of zeolites have been documented in many studies using daily gain and feed conversion in pigs,[72] calves[72] and sheep.[108,109] Additionally, zeolites enrich the reproductive performance of sows[72] and increase the milk yield of dairy cows.[110] One of the earlier studies in Japan employing $\leq$ 10% clinoptilolite and mordenite as dietary supplements for swine and poultry reported a faster growth for test animals compared to the control group, such as 5% clinoptilolite mixed with feed resulting in 16% more weight and a simultaneous decrease in the amount and cost of the feed.[111,112] The admittance of both synthetic and natural zeolites into the rumen of test animals and the gradual release of the excess nitrogen allowed rumen organisms to integrate cellular protein by assimilation into the animal digestive system.[113]

The effect of dietary supplementation with clinoptilolite on performance and biochemical serum values in dairy goats was investigated by Katsoulos and Christodoulopoulos.[114] The use of clinoptilolite on food intake and the performance of growing lambs contaminated with gastrointestinal nematodes was increased and it was suggested that this compound could be utilized as a natural alternative to prevent gastrointenstinal nematodes in sheep rations.[115] The influence of dietary fiber, protein and zeolites on zearalenone toxicosis in female weaning rats and swine was also investigated by Smith.[116] Another study concluded that a 3% addition to the feed of gilthead sea bream (*Sparus aurata*) resulted in a positive impact of growth.[117] The inclusion of additives such as the plant *Yucca schidigera* Roezl ex Ortgies and zeolite (clinoptilolite) in commercial wet food for adult cats eliminated fecal odor without any negative interference in the health of animals.[118,119] For adult dogs, the effects of adding *Y. schidigera* and zeolite (clinoptilolite) to their food were evaluated regarding the acceptability of the feed, stool characteristics and the apparent indigestibility coefficient of minerals.[119] It was found that the inclusion of additives may interrupt the excretion of some minerals in the diet[119] and also notably increase crop yield.[120]

Natural zeolites have three major impacts on aquaculture according to Mumpton;[1] removal of ammonium from hatchery, transport and aquarium waters; generation of oxygen for aeration systems in aquaria and transport; and supplementation of fish rations. Phillipsite from the Neapolitan Yellow Tuff was used to remove ammonium from saline water effluent in shrimp-culture tanks and its limited use in seawater was recommended.[121]

Natural zeolites have been used heavily in animal nutrition to promote health and performance ever since the early 1980s. Nevertheless, the exact mechanism of the effect of zeolites is poorly understood, despite the fact that there are many published works on the dietary use of natural zeolites in terms of gastrointestinal disturbances together with intestinal parasite infections in farm animals.[105] Moreover, zeolites that possess high ion-exchange capacity have been used effectively for the prevention of heavy metal toxicity and the prevention of organophosphates poisoning. Clinoptilolite has been recorded to protect mice from lead (Pb) toxicity[108] when added to their ration in a ratio of clinoptilolite/Pb of 10:1 and similar results have also been reported with swine.[109] The dietary use of clinoptilolite was demonstrated to be effective in the prevention of organophosphate poisoning. The protective effect of clinoptilolite on cholinesterase activity has been recognized in mice receiving higher doses of organophosphates.[122] Extensive scientific data demonstrate that the dietary use of zeolites improves the health status of animals, as well as the quality of meat and dairy products.

APPLICATION OF FOOD PRODUCTION

Aluminosilicate natural mineral raw materials, such as zeolites, as a result of their high content of SiO_2 and appropriate pH levels, can be useful for drying and the storage protection of food products from insects. Agricultural practices and industrial activities lead to organic and inorganic pollutants of soil that have negative effects on food quality and safety.[123] Therefore, zeolites may be used in applications ranging from the proper drying of harvested food products to active and intelligent packaging in the food industry. Active packaging involves interactions among package, food and the internal gas atmosphere to comply with consumer demands for high-quality, fresh and safe products.[124] The market for active packaging films, which suppress the growth of pathogenic and spoilage microorganisms, block migration of contaminants and maintain nutritional quality, is expected to grow rapidly. The important active packaging systems include oxygen scavengers, carbon dioxide emitters/absorbers, moisture absorbers, ethylene absorbers, ethanol emitters, flavor releasing/absorbing systems, antimicrobial containing films and time-temperature indicators. Among these, zeolites are used as ethylene absorbing agents and silver-zeolites are used as antimicrobial releasing agents in active packaging systems.[124]

There are many studies that report the use of zeolites as coatings in food packages. Their application in vacuum packaged sardine fillets with natural zeolites was investigated to determine quality changes at $4 \pm 1\,^{\circ}$C when doses of 1% and 5% were applied for 19 days.[125] Zeolite improved the sensory quality of sardines by removing off-odor and provided a longer shelf life, and also reduced ammonia and biogenic amine accumulation, especially for histamine and tyramine. The efficacy of zeolite as a natural antimicrobial was quite high even at low doses.[125] Additionally, the use of edible coatings such as chitosan reduces water transfer, protects fruit skins from physical damage and seals small wounds on skins, hence delaying dehydration and mould infections. The effect of a chitosan coating combined with zeolite on tomato (*Lycopersicon esculentum* Mill.) quality during refrigerated storage was investigated and fruit shelf life, fungal decay, respiration rate and visual appearance were evaluated.[126] No sign of fungal decay was found during the storage period. Moreover, the addition of 3% (w/w based on chitosan) zeolite and Tween 80 at 0.1% (v/v) in chitosan solution appears to improve its coating properties and delay the ripening of tomatoes. The incorporation of zeolite into the film-forming solution did not result in any weight loss in tomatoes. Mechanical and barrier properties of chitosan films were affected through the intercalation of nanoparticles such as Ag-zeolite reported by Rhim *et al.*[127]

Drying applications represent a major operation in the food industry, especially the drying capacity of air in the convective dryers. It is cited that the water adsorption capacity of zeolites, which is very high, can be used in dryers to promote the water uptake capability of air at low temperatures.[128] Zeolites have the potential to increase drying efficiency at a medium temperature in the food industry.[129] Dryers using air dehumidified by zeolite and conventional dryers were compared with respect to energy recovery and steady-state mass over a range of temperatures from 52 to 72 °C. Zeolite dryers were found to be 10–18% more efficient than conventional dryers.[129]

The FAO and IPGRI (International Plant Genetic Resources Institute) Genebank Standards[130] suggests drying seed germplasm immediately after it is received, at 10–25 °C and 10–15% relative humidity, either in a drying chamber or using a desiccant.[131] The most common application is the use of silica gel to reach a target moisture content of 3–7% (fresh weight basis). However, in wet tropical regions of the world, especially those in developing countries with limited energy sources, drying can be a real problem.[132,133] Desiccant drying including silica gel (sodium silicate), charcoal or a molecular sieve in a closed container is often recommended as a low-technology method for reaching the optimum moisture content of seed germplasms. Aluminum silicate ceramics are marketed as seed 'drying beads' and comprise a type of molecular sieve with small, uniform pores. They absorb water molecules and have a re-use ability after heating to 200 °C for 2 h. After examining the potential of drying beads to dry rice seeds according to long-term genebank storage requirements, it was found that formal moisture content of the seeds depended on the ratio of beads to seed and temperature of the place. The beads helped to dry seeds very rapidly and more drying was recorded at 30 °C compared to that achieved at 15 or 5 °C, although further study is required to optimize target moisture contents and better germination rates.[132]

The storage of seeds was studied using zeolite on dolichos bean (*Lablab purpureus* L.), soybean (*Glycine max* L.) and forage sorghum (*Sorghum bicolor* (L.) Moench.) by Crespo *et al.*[133] Seeds were mixed with 25 and 50 g kg^{-1} zeolite and stored for 10 months. There was a significantly higher germination of sorghum and soybean seeds observed after 4 months of storage in seed mixed with zeolite, whereas rotten seeds, mainly in soybeans and sorghum, were reduced by zeolite. However, after 10 months of storage, soybean seed lost all viability in all treatments. Immersion drying of wheat (*Triticum durum* Desf.) was tested in a particulate medium grain dryer using natural clay, pillared aluminum clay (Al-PILC), zeolite 13X and sand as media. The results obtained at different initial bed temperatures and times in the dryer revealed that zeolite resulted in the highest grain moisture loss for a given time. After zeolite, other materials followed, such as Al-PILC, natural clay and sand. The best heat and mass transfer features were found for Zeolite and Al-PILC.[134]

Trading quality and bread-making performances of wheat treated with natural zeolite and diatomaceous earth were investigated after inert dust approval for use in pest control during certified organic crop production.[135] It was confirmed that there is no change in the bread-making properties of treated wheat.[135] However, treatments with natural zeolite significantly decreased the test weight (volume to weight ratio) of wheat, which is a major disadvantage[48] because test weight is one of the most important trading characteristics of grains. Similar results have been also reported for diatomaceous earths.[136]

PROSPECTS FOR THE FUTURE

Zeolites, crystalline hydrated aluminosilicates, are versatile materials that have unique physical and chemical characteristics and function as being capable of losing and gaining water reversibly, adsorbing molecules when acting as molecular sieves, and exchanging their constituent cations without structural change. Their applications have been growing in a wide range of cases, such as in agriculture, animal husbandry and fisheries, environmental protection, and food production. Environmental concerns and a strong public demand to use natural products without any toxic residues has encouraged research on future industrial applications in this respect.

To outline the advantages and disadvantages of inert dusts, the perspectives of the small farmers and potential industrial size applications should be evaluated. Many advantages of inert dust application against stored product pests, including diatomaceous earth, synthetic inert dusts, zeolite, kaolin, clay, etc., have been recorded over recent decades.[37,41,42,45] Traditional usage by small-scale farmers (especially in Africa and India), an estimated lower cost compared to conventional chemicals, low mammalian toxicity, slow and eco-friendly action, and the potential of easily being part of an IPM are the leading attributes.[35,37,41,42,45,137] Inert dusts are applied in three ways by the bulk grain handling industry: structural treatments, admixture treatments on the entire mass of the commodity, and surface admixture treatments.[35,45,54] Separation from grain is easily achieved via standard grain processing and there are no adverse effects on the properties of the final commodity. Zeolite application to wheat grain and flour was reported to significantly decrease insect damage and test weight, at the same time as significantly improve the technological quality of insect-damaged wheat and dough energy.[135] Moreover, inert dusts are established as a promising alternative to conventional insecticides in the management of resistant populations.[45]

Zeolites are comparable in toxicity to diatomaceous earth and have a great potential for use in stored-product protection.[48] They are non-toxic[138] and safe for human consumption.[139] The Codex Alimentarius Commission[17] recommends Zeolite under 'Silicates, clay, sodium silicate' for the control of insect pests in food communities and lists zeolites as permitted substances for plant pest and disease control. According to the FDA, GRAS Substances[140] do not pose a hazard to public. Silicon compounds under this listing are consumed as direct food ingredients, food packaging and filter aids.[140] Naturally occurring zeolites are distributed worldwide and exposure may occur during the mining, production and use of zeolites. However, no human carcinogencity effects were recorded in studies reported by the IARC[138] among 218 forms, except for erionite.

Prices for natural zeolite change based on the content, country and processing type, ranging from \$75 to \$300 per metric ton in 2004, as released by the US Geological Survey canvass of domestic zeolite producers.[141] Another report highlights the prices for industrial or agricultural applications ranging from US \$30 to \$70 per ton for granular products down to 40 mesh and from US \$50 to \$120 per ton for finer (−40 to +325 mesh) ground material.[142] Prices for Asian and European zeolite (mainly clinoptilolite) were between US \$60 and \$165 per ton.[141] The latest USGS archive reported a price range of US \$50 to \$800 per ton for natural zeolite,[143] indicating the affordability of all stored product with respect to pest control.

On the other hand, the efficacy of inert dust treatment varies according to particle size, pore diameter, specific surface area, and bulk density, which heavily rely all on geographical and geological conditions.[45,136,137] Inert dust applications negatively affect the weight to volume ratio known as the bulk density on grains.[45,48,136,137] The angle of repose of the treated wheat is also affected and increased by these treatments.[45] Furthermore, health hazards from inhalation and an excessively dusty atmosphere during application may produce respiration problems for workers after long exposure intervals.

As a result of new alternative methods of organic agriculture and IPM programs, zeolite applications on agriculture and crop protection have gained distinct attention from scientists, although such applications have not been regulated or licensed in most countries. There are very limited studies investigating different zeolite formations against stored product pests locally, although zeolite mining industries are common in many countries and large amounts of diverse products are exported. Apart from a lack of validated data from experiments, there is also a serious gap regarding the implementation of these materials in inorganic control programs, the existence of an adequate infrastructure to produce and supply continuous product for stored product pest control locally and abroad, and both farmer and consumer awareness regarding inert material use in stored durable food. Additional investigations are required to encourage wider application as an agent in IPM programs. In this context, it is estimated that zeolites will achieve more important roles in agricultural practices and food safety in the near future.

REFERENCES

1 Mumpton FA, La roca magica: uses of natural zeolites in agriculture and industry. *Proc Natl Acad Sci USA* **96**:3463–3470 (1999).
2 Adamovic M, Stojanovic M, Grubisic M, Iles D, and Milojkovic J, Importance of aluminosilicate minerals in safe food production. *Maced J Anim Sci* **1**:175–180 (2011).
3 McBain JW, *The Sorption of Gases and Vapors by Solids*. Rutledge and Sons, London (1932).
4 Colella C, Recent advances in natural zeolite applications based on external surface interaction with cations and molecules, in *From Zeolites to Porous MOF Materials. The 40th Anniversary of International Zeolite* Conference, 12–17 August 2007, Beijing, PR China, ed. by Xu R, Chen J, Gao Z and Yan W. *Stud Surf Sci Catal* **170**:2063–2073) (2007).
5 Barrer RM, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves.* FRS Academic Press, Inc., London (1978).
6 EPO, *Espacenet Patent Search* [Online]. Available: http:/www.epo.org/searching/free/espacenet.html [20 October 2016].
7 Pharos, *Zeolites* [Online]. Available: https://www.pharosproject.net/uploads/files/cml/1397836670.pdf [20 October 2016].
8 Allen ER and Ming DW, Recent progress in the use of natural zeolites in agronomy and horticulture, in *Natural Zeolites '93: Occurrence, Properties, Use. International Committee on Natural Zeolites*, ed. by Ming DW and Mumpton FA. Brockport, New York, pp. 477–490. (1995).
9 Campbell LS and Davies BE, Experimental investigation of plant uptake of caesium from soils amended with Clinoptilolite and calcium carbonate. *Plant and Soil* **189**:65–74 (1997).
10 Polat E, Karaca M, Demir H and Onus N, Use of natural zeolite (Clinoptilolite) in agriculture. Orchard management in sustainable fruit production. *J Fruit Ornam Plant Res* **12**: 183–189 (special edition) (2004).
11 Moreno-Tost R, Santamaria-Gonzalez J, Rodriguez-Castellon E, Jimenez-Lopeza A, Autie MA, Glacial MC *et al.*, Selective catalytic reduction of nitric oxide by ammonia over Ag and Zn exchanged cuban natural zeolites. *Z Anorg Allg Chem* **631** (2005).
12 Virta RL, Zeolites (Advance Release). [Online]. USGS2009 Minerals Yearbook. Available: https://minerals.usgs.gov/minerals/pubs/commodity/zeolites/myb1-2009-zeoli.pdf [15 September 2016].
13 Virta RL, Zeolites (Natural) [Online]. U.S. Geological Survey, Mineral Commodity Summaries, January 2011. Available: https://minerals.usgs.gov/minerals/pubs/commodity/zeolites/mcs-2014-zeoli.pdf [10 September 2016].
14 IARC, *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Supplement. Silica, Some Silicates, Coal Dust and Para-Aramid Fibrils*. IARC, Lyon, Vol. 68, p. 506 (1997).
15 IARC, *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Zeolites other than Erionite*, IARC, *Lyon*, Vol. **68**, p. 307–333 (1997).
16 FDA, *Code of Federal Regulations*, Title 21, Volume 3, revised as of 1 April, 2015, cites; 21CFR182.2729 [Online]. Available: http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=182.2729 [15 September 2016].
17 GL 32-1999, *Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods*. Codex Alimentarius Commission. [Online]. Available: http://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FStandards%252FCAC%2BGL%2B32-1999%252Fcxg_032e.pdf [10 August 2016].
18 European Food Safety Authority (EFSA) Panel on Food Contact Materials, Enyzmes, Flavourings and Processing Aids (CEF), *EFSA J* **11**:3155 (2013).
19 European Food Safety Authority (EFSA), The Panel of Additives and Products or Substances used in Animal Feed (FEEDAP), *EFSA J* **11**:3039 (2013).
20 EPA, Potential Nano-Enabled Environmental Applications for Radionuclides. [Online]. Available: https://nepis.epa.gov/Exe/ZyNET.exe/P1005GR1.txt?ZyActionD=ZyDocument&Client=EPA&Index=2006%20Thru%202010&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C06THRU10%5CTXT%5C00000012%5CP1005GR1.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=7 [10 August 2016].
21 Ilgren EB, Breña MO, Larragoitia JC, Navarrete AL, Breña F, Krauss E *et al*, A reconnaissance study of a potential emerging Mexican mesothelioma epidemic due to fibrous zeolite exposure. *Indoor Built Environ* **17**:496–515 (2008).
22 Virta RL, Zeolites (Natural). [Online]. U.S. Geological Survey, Mineral Commodity Summaries, January 2015. Available: https://minerals.usgs.gov/minerals/pubs/commodity/zeolites/mcs-2015-zeoli.pdf [12 September 2016].
23 Ryan P, Dihle M, Griffin S, Partridge C, Hilbert T, Taylor R *et al*, Erionite in road gravel associated with interstitial and pleural changes an occupational hazard in Western United States. *J Occup Environ Med* **53**:892–898 (2011).
24 Rom W, Casey K, Parry W, Mjaatvedt C and Moatamed F, Health implications of natural fibrous zeolites in the intermountain west. *Environ Res* **30**:1–8 (1983).
25 Breck DW, *Zeolite Molecular Sieves*. Wiley, New York, NY (1974).
26 Chen NY, *Shape Selective Catalysis in Industrial Applications*, 2nd edn. Marcel Dekker Inc., New York, NY (1996).
27 Busca G, *Heterogeneous Catalytic Materials: Solid State Chemistry, Surface Chemistry and Catalytic Behavior*. Elsevier Science, San Francisco, CA (2014).
28 Meier WM, Olson DH and Baerlocher C, Atlas of zeolite structure types. *Zeolites* **17**:1–230 (1996).
29 Armbruster T and Gunter ME, Crystal structures of natural zeolites, in *Natural Zeolites: Occurrence, Properties, Application*, ed. by Bish DL and Ming DW. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society, Chantilly, VA, Vol. 45, pp. 1–57 (2001).
30 Gottardi G and Galli E, *Natural Zeolites*. Springer-Verlag, Berlin (1985).
31 Gaines RV, Skinner HC, Foord EE, Mason B and Rosenzweig A, *Dana's New Mineralogy*. John Wiley & Sons, Inc. New York, NY (1997).
32 Mindat, *Nickel-Strunz Classification – SILICATES (Germanates) 10th edition* [Online]. Available: https://www.mindat.org/strunz.php?a=9 [13 July 2016].
33 Alp E, *Transalkylation and disproportionation of aromatic compounds over zeolite catalysts*. Master's Thesis, Ankara University Graduate School of Natural and Applied Sciences Department of Chemical Engineering (2005).
34 Eyde TH and Holmes DA, Zeolites, in *Industrial Minerals & Rocks: Commodities, Markets, and Uses*, 6th edn, ed. by Kogel JE, Trivedi NC, Barker JM and Krukowski ST. Society for Mining, Metallurgy, and Exploration Inc, Littleton, CO, pp. 1–26 (2006).
35 Korunic Z, Diatomaceous earths, a group of natural insecticides. *J Stored Prod Res* **34**:87–97 (1998).
36 Fields PG and Korunic Z, The effect of grain moisture content and temperature on the efficacy of diatomaceous earths from different geographical locations against stored-product beetles. *J Stored Prod Res* **36**:1–13 (2000).
37 Subramanyam B and Roesli R, Inert dusts, in *Alternatives to Pesticides in Stored-Product IPM*, ed. by Subramanyam B and Hagstrum DW. Kluwer Academic Publishers, Boston, MA, pp. 321–380 (2000).
38 Arthur FH, Immediate and delayed mortality of *Oryzaephilus surinamensis* (L.) exposed on wheat treated with diatomaceous earth: effects of temperature, relative humidity and exposure interval. *J Stored Prod Res* **37**:13–21 (2001).
39 Athanassiou CG, Vayias BJ, Dimizas CB, Kavallieratos NG, Papagregoriou AS and Buchelos C, Insecticidal efficacy of diatomaceous earth against *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae) and *Tribolium confusum* du Val (Coleoptera: Tenebrionidae) on stored wheat: influence of dose rate, temperature and exposure interval. *J Stored Prod Res* **41**:47–55 (2005).
40 Athanassiou CG, Kavallieratos NG and Meletis CM, Insecticidal effect of three diatomaceous earth formulations, applied alone or in combination, against three stored-product beetle species on wheat and maize. *J Stored Prod Res* **43**:330–334 (2007).
41 Kljajic P, Andric G, Adamovic M and Golic MP, Laboratory evaluation of insecticidal effectiveness of a natural zeolite formulation against *Sitophilus oryzae* (L.), *Rhyzopertha dominica* (F.) and *Tribolium castaneum* (Herbst) in treated wheat, in *Proceedings of the 10th International Working Conference on Stored Product Protection*, 27 June to 2

July 2010, Estoril, Portugal, ed. by Carvalho MO, Fields PG, Adler CS, Arthur FH, Athanassiou CG, Campbell JF *et al.*, Julius-Kuhn-Archive, Julius Kühn-Institut, Berlin, pp. 863–868 (2010).
42 Kljajic P, Andric G, Adamovic M, Bodroza-Solarov M, Markovic M and Peric I, Laboratory assessment of insecticidal effectiveness of natural zeolite and diatomaceous earth formulations against three stored-product beetle pests. *J Stored Prod Res* **46**:1–6 (2010).
43 Korunic Z, *Mycotoxins problems in stored grains, in* The Proceedings of the Seminar Medunarodno savjetovanje tehnologa susenja i skladistenja, Zavod za prehranbenu tehnologiju, Poljoprivredni Fakultet Zagreb*, January 1992, Stubicke Toplice* (1992).
44 Vayias BJ, Athanassiou CG, Korunic Z and Rozman V, Evaluation of natural diatomaceous earth deposits from south-eastern Europe for stored-grain protection: the effect of particle size. *Pest Manag Sci* **65**:1118–1123 (2009).
45 Golob P, Current status and future perspectives for inert dusts for control of stored product insects. *J Stored Prod Res* **33**:69–79 (1997).
46 Cook DA and Armitage DM, Efficacy of a diatomaceous earth against mite and insect populations in small bins of wheat under conditions of low temperature and high humidity. *Pest Manag Sci* **56**:591–596 (2007).
47 Pezzutti R, Effects of dry air on some beetles infesting stored cereals, in Second Symposium on Pest Control in Food Processing Plant and the Protection of Food Stuffs, Piacenza, Italy, ed. by Domenichini G. Tipolitografia, Piacenza, Italy. pp. 135–144 (1979).
48 Rumbos CI, Sakka M, Berillis P and Athanassiou CG, Insecticidal potential of zeolite formulations against three major stored-grain insects: particle size effect, adherence ratio and effect of test weight on grains. *J Stored Prod Res* **68**:93–101 (2016).
49 Haryadi Y, Syarief R, Hubeis M and Herawati I, Effect of zeolite on the development of *Sitophilus zeamais* Motsch, in *Stored Products Protection. Proceedings of the Sixth International Working Conference on Stored-Product* Protection, 17–23 April 1994, Canberra, Australia, ed. by Highley E, Wright EJ, Banks HJ and Champ BR. CAB International, Wallingford, pp. 633–634 (1994).
50 Andric GG, Markovic MM, Adamovic M, Dakovic A, Golic MP and Kljajic PJ, Insecticidal potential of natural zeolite and diatomaceous earth formulations against rice weevil (Coleoptera: Curculionidae) and red flour beetle (Coleoptera: Tenebrionidae). *J Econ Entomol* **105**:670–678 (2012).
51 Perez JC, Pino O, Ramirez S and Suris M, Evaluation of natural products in the control of *Lasioderma serricorne* (F.) (Coleopteran: Anobiidae) in chickpea under laboratory conditions. *Rev Proteccion Veg* **27**:26–32 (2012).
52 Daniel C, Dieraurer H and Clerc M, The potential of silicate rock dust to control pollen beetles (*Meligethes* spp.). *IOBC-WPRS Bull* **96**:47–55 (2013).
53 Mulla MS, Thavara U, Tawatsin A and Chompoosri J, Procedures for evaluation of field efficacy of slow-release formulations of larvicides against *Aedes aegypti* in water-storage containers. *J Am Mosq Control Assoc* **20**:73–92 (2004).
54 Ming DW and Allen ER, Applications in agronomy and horticulture, in *Natural Zeolites: Occurrence, Properties, Application*, ed. by Bish DL and Ming DW. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society, Chantilly, *VA*, vol. **45**, pp. 619–654 (2001).
55 Petrovic AM, Barrett WC, Larsson-Kovach IM, Reid CM and Lisk DJ, Downward migration of metalaxyl fungicide in creeping bentgrass sand lysimeters as affected by organic waste, peat and zeolite amendments. *Chemosphere* **37**:249–256 (1998).
56 Kvachantiradze M, Tvalchrelidze E, Kotetishvili M and Tsitsishvili T, Porous materials in environmental friendly processes. *Stud Surf Sci Catal* **125**:731 (1999).
57 Casal B, Lami L, Quadra LMJ, Alvarez A and Ruiz-Hitsky E, Synthesis of 2,4-D ester herbicides. *New routes using inorganic solid supports. Green Chem* **1**:199–204 (1999).
58 Garcia-Hernandez JE, Notario-del-Pino JS, Arteaga-Padron IJ and Gonzalez-Martin MM, Phosphate and potassium fixation on a phillipsite-rich tuff as a slow-release fertiliser. Experiments with KH_2PO_4. *Agrochimica* **32**:1–11 (2002).
59 Sopkova A and Mezes P, About the inclusion of an insecticide in zeolitic materials. *J Therm Anal* **46**:471–478 (1996).
60 Sopkova A and Janokova E, *An insecticide stabilized of the zeolite type, properties and possibility of their application*. Thesis, University Pavol Jozef Safarika, Kosice (1997).
61 Scrinis G and Lyons K, The emerging nano-corporate paradigm: nanotechnology and the transformation of nature, food and agri-food systems. *Int J Sociol Food Agric* **15**:22–44 (2007).
62 Barik TK, Sahu B and Swain V, Nanosilica-from medicine to pest control. *Parasitolol Res* **103**:253–258 (2008).
63 Yang FL, Li XG, Zhu F and Lei CL, Structural characterization of nanoparticles loaded with garlic essential oil and their insecticidal activity against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). *J Agric Food Chem* **57**:10156–10162 (2009).
64 Bhattacharyya A, Bhaumik A, Pathipati UR, Mandal S and Epidi TT, Nanoparticles – a recent approach to insect pest control. *Afr J Biotechnol* **9**:3489–3493 (2010).
65 Neethirajan S and Jayas DS, Nanotechnology for the food and bioprocessing industries. *Food Bioprocess Technol* **4**:39–47 (2010).
66 Prasad R, Kumar V and Prasad KS, Nanotechnology in sustainable agriculture: present concerns and future aspects. *Afr J Biotechnol* **13**:705–713 (2014).
67 Stadler T, Buteler M and Weaver DK, Novel use of nanostructured alumina as an insecticide. *Pest Manag Sci* **66**:577–579 (2010).
68 Kabak B, Dobson AD and Var I, Strategies to prevent mycotoxin contamination of food and animal feed: a review. *Crit Rev Food Sci Nutr* **46**:593–619 (2006).
69 Phillips, TD, Sarr BA, Clement BA, Kubena LF and Harvey RB, Prevention of aflatoxicosis in farm animals via selective chemisorptions of aflatoxin, in *Mycotoxins, Cancer and Health*, ed. by Bray GA and Ryan DH. Louisiana State University Press, Baton Rouge, FL, pp. 223–237 (1991).
70 Galvano F, Piva A, Ritieni A and Galvano G, Dietary strategies to counteract the effects of mycotoxins: a review. *J Food Prot* **64**:120–131 (2001).
71 Phillips TD, Kubena LF, Harvey RB, Taylor DR and Heidelbaugh ND, Hydrated sodium calcium aluminosilicate: a high affinity sorbent for aflatoxin. *Poult Sci* **67**:253–260 (1988).
72 Mumpton FA and Fishman PH, The application of natural zeolites in animal science and aquaculture. *J Anim Sci* **45**:1188–1203 (1977).
73 Masimango N, Remacle J and Ramaut J, The role of adsorption in the elimination of aflatoxin B1 from contaminated media. *Eur J Appl Microbiol Biotechnol* **6**:101–105 (1978).
74 Davidson JN, Babish JG, Delaney KA, Taylor DR and Phillips TD, Hydrated sodium calcium aluminosili cate decrease the bioavailability of aflatoxin in the chicken. *Poult Sci* **66**:89 (1987).
75 Ramos AJ and Hernandez E, Prevention of aflatoxicosis in farm animals by means of hydrated sodium calcium aluminosilicate addition to feedstuffs. *A review. Anim Feed Sci Technol* **65**:197–206 (1997).
76 Huff WE, Kubena LF, Harvey RB and Phillips TD, Efficacy of hydrated sodium calcium aluminosilicate to reduce the individual and combined toxicity of aflatoxin and ochratoxin A. *Poult Sci* **71**:64–69 (1992).
77 Kubena LF, Harvey RB, Huff WE, Elissalde MH, Yersin AG, Phillips TD *et al.*, Efficacy of a hydrated sodium calcium aluminosilicate to reduce the toxicity of aflatoxin and diacetoxyscirpenol. *Poult Sci* **72**:51–59 (1993).
78 Ledoux DR, Rottinghaus GE, Bermudez AJ and Alonso-Debolt M, Efficacy of a hydrated sodium calcium aluminosilicate to ameliorate the toxic effects of aflatoxin in broiler chicks. *Poult Sci* **78**:204–210 (1999).
79 Kubena LF, Huff WE, Harvey RB, Yersin EG, Elissalde MH, Witzel DA *et al.*, Effects of a hydrated sodium calcium aluminosilicate on growing turkey poults during aflatoxicosis. *Poult Sci* **70**:1823–1830 (1991).
80 Harvey RB, Phillips TD, Ellis J, Kubena LF, Huff WE and Petersen HD, Effects on aflatoxin M1 residues in milk by addition of hydrated sodium calcium aluminosilicate to aflatoxin contaminated diets of dairy cows. *Am J Vet Res* **52**:1556–1559 (1991).
81 Smith EE, Phillips TD, Ellis JA, Harvey RB, Kubena LF, Thompson J *et al.*, Hydrated sodium calcium aluminosilicate reduction of AFM1 residues in dairy goat milk. *J Anim Sci* **72**:677–682 (1994).
82 Dwyer MR, Kubena RB, Harvey LF, Mayura K, Sarr AB, Buckley S *et al.*, Effects of inorganic adsorbents and cylcopiazonic acid in broiler chicks. *Poult Sci* **76**:1141–1149 (1997).
83 Phillips TD, Dietary clay in the chemoprevention of aflatoxin-induced disease. *Toxicol Sci* **52**:118–126 (1999).
84 Parlat SS, Yildiz AO and Oguz H, Effect of clinoptilolite on performance of Japanese quail *Coturnix japonica* during experimental aflatoxicosis. *Br Poult Sci* **40**:495–500 (1999).

85 Schell TC, Lindemann MD, Kornegay ET, Blodgett DJ and Doerr JA, Effectiveness of different types of clays for reducing the detrimental effects of aflatoxin-contaminated diets on performance and serum profiles of weanling pigs. *J Anim Sci* **71**:1226–1231 (1993).
86 Tomasevic-Canovic M, Dacovic A, Markovic V and Stojcic D, The effect of exchangeable cations in clinoptililite and montmorillonite on the adsorbtion of aflatoxin B1. *J Serb Chem Soc* **66**:555–561 (2001).
87 Tomasevic-Canovic M, Dakovic A, Rottinghaus G, Matijasevic S and Duricic M, Surfactant modified zeolite-new efficient adsorbents for mycotoxins. *Micro Meso Materials* **61**:173–180 (2003).
88 Adamovic M, Magdalena T-C, Milosevic S, Aleksandra D and Lemic J, The contribution of mineral adsorbent in the improvement of animal performance, health and quality of animal products. *Biotechnol Anim Husb* **5–6**:383–395 (2003).
89 Huwig A, Freimund S, Kappeli O and Dutler H, Mycotoxin detoxication of animal feed by different adsorbents. *Toxicol Lett* **122**:179–188 (2001).
90 Avantaggiato G, Solfrizzo M and Visconti A, Recent advances on the use of adsorbent materials for detoxification of *Fusarium* mycotoxins. *Food Addit Contam* **22**:379–388 (2005).
91 Jouany JP, Methods for preventing, decontaminating and minimizing the toxicity of mycotoxins in feeds. *Anim Feed Sci Technol* **13**:342–362.
92 Torii K, Utilization of natural zeolites in Japan, in *Natural Zeolites: Occurrence, Properties, Use*, ed. by Sand LB and Mumpton FA. Pergamon Press, Elmsford, NY, pp. 235–244 (1978).
93 Mazur GA, Medvid GK and Grigora TI, Use of natural zeolites for increasing the fertility of light textured soils. *Pochvovedenie* **10**:73–75 (1984).
94 Allen ER, Ming D, Hossner L, Henninger D and Galindo C, Growth and nutrient uptake of wheat in a clinoptilolite-phosphate rock substrate. *Agron J* **87**:1052–1059 (1995).
95 Bernardi ACC, Oliviera PPE, Monte MMB, Polidoro JC and Souza-Barros F, Brazilian sedimentary zeolite use in agriculture, in *Proceedings of the 19th World Congress of Soil Science: Soil Solution for a Changing World*, 1–6 August 2010, Brisbane, Australia, ed. by Gilkes R and Prakongkep N, pp. 37–40. Elecronic Proceedings: International Union of Soil Sciences, Brisbane, Australia (2010).
96 Rodriguez-Fuentes G, Ed. by Rodriguez-Fuentes G and Andres Gonzales J, *Zeolites '91: Memoirs of the 3rd International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Part 1*, Havana, 1991. Sine nomine, Sine loco, pp. **25–36** (1993).
97 Ivanova TN, Bercovich YA, Mashinsky AL and Meleshko GI, The 1st space vegetables have been grown in the Svet greenhouse using controlled environmental conditions. *Acta Astronaut* **29**:639–644 (1993).
98 Ming DW, Barta DJ, Golden DC, Galindo C Jr, Henninger DL, *Natural Zeolites '93: Occurrence, Properties, Use. International Committee on Natural Zeolites*, ed. by Ming DW and Mumpton FA. Brockport, New York, pp. 505–513 (1995).
99 Klaus A, Grubisic M and Niksic M, Influence of some zeolits on the growth of mycelia of industrial fungi *Agaricus bisporus, Ganoderma lucidum, Pleurotus ostreatus* and *Lentinus edodes*, in *First South East European Congress of Chemical Engineering, Book of Abstracts*, ed. by Skala D, Grbavčić Ž and Dekanski A, 25–28 September 2005. Faculty of Technology and Metallurgy, *Belgrade, p.* **94** (2005).
100 Malekian R, Abedi-Koupai J and Eslamian SS, Influences of clinoptilolite and surfactant-modified clinoptilolite zeolite on nitrate leaching and plant growth. *J Hazard Mater* **185**:970–976 (2011).
101 Er G, The effect on dry matter yıeld and mıneral content of corn (*Zea mays* L. Akpinar, Karadeniz Yildizi) plants applied diatomite and zeolite to acidic soils. MSc Thesis, Ataturk University, Graduate School of Natural and Applied Sciences Department of Soil Science (2011).
102 Michalev T and Petrov I, The removal of heavy metal ions by synthetic zeolites: a review. *Proc Univ Ruse* **51**:79–84 (2012).
103 Tsalidas CD, Dimoyiannis D and Samaras V, Effect of zeolite application and soil pH on cadmium sorption in soils. *Commun Soil Sci Plan* **28**:1591–1602 (1997).
104 Ghuman GS, Sajwan KS and Alva AK, Remediation of an acid soil using hydroxyapatite and zeolites, in *Proceedings of the Extended Abstracts from the 5th International Conference on the Biogeochemistry of Trace Elements*, 11–15 July 1999, Vienna, Austria, ed. by Wenzel WW, Adriano DC, Alloway B, Doner HE and Keller C. International Society for Trace Element Research, Vienna, Austria, pp. 1018–1019 (1999).
105 Chlopecka A, Adriano DC, Inactivation of metals in polluted soils using natural zeolite and apatite, in *Proceedings of the Extended Abstracts from the 4th International Conference on the Biogeochemistry of Trace Elements*, ed. by Iskandar SE, Hardy AC and Chang GM. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, pp. 415–416, (1997).
106 Papaioannou D, Katsoulos PD, Panousis N and Karatzias H, The role of natural and synthetic zeolites as feed additives on the prevention and/or the treatment of certain farm animal diseases: a review. *Micropor Mesopor Mat* **84**:161–17 (2005).
107 Shariatmadari F, The application of zeolite in poultry production. *World's Poult Sci J* **64**:76–84 (2008).
108 Pond WG and Yen JT, Reproduction and progeny growth in rats fed clinoptilolite in the presence or absence of dietary cadmium. *B Environ Contam Tox* **31**:666–672 (1983)
109 Pond WG and Yen JT, Protection by clinoptilolite or zeolite NaA against cadmium-induced anemia in growing swine. *Proc Soc Exp Biol Med* **173**:327–337 (1983).
110 Garcia-Lopez R, Elias A and Menchaca MA, The utilization of zeolite by dairy cows. *II. effect on milk yield. Cuban J Agric Sci* **26**:131 (1992).
111 Onagi T, Treating experiments of chicken droppings with zeolitic tuff powder. 2. Experimental use of zeolite-tufts as dietary supplements for chickens. *Rep Yamagata Stock Raising Inst* 7–18 (1966).
112 Kondo N, Wagai B, Experimental use of clinoptilolite-tuff as a dietary supplement for pigs. *Yotonkai* May 1–4 (1968).
113 White JL and Ohlrogge AJ, Ion exchange materials to increase consumption of non-protein nitrogen in ruminants. Canadian Patent: 939186, January 2. 30 pp. (1974).
114 Katsoulos Z and Christodoulopoulos R, Effect of long-term dietary supplementation with clinoptilolite on performance and selected serum biochemical values in dairy goats. *Am J Vet Res* **70**:346–352 (2009).
115 Deligiannis K, Lainas T, Arsenos G, Papadopoulos E, Fortomaris P, Kufidis D *et al.*, The effect of feeding clinoptilolite on food intake and performance of growing lambs infected or not with gastrointestinal nematodes. *Livest Prod Sci* **96**:195–203 (2005).
116 Smith TK, Influence of dietary fiber, protein and zeolite on zearalenone toxicosis in rats and swine. *J Anim Sci* **50**:278–285 (1980).
117 Kanyilmaz M, The use of natural zeolite (Clinoptilolite) in gilthead sea brem (*Sparus aurata*) culture. PhD Thesis, Cukurova University, Adana (with english abstract) (2012).
118 Roque NC, Saad FMOB, Santos JPF, Ebina FS, Chizzotti AF, Silva RC *et al.*, Increasing levels of zeolite and Yucca schidigerain diets for adult cats. *R Bras Zootec* **40**:2471–2475 (2011).
119 Santos JPF, Saad FMOB, Maia GVC, Pires CP, Reis JS, Roque NC *et al.*, Inclusion of *Yucca schidigera* and zeolite in dog feed: influence on mineral excretion. *Arq Bras Med Vet Zootec* **65**:918–926 (2013).
120 Noori M, Zendehdel M and Ahmadi A, Using natural zeolite for the improvement of soil salinity and crop yield. *Toxicol Environ Chem* **88**:77–84 (2006).
121 Ciambelli P, Corbo P, Lumare F and Porcelli C, *Zeo-Agriculture: Use of Natural Zeolites in Agriculture & Aquaculture*, ed. by Pond WG and Mumpton FA, Westview Press, Boulder, CO, pp. 251–258 (1984).
122 Mojzis J, Nistiar F and Kovac G, Tissue and erythrocyte cholinesterase inhibition and protection by clinoptilolite pretreatment. *Vet Hum Toxicol* **36**:533 (1994).
123 Adriano DC, *Trace Elements in the Terrestrial Environment*, 1st edn. Springer, New York, NY (2001).
124 Ozdemir M and Floros JD, Active food packaging technologies. *Crit Rev Food Sci Nutr* **44**:185–193 (2004).
125 Kuley E, Ozogul F, Durmus M, Gokdogan S, Kacar C, Ozogul Y *et al.*, The impact of applying natural clinoptilolite (zeolite) on the chemical, sensory and microbiological changes of vacuum packed sardine fillets. *Int J Food Sci Tech* **47**:1977–1985 (2012).
126 Garcia M, Casariego A, Diaz R and Roblejo L, Effect of edible chitosan/zeolite coating on tomatoes quality during refrigerated storage. *Emir J Food Agric* **26**:238–246 (2014).
127 Rhim JW, Hong SI, Park HM and Perry KW, Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. *J Agric Food Chem* **54**:5814–5822 (2006).
128 Tutova EG, Fundamentals of contact-sorption dehydration of labile materials. *Dry Technol* **6**:1–20 (1988).
129 Djaeni M, Bartels P, Sanders J, van Straten G and van Boxtel AJB, Process integration for food drying with air dehumidified by zeolites. *Dry Technol* **25**:225–239 (2007).

130 FAO and IPGRI, *Genebank Standards.* Food and Agriculture Organization and International Plant Genetic Resources Institute, Rome (1994).
131 Somado EA, Sanchez IM, Nwilene F, Sie M, Ogunbayo AA, Sanni K *et al.*, Comparative studies of drying methods on the seed quality of interspecific NERICA rice varieties (*Oryza glaberrima* × *Oryza sativa*) and their parents. *Afr J Biotechnol* **5**:1618–1624 (2006).
132 Hay FR, Thavong P, Taridno P and Timple S, Evaluation of zeolite seed 'Drying Beads®' for drying rice seeds to low moisture content prior to long-term storage. *Seed Sci Technol* **40**:374–395 (2012).
133 Crespo G, Febles G and Aguiar M, Effect of zeolite on the performance of seeds during storage I. Dolicahos (*Lablab purpureus*), soybean (*Glycine max*) and forage sorghum (*Sorghum bicolor*). *Cuban J Agr Sci* **27**:217–222 (1993).
134 Osorio-Revilla G, Gallardo-Velazquez T, Lopez-Cortes S and Arellano-Cardenas S, Immersion drying of wheat using Al-PILC, zeolite, clay, and sand as participate media. *Drying Technol* **24**:1033–1038 (2006).
135 Solarov MB, Kljajic P, Goran A, Bojana F, Olivera S, Prazic-Golic M *et al.*, Application of principal component analysis in assessment of relation between the parameters of tehcnological quality of wheat grains treated with inert dusts against rice weevil (*Sitophilus oryzae* L.). *Pestic Phytomed* **26**:385–390 (2011).
136 Korunic Z, Fields PG, Kovacs MI, Noll JS, Lukow OM, Demianyk CJ *et al.*, The effect of diatomaceous earth on grain quality. *Postharvest Biol Tech* **31**:373–87 (1996).
137 Korunic Z, Rapid assessment of the insecticidal value of diatomaceous earths without conducting bioassays. *J Stored Prod Res* **33**:219–229 (1997).
138 IARC, *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Supplement 7, Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs, Vols 1 to 42*. IARC, Lyon, p. 203 (1987) [Online]. Available: http://monographs.iarc.fr/ENG/Monographs/vol68/ [15 September 2016].
139 FDA GRAS List, *Database of Select Committee on GRAS Substances (SCOGS) Reviews*. *Sodium Aluminasilicates* [Online]. Available: http://www.accessdata.fda.gov/scripts/fcn/fcnDetailNavigation.cfm?rpt=scogsListing &id=281 [15 September 2016].
140 SCOGS, *Database of Select Committee on GRAS Substances (SCOGS) Reviews. Sodium Aluminasilicates* [Online]. Available: http://www.accessdata.fda.gov/scripts/fcn/fcnDetailNavigation.cfm?rpt=scogsListing&id=281 [15 September 2016].
141 Virta RL, Zeolites. [Online]. USGS Minerals Yearbook-2004. Available: https://minerals.usgs.gov/minerals/pubs/commodity/zeolites/zeolimyb04.pdf [10 September 2016].
142 Holmes D, Zeolites, in *Industrial Minerals and Rocks*, ed. by Carr DI, Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, pp. 1150–1151 (1994).
143 USGS, *Chemical and Morphological Comparison of Erionite from Oregon, North Dakota, and Turkey*. [Online]. Available: https://pubs.usgs.gov/of/2010/1286/pdf/OF10-1286.pdf [10 September 2016].

