Mechanochemical modification of natural zeolite to improve the adsorption and hydrolysis properties of metsulfuron-methyl

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Abstract. For the first time, potentially active samples of zeolites were obtained by their mechanochemical modification with the polysaccharide arabinogalactan and aerosil. The most positive effect on the desorption properties of aerosil addition is shown.

1. Introduction
Modern society is at a sufficiently high level of development, so that, along with the achievements of science and technology in the field of consumption, we can think about the accompanying technogenic and agrogenic pollution of the surrounding soil and water, the issues of rational nature management, monitoring and forecasting the state of the environment, preventing and eliminating its pollution.

The use of chemical reagents, in particular for protecting plants from pathogens and pests, is an integral part of modern agriculture, which must be distinguished by high productivity. The volume of pesticides used is growing from year to year. At the same time, from 70 to 90% of chemicals at the time of their application enters the soil and this leads to soil pollution with pesticides [1], which accumulate in the environment and affect its characteristics and the totality of species of living organisms in it. In this connection, active attention is attracted by studies on soil detoxification as a result of chemical hydrolysis, photolysis under the influence of light and microbiological transformation under the influence of microorganisms [2-5].

An essential role in these studies is played by materials that are artificially introduced into the environment and are capable of acting as catalysts for decomposition and sorbents of toxic substances. Such materials potentially include minerals of the zeolite group.

The crystal structure of natural and artificial zeolites is formed by tetrahedral groups SiO2 / 4 and AlO2 / 4, united by common vertices into a three-dimensional framework, pierced by cavities and channels (windows) 2-15 angstroms in size. The open frame-cavity structure of [AlSi] O4– zeolites has a negative charge, which is compensated by counterions (metal cations, ammonium, alkylammonium and other ions introduced by the ion exchange mechanism) and easily dehydrated water molecules.
The following properties of zeolites are distinguished, due to which they are widely used:
adsorptive - the ability to absorb and release various substances,
ion exchange - the ability to exchange cations,
catalytic - the ability to speed up chemical reactions.

Each type of zeolite is characterized by a certain size of windows, therefore, molecules of other substances are absorbed and passed (during filtration) by zeolites selectively. This phenomenon is called the molecular sieve effect.

There are examples of various uses of zeolites [6-14]. Zeolites are widely used in water purification devices as adsorbents, ion exchangers, molecular sieves; used as electron donors and acceptors. Used in sorption vacuum pumps. Zeolites are also widely used as catalysts for many petrochemical and oil refining processes and as heterogeneous catalysts. They are widely used in analytical chemistry as zeolite-modified electrodes; for gas detection; for separation and concentration methods. Due to their pozzolanic activity, zeolites are used in construction as an active mineral additive for cements, concrete and mortars. It is also used in life support systems of space stations (MIR, ISS, Skylab) to absorb carbon dioxide released during breathing.

Zeolite adsorbents are used many times, which is important from an economic point of view.

The use of zeolites to remove the toxicity of soils contaminated with herbicide residues is a new approach, and there are no such works in the literature.

Mechanical activation - activation of solids by their mechanical treatment. Milling in shock, shock-abrasion or abrasion modes leads to the accumulation of structural defects, an increase in surface curvature, phase transformations, and even amorphization of crystals, which affects their chemical activity. In cases where the rate of accumulation of defects exceeds the rate of their disappearance, mechanical activation occurs.

The mechanical activation of materials in mills is the most common technological operation in modern production and is aimed at creating materials with the required properties.

Mechanochemical treatment, mechanical milling and alloying - mechanical treatment of solid mixtures, as a result of which plastic deformation of substances occurs, mass transfer is accelerated, the mixture components are mixed at the atomic level and the chemical interaction of solid reagents is activated.

Mechanical alloying provides mass transfer and chemical interaction of powders of pure elements, compounds or alloys. With the help of mechanical alloying, it is possible to obtain substances in both crystalline and amorphous states. In addition, as a result of mechanical fusion, complete mutual solubility in the solid state of such elements can be achieved, the mutual solubility of which is negligible under equilibrium conditions.

Mechanochemical action is one of the most productive methods for obtaining large quantities of nanopowders of various materials - metals, alloys, intermetallic compounds, ceramics, composites. The average particle size of the resulting powders is from 200 to 5-10 nm, which has a significant effect on the properties of the final material.

The aim of this work was to study the parameters of mechanochemical modification of natural zeolite to improve the metsulfuron-methyl (MSM, a herbicide used to destroy a wide range of weeds in cereal crops - winter wheat and barley) adsorptive and hydrolyzing properties.

2. Materials and methods
In the literature there is only one work by Bottero and co-authors (1994), who, while studying the sorption of the herbicide atrazine on various zeolites, found that the chitosan-modified zeolite "ZSM 5" better adsorbs atrazine.

Continuing this line of research, we studied the sorption activity towards MSM of mechanically modified zeolites of the following compositions:
- mechanically activated zeolite (Zeolite 1);
- zeolite mechanically modified with the polysaccharide arabinogalactan (Zeolite 2) with the ratio "zeolite: AG = 10: 1";
The mechanochemical modification of the ZP with the selected modifiers (AG and AS) at a weight ratio of the components (1:10) was carried out in the metal and capralon drums of the LE-101 roller mill with metal balls 25 mm in diameter at a modulus of 1:16 and a drum rotation speed of 60-70 rpm. / min for 1-2 hours. In this case, nanodispersed solid dispersions (TD) of the composition ZP / AS (1/10) and ZP / AG (1/10) were obtained in the form of loose light green powders.

To solve the problem, we used:
- natural zeolite (ZP), with a content of 60-70% clinoptilolite, produced by ALSIS, Yekaterinburg, RF;
- arabinogalactan (AG) from Siberian larch Larix sibirica according to TU 9363-021-39094141-08, series 02042013;
- aerosil (AC) - according to GOST 14922-77 - colloidal silicon dioxide, which is a very light white highly dispersed micronized powder with a large specific surface area of the powder.

The ability of mechanically modified zeolites to adsorb MSM was studied by their joint mechanical treatment with further study of the desorption process of MSM from the obtained TD of the following compositions:
- zeolite: AG: MSM = 10: 1: 0.1;
- zeolite: aerosil: MSM = 10: 1: 0.1.

The study of the sorption properties of the obtained TD was carried out by extraction of samples (weighed portion of 2 g in 10 g of distilled water in a closed 50 ml conical flask) with sampling of acetonitrile after 30; 90; 180; 1260 and 1320 min. The analysis of samples for the content of MSM was carried out by HPLC. In this case, an Agilent 1100 liquid chromatograph (Germany) with a UV detector and an analytical column Diasfer-100-C18 (4.6 * 250 mm, 5 μm) were used. Eluent composition 70:30 (0.05 M phosphoric acid / acetonitrile) was fed at a rate of 1 ml / min in an isocratic mode. Column oven temperature 250C, UV detection at 230 nm. Data reception and processing were carried out using the Chemstation program.

3. Results and discussion
According to preliminary data on the assessment of the sorption activity of mechanically modified zeolites, it can be seen that, according to the sorption activity, they are in the following order:
- Zeolite 2> Zeolite 1> Zeolite 3.

The obtained results of the analysis of solid dispersions are recalculated and shown in Figures 1 and 2.
According to the results of HPLC analysis (Figures 1-2), it can be concluded that the TD of the "zeolite-aerosil" composition holds MSM more strongly than the TD of the "zeolite-AG" composition. The extraction time is also less important in the case of samples with Aerosil.

4. Conclusions
For the first time, potentially active samples of zeolites were obtained by their mechanochemical modification with the polysaccharide arabinogalactan and aerosil. The most positive effect on the desorption properties of aerosil addition is shown.

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