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IMPORTANCE OF ALUMINOSILICATE MINERALS IN SAFE FOOD PRODUCTION

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In this paper certain natural minerals (zeolite, apatite, diatomite, sepiolite, kaolin etc.) are emphasized, thanks to their physical and chemical characteristics, in natural or modified/refined form, they can be very good adsorbents of: mycotoxins, toxic metals, radionuclide, ammonia and other unacceptable matters. They can help by providing nutrients to plants and animals. Eminently there are certain convictions that particular aluminosilicate minerals, because of high content of SiO_2 and convenient content of pH, can be used for drying and storage protection of wheat from insects. Although they react slower than synthetic insecticides, main benefit for their apply as inert farrows is that they have natural source and that they have non-toxic influence on mammals. It is concluded that aluminosilicate minerals lessen or eliminate detrimental influence of suppressive factors. Those factors destruct reproductive capabilities and helth of herbs and animals, also quality of their products. According to this aluminosilicate minerals are contributing to the production of food with high quality and safety and environmental protection.

Key words: safe food; harmful matters; aluminosilicate raw mineral materials; soil; plants; animals

ЗНАЧЕЊЕ НА АЛУМОСИЛИКАТНИ МИНЕРАЛНИ СУРОВИНИ ВО ПРОИЗВОДСТВОТО НА БЕЗБЕДНА ХРАНА

Во трудот е даден приказ на карактеристиките на важните природни алумосиликатни минерални суровини и на можноста за нивно користење во производството на безбедна храна. Истакнато е дека одредени природни минерални суровини, благодарение на нивните физичко-хемиски карактеристики (зеолит, бентонит, апатит, диатомит, сепиолит, каолин и др.) во дадени услови, во природен и/или модифициран/облагороден облик, можат да бидат добри атсорбенти на микотоксини, токсични метали, радионуклиди, амонијак и други штетни материи, а можат да бидат извор на минерални елементи неопходни за растенијата и животните. Истакнато е дека постојат сосема извесни потврди дека одредени алумосиликатни минерални суровини, поради високата содржина на SiO_2 и поволен pH (диатомејска земја, зеолит), можат да се користат и како средство за заштита на житата од складишните инсекти. Иако нивното дејство е побавно од синтетичките инсектициди, доминантната предност на нивната примена како инертни прашоци е дека се од природно потекло и немаат токсично влијание врз цицачите. Заклучено е дека алумосиликатните суровини го ублажуваат и/или го елиминираат штетното влијание на супресивните фактори кои ги загрозуваат производните и репродуктивните способности и здравјето на растенијата и животните, како и за квалитетот на производите, придонесувајќи така за производство на безбедна храна и за аштита на животната средина.

Клучни зборови: безбедна храна; штетни материи; алумосиликатни минерални суровини; почва; растенија; животни

1. INTRODUCTION

Human activities in the field of industry, energy production, and exploitation of ore deposits, agriculture, military engagement, traffic and urbanization continually generate primary and secondary organic, inorganic and radioactive pollutants which are contributed to the permanent degradation of soil with long-term effects on biodiversity, food quality and safety. Annually in the European Union about 30 million tons of health harmful waste is produced (50–60% remains in the soil)

and about 7 million hectares of agricultural land is lost. Increasing content of radioactive uranium and toxic metals (chromium, cadmium and strontium) in the mineral fertilizer is evident. It is known that the pollutants in mineral fertilizers in easily dissolvable form, can attain and accumulate in the floral organs (especially in the vegetative), and biogenic elements, and the use of such food may have negative consequences on the health of people and animals (Stojanović, 2008).

Aluminosilicate natural mineral raw materials, thanks to their physical-chemical characteristics (zeolite, bentonite, apatite, diatomite, sepiolite, koalin, etc.), in natural or modified form, in given conditions, can be a good adsorbent of toxins, toxic metals (Pb, Cu, Cd, Mn, Zn, Cr, Ni), radionuclides (Cs, U, Ra, I), ammonia, carbon dioxide, methane and other organic pollutants. They have been used as a corrector of soil acidity, chemical and physical-mechanical properties of soil, donor's macro and microelements, funds for the preservation of the quality and germinability seeds, carriers of active substances of pesticides, biologically active substances, reaction filters, filtered and rheological additives. In this way, at the same time, they contribute limiting influence of suppressive factors that prevents the realization of production and reproductive potential of plants and animals and threaten their health and quality of products.

The aim of this paper is to point out these problems and draw attention to new knowledge about the possibilities of aluminosilicate mineral raw materials in the production of safe food.

2. USAGE OF ALUMINOSILICATE MINERAL RAW MATERIALS IN THE PRODUCTION OF SAFE FOOD

Natural mineral raw materials can't be used without the chemical, physical, crystallochemical and/or thermal treatment. Previously they must be investigated and then with appropriate technological procedures to prepare for implementation.

Zeolite. Natural and/or modified zeolite can be used as an adsorbent of mycotoxins, radionuclides, toxic metals, ammonia, harmful gases smelly and humidity in the stalls. Zeolite preserves the optimal value of pH in rumen and improves the immunity of newborn mammals (Tomašević et al. 2003; Adamović et al, 2003; Dobiec et al., 1994; Kubena et al., 1993, and others). It is most applicable as a mycotoxin adsorbent. Tomašević et al. (2001) have found that the natural zeolite with a high proportion of clinoptilolite (over 80%) effectively adsorbs aflatoxins (B_1, B_2 and G_2). On the other hand, zeolite whose surface was modified with ammonium ion, adsorbed well zearalenone, ochratoxin A and T-2 toxin, beside aflatoxins (Table 1).

Table 1

Index of major mycotoxins adsorption with natural zeolite (%)

	Natural zeolite	Modified zeolite
Aflatoxin B_1	99	99
Aflatoxin B_2	85	–
Aflatoxin G_2	82	–
Zearalenone	33	94
Ochratoxin A	40	96
T-2 toxin	35	83

Animals that have been fed with mycotoxins contaminated food, with addition of adsorbents based on the zeolite, have a higher yield of meat, milk and eggs (3-–7%), also have better performance using food (2–5%), less losses, more vitality, better reproductive performance, immune status and better health and less residua of harmful substances in contrary to the animals that received the same food, but without adsorbents. Modified zeolite complement to silage corn (0.2%) was influenced on better silage fermentation, decrease number of mould and quantity of zearalenone, T-2 toxin and DAS (Adamović et al., 2003).

Due to the large affinity towards the radionuclides cesium (^{137}Cs) zeolite can be used to remove caesium from contaminated water and soil, (Abusafa and Yucel, 2002, and others). Matijašević et al. (2006) have found that modified natural zeolite (ammonium ions or amin) can be an effective tool for removing uranium from solution, in the interval pH 3–8 (Table 2).

Positive impact of natural and modified zeolites was established on the vegetative development of mycelium mushroom (*Agaricus blazei. Ganoderma lucidum, Lentinula edodus, Pleurotus ostreatus*) like earlier realization of the yield and higher quantity of yield. It was also noticed better

chemical composition of the mushroom. The mushroom (*Pleurotus ostreatus* and *Agaricus biosporus*) cultivated in substrates with addition of modified zeolite (0.2% and 0.5%) was found higher content of minerals (Ca, P, K, Na, Mg, Fe, and Cu). Addition of natural and modified zeolite in overlay for growing mushroom *Agaricus biosporus*, influenced on increase (10%) of mushroom (Adamović et al., 2006; Anita Klaus et al., 2005).

Table 2

Results uranyl ion adsorption with organically modified zeolite

Organically modified zeolite	Organic phase mmol M^+/100g.	Adsorption index, %	C_{fil}, mg/dm^3
Zeolite + octadecyl dimethyl benzyl ammonium ion	2	20.4	38.06
	5	24.1	36.25
	10	50.4	21.71
Zeolite + hexadecyl dimethyl benzyl ammonium ion	2	29.8	33.50
	5	92.0	3.81
	10	98.0	0.95
Zeolite + octadecyl amin	2	25.0	35.83
	5	50.5	23.65
	10	97.7	1.19

M^+ – organic cation, which is activated zeolite; C_{fil} – *non*-adsorptive concentration uranyl ion in the filtrate (at the beginning of the experiment it was 49.2 mg/dm^3)

Bentonite. Thanks to its characteristics, similary as zeolite, it can be used as an adsorbent of mycotoxins. Bentonite shows a good affinity to aflatoxin. In investigation of Ramos et al. (1996), where bentonite was added in the environment (fluid) similar to gastric contents, (1%) adsorption aflatoxins (B_1, B_2, G_1 and G_2) was close to 100%. Applebaum et al. (1982) have found that the addition of bentonites in feed mixture (2%) contributed to the reduction of aflatoxin M_1 in milk for 89%. Incorporating different amounts of Na-bentonites in the ration of pigs that contained 800 ppb aflatoxin B_1, resulted with increased average daily gain and food consumption (Lindeman et al., 1993). The optimum amount of Na-bentonites was 0.5%. Na-bentonite on the feed mixture (1.1%) had a positive impact on residua reduction of aflatoxin M_1 in milk in the amount of 64.6% (Yermolenko et al., 1996). If bentonites were included in ration for cows (Piva et al., 1988), they reduced contamination of milk with caesium (^{137}Cs and ^{134}Cs). Addition of bentonites 300 g/day in meal effected on the radionuclide reduction in the milk of 50%, and with dose of 600 g/day the reduction was 80%. Bentonite has a very good affinity for the binding of ammonia and toxic metal. It is used as agens for preserving the optimal values of pH (6–7) content of rumen. Adamović et al. (2009) have found that the 1.5% addition of bentonites in the feed mixture for calves, impact on increasing the quality of pellet, increase in growth, consumption and utilization of food (Table 3).

Table 3

Results of application of bentonites in diet calves

Index	Control group	Sample group of 1.5% bentonites in mixture
Daily gain, kg	0.972	1.084
Consuming mixture, kg/day	1.81	1.84
Consumption mixture, kg/gain, kg	1.86	1.70

It wasn't found bad influence bentonite on important biochemical parameters of blood. It is a well known ability application of bentonites as a carrier of non protein nitrogen (from urea). This ability is used as basis for ruminant food products.

It is known that the bentonite (as well as zeolite and sepiolit) in natural or modified form can be used as a reaction filter for the purification of water contaminated with pesticides (Andrades et

al., 2004). The same minerals can be used as carriers of active substances in the production of pesticides with slower reliving of active components (Celis et al., 2005).

Diatomite. It is very effective adsorbent uranium ions. Results diatomite efficiency, in comparison with natural and modified bentonites (Milojković et al, 2009), is given in Table 4.

Diatomite and organically modified bentonite can be used for "in situ" remediation contaminated soil with uranium ion. They are efficient, cheap and available in larger quantities. It is recommended to use these adsorbents for soil with a high content of uranium as a layer or geological barrier. Using adsorbents with faster action (diatomite, organically modified zeolite and bentonite) with a slower acting adsorbent (natural phosphate), the synergistic effect will be achieved by a mixture of reactive materials as a permanent solution "in situ" stabilization of uranium ions in soil.

Table 4

Efficiency diatomite and bentonite in the uranyl ion adsorption

Type of materials	pH at the beginning	Adsorption 7.day, %	pH 7. day	Adsorption 14.day, %	pH 14.day
Diatomite	8.03	89.76	6.96	81.12	6.97
Bentonite	8.39	47.77	8.07	42.49	7.96
Organically modified bentonite	7.27	89.46	7.49	89.64	7.5

In the study of Kljajić et al., 2007, the product for the protection of storage insects on the basis of diatomite, contained 83.7% amorphous SiO_2, with an average particle size of 5 μm. That was used for suppression of rice weevil *Sitophilus oryzae* and red flour beetle *Tribolium castaneum*. The test sample in a dose of 0.15 g/kg of wheat for the types of *S. oryzae*, and 0.30 g/kg of wheat for the type *T. castaneum* gave better results than inert dusts based on zeolite and organozeolite used in the amount of 0.50 g/kg wheat (Table 5).

Table 5

Dying out of adult insects , %

Inert dusts	dust, g/kg wheat	7. day	14.day
Sitophilus oryzae			
Zeolite	0.50	66± 1.73	100
Organozeolite	0.50	40 ± 1.63	87 ± 2.06
Diatomite	0.15	69 ± 1.50	100
Tribolium castaneum			
Zeolit	0.50	34 ± 3.70	95 ± 1.26
Organozeolite	0.50	23 ± 1.26	72 ± 3.16
Diatomite	0.30	83 ± 2.06	100

Diatomite is used as a thermal, hydroisolation and filtration product, as a holder of chemical active substances, for making uninflammable pastes, plastic compound, as sound isolation, in production of water glass, enamel, varnish, cement, nitroglycerine etc. Similar to bentonite and zeolite, diatomite can be added to food for animals. In animal food like addition diatomite contributes not only for adsorption of mycotoxins but also for recovery from diarrhea.

Apatite. Interesting results were obtained in remediation soil contaminated with uranium. Phosphate-induced metal stabilization, using apatite, is based on the mechanism precipitation of a new phase. Apatite is then chemically bonded in a new low solubility phase (Ksp = 10^{-49}) uranium-phosphate-autonite which is stable across a wide range of geological conditions for millions of years. Investigations show that the mechanism which forms a new phase immobilized uranium at least ten times more than sorption. Apatite has a buffer effect, which contributes to the efficiency of precipitation of metal. Apatite acts as a biostimulator, because during the long period of time it provides phosphorus and organic substances which stimulate microbial reactions and has the ability of semi-surface adsorption. In the investigation of Stojanović et al. 2008, it was found that the

phosphate concentrate (14.43% P_2O_5) in relation to the natural phosphate (34.95% P_2O_5) had better immobilization properties. That is why as one of the possible solutions is recommended in the remediation technology of soil (Table 6).

Process of mechanochemical activation adsorbent whose adsorption ability in relation to the natural apatite increased by about 70%, which, during the first 7 days, adsorption reaches approximately 90% of the uranium from solution.

Table 6

Sorption of uranyl ion with different forms of phosphate, %

pH	30. day		60. day	
	Nature phosphate	Phosphate concentrate	Nature phosphate	Phosphate concentrate
7	18.07	48.53	37.19	91.92
	24.61	81.01	72.38	95.19
5.5	44.74	97.17	64.04	~100%
	94.54	97.96	98.09	~100%

Kaolin. Because of its crystal properties, kaolin application in agriculture is limited. It is used as a carrier of low cost pesticides. In animal feed industry it is used (as well as sepiolite) against formation balling, for improving the transport of food (fluid transport) and as a binder for pelleting food. Kaolin is used in the production of ceramics, rubber, paints, plastics and paper.

3. CONCLUSION

Aluminosilicate mineral raw materials (zeolite, bentonite, apatite, diatomite, kaolin, sepiolite, etc.) in natural or modified/refined form can adsorb and bind mycotoxins, radionuclides, toxic metals and other harmful substances. In that way, they at the same time contribute to the protection of resources for the production of safe food (land, water and air) and also to the health of people, plants and animals and maintaining the quality of the environment.

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