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USING OF SILICATE MATERIALS FOR SEWAGE SORPTION TREATMENT FROM HEAVY METALS

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The article presents the research results of using different types of silicate minerals, their modified forms for sewage sorption treatment. Their physical and chemical properties, the mechanisms of action and sorption efficiency of the widespread natural minerals are characterized in this paper.

Key words: silicate minerals, sorption, zeolites, mica, vermiculite, clays, heavy metals, isotopes, sewage.

Подано результати досліджень використання різних типів силікатних мінералів, їх модифікованих форм для сорбційного очищення стоків. Охарактеризовано їх фізико-хімічні властивості, механізми дії та ефективність сорбції найпоширеніших мінералів.

Ключові слова: силікатні мінерали, сорбція, цеоліти, слюди, вермикуліт, глини, важкі метали, ізотопи, стічні води.

Introduction

Sorption method is the most promising method among the known effective and inexpensive reagentless methods of sewage treatment according to the relevant quality standards. However, it is true assumption that a prolonged adsorbent functioning as the water purifier and the possibility of its regeneration must be carried out directly in the filtering structures.

Effective base for obtaining adsorbents with high surface activity of grains and purposefully adjustable properties is the natural aluminosilicate minerals as well as the artificially obtained (or modified natural) ones, because it is possible to incorporate into their structure any additives of the organic and mineral origin. These additives will provide the grain surface with the required properties.

Ukraine has many deposits of silicate materials. But not all the deposits virtually have minerals with relevant sorption characteristics. However, even this potential is used only for a quarter. Among the natural silicate minerals and sorbents there are clay materials (montmorillonite, saponite, natronite, sokolite and other clays such as bentonite, kaolin, palygorskite, palygorskite-morilonite); mica materials (hydromica,

vermiculite, glauconite, perlite); monolithic rocks: perlites, zeolites and their subgroups (clinoptilolite, modernite) and so on [1, 2].

Problem statement

For wider applicability, increase of selectivity and efficiency of natural sorbents their modifying (coating the surface of natural sorbents with organic substances with their subsequent high-temperature pyrolysis; hydrophobization by organic-silicon substances of the expanded minerals or the thermooxidation of the modified minerals at 320-350 °C (perlite); modifying of zeolites by manganese dioxide (clinoptilolite); acid activation of clays [3], etc.) is possible. However, the mechanisms of action of these factors-activators on the minerals structure cause a lot of questions that have not been studied thoroughly yet.

Aim and objectives of the research are the following: to investigate the sorption capabilities and mechanisms of action of natural and modified silicate sorbents intended for the industrial sewage treatment from the man-triggered pollutants, in particular heavy metals.

Materials

Both natural and modified materials are mainly used in processes of water treatment by filtration. The natural materials (quartz sand, anthracite), are traditionally used for loading filters, ensure the removal of suspended solids from water, mechanical admixtures and, as a rule, are rather inert to the real solutes and colloids. Thus, when using the clinoptilolite (group of zeolites) as a filtering material at water treatment stations instead of quartz sand, the filtering rate increases 1,5-1,7 times, the filtrate turbidity decreases by 0,1-1,0 mg/dm³, chromaticity decreases by 1-8 degrees [4].

The efficiency assessment of the natural sorbents is carried out by considering their versatility, i.e. the effectiveness of the specific sorbent with regard to a particular substance. Herein, it should be taken into account the diversity of the mechanisms of action of various adsorbents[5].

Natural mineral-based sorbents, as a rule, start to physically adsorb by the entire surface of the adsorbent. Adsorbate molecules are kept on the surface of the adsorbent by the intermolecular force through the catalytic principle (the energy of the molecules activity in the minerals lattice is getting reduced), forming an adsorption layer thickness of one molecule (monomolecular adsorption) and retaining the property to diffuse parallel to the surface and leave it due to the thermal motion[6].

All natural sorbents have the shape selective properties, adsorbing only molecules of a specific size. So, for example, mineral sorbents of the zeolite group have the appropriate cell sizes: analcime is 2,2 Å; shozibite is 3,9 Å; modernite and clinoptilolite – 4,0 Å; erionite– 5,0 Å; foshazite– 9,0 Å.

The adsorption process in natural sorbents usually passes through the cation-exchange principle with high-quality selection to the ions of the big sizes (Caesium-137, Strontium-90 and others). The isomorphism in the structure of complex silicates causes cation-exchange capacity of the latter. During the replacement of ions to the multicharged ones (for example, Fe³⁺) on the surface of complex silicates there are formed the active coordinatively unsaturated centres which play an important role in acid-base and redox heterogeneous catalysis.

Another source of the exchange centers is subacidic hydroxyl group of Si–OH and of Al–OH on the side faces and edges, which, depending on the pH, to some extent are also exchanged to the cations. It is suggested that up to 80% of the exchange cations are in the interlayer space and up to 20% on the lateral face [2].

The composition of a number of clay sorbents of the silicate class changes in a range of silicates and aluminosilicates of calcium, sodium, magnesium, iron and other metals, including montmorillonite, beidellite and other minerals. Due to the fact that the crystal structure of the rock-forming minerals differ from each other, their physical and chemical properties, including adsorption and ion-exchange properties, emerge in different ways. So, cation-exchange properties are

determinative to bentonite clays, glauconites, zeolites. Thixotropic and catalytic properties are determinative to palygorskites, bentonites, saponites.

The effective natural sorbents are the zeolite class minerals, which are natural crystals of aluminosilicates, i.e. tectoaluminates of alkaline and alkaline-earth elements which contain the water molecules in their structure ($M_x/n \cdot [(AlO_2)_x \cdot (SiO_2)_y] \cdot y H_2O$). Characteristic peculiarities of the zeolites is that the water in their structure tends to evolve from mineral and turn back without destroying its structure.

The elementary building block of the zeolite crystal lattice is silica-aluminoxygenous tetrahedra in which the oxygen atoms are located in the centre or on the top of the pyramid. Tetrahedra creates a complex structure of cuboctahedron.

Among all the explored zeolite deposits in Ukraine (Hanychske, Podpoleshanske, Verkhnie, Novoselytske, Vulkhovske and others) only a few can be attributed to the deposits of the effective sorption materials. Zeolites in the above mentioned deposits have low parameters of porosity (6–8 %), water absorption (1.5–5 %) and volume capacity (3–6 mEq/100 g).

Research has shown that two zeolite deposits in Ukraine have high sorption characteristics with respect to strontium and cesium. For example, the clinoptilolite tuff of Sokernitske deposit in the Transcarpathian region absorbs Cs-137 (78–94%) and Sr-90 (35–60%) from the environment by the fraction of 0.071–0.25 mm and a specific surface area of 15–18 m²/g. Clinoptilolite-modernite tuff of the Rodyshchynska plane can absorb the radioactive Cs-137 (approximately 97.5–99.8%) and Sr-90 (5–10%) by the fraction of 0.071–0.25 mm [7].

The high sorption capacity of the Transcarpathian clinoptilolite, the ability to absorb both the low and high concentration of Zn(II) and the most effective of the cation forms of Zn^{2+} and $ZnOH^+$, the existence of the effective sorbent (solutions of hydrochloric, nitric, sulphuric acids and strontium nitrate) give grounds to suggest this sorbent for water purification from Zn (II) ions, separation of these ions from the technological solutions as well as for the concentration of Zn (II) ions at the preparation of water samples for the analysis [8].

Through the research on biotite, phlogopite, vermiculite [2, 9] and other clay minerals it is found out that the modified micaceous materials have a defective surface and, consequently, a large number of transport pores (mesopores, micropores, macropores) that contribute to a significant increase in sorption activity of the material. The pores of different size, different nature of the pore surface wetting determine the multifunctionality of the modified sorbent, its ability to absorb the organic chemicals and ion exchange.

Another example of a new efficient modified silicate-based sorbent is a *Versoil* bioreactive vermiculite for the oil spills removing from the water surface (purification of aquatories of the sea and river ports), from soil; for the liquidation of the undersea pipelines accidents; for ensuring the safety measures in the offshore oil extraction; for the industrial and sewage waters purification from the multicomponent pollution in treatment facilities; for the localization of heavy metals, radionuclides and petroleum products in the soil substrates. According to the results of [9], the value of the *Versoil* total exchange capacity is 1.9 mEq/g (at the 86–98% purification level and the sorbent losses after the collection and regeneration that comprise 3%).

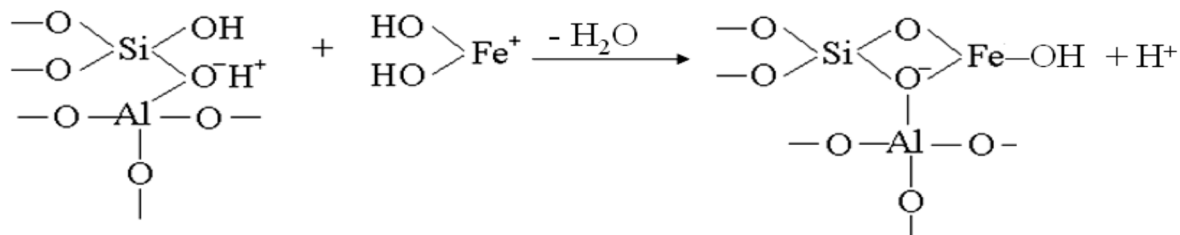
Versoil is especially effective as the excipient of the oil oxydic microflora. Bioreactive sorbent addition, a complete adaptation of *Pseudomonas putida* culture, its high oil oxydic activity made it possible to cope with the emergency admission of a large number of petroleum products into the buffer pool [9].

A large specific surface of the biofilm on the sorbent reduces in several orders the load of the organic substances per unit of the surface area of the attached microorganisms. This leads to the formation of the specific, qualitatively different microflora being a part of the biofilm, capable for more complete oxidation of pollutants. The consequence of the above mentioned is the intensification of the biochemical oxidation of hydrocarbons in water and bottom sediments.

Bioreactive sorbent use significantly accelerates the oil spill in reservoirs. Biosorbent addition reduces the oil level in all the forms: in the soil, in water and in bottom sediments; that corresponds to the modern views on the problem of using inexpensive simple methods of the environment purification from oil which stimulate the natural self-purification processes.

The layer silicates contained in different types of clay minerals and loams are divided into two main types of ion-exchange centers: the exchange cations that are located on the minerals basal plane and torn silica- or alumooxygenous bonds that are located on the side faces [10, 11].

Research of the sorption isotherms allows to make a conclusion about the adsorption mechanisms. So, by Fe (III) ionadsorption it is likely that the chemical sorption occurs on the most samples (as indicated by the H-type isotherm) where the interaction between iron ions and hydroxyl ions of siliconoxygenous tetrahedra, forming 2- and 3-layer packets in clay minerals. Consequently, iron ions bind to the surface with the hydroxocomplexes formation, and so occurs their incorporation into the adsorbent structure. In addition, one should not exclude the physical deposition of the insoluble Fe(OH)₃ formed as a result of suspension contact with the air oxidants when mixing [12]. By the contact of the “solution-adsorbent” mixture with oxygen there is a partial oxidation of iron ions. After that the deposition on clay matrix of the equivalent amounts of the insoluble iron hydroxide occurs on possible scheme:



The dependence of the adsorption properties of the samples from the qualitative and quantitative indicators of their mineral composition is experimentally confirmed. According to the presented data [12] if the clay structures contain montmorillonite it will improve their ability to absorb ions from the solutions, and the prevalence of kaolinite in this rock composition defines poor adsorption capacity of sorbents. It is especially noticeable by the absorption of single-charged and highly hydrated ammonium ions from the low concentration solutions; under such conditions kaolinite sorbents use is impractical. However, by the absorption of closely related iron ions in terms of low concentrations such rocks can be used quite successfully.

The influence of acid and alkaline activation of montmorillonite and kaolinite sorbent groups is determined the sorption capacity decrease using mineral acids as activators and the low efficiency of alkaline activation in both groups of sorbents [12]. By the conducted research

Promising investigations are state the possibilities of the ceramic technology using for processing of clay- and zeolite slurries to dispose and safely store the water purification wastes of radioactively contaminated water from the isotopes. According to the studies [13, 14] the physical and mechanical characteristics of the ceramic samples and the research results of the processes of leaching by various aggressive environments confirm the high strength of the radionuclides fixation in the ceramic matrices, which can hold Cs-137 isotopes in a safe immobilized state for long time.

The modifying of the clay minerals by the surface-active substances (SAS) is one of the methods used to change the hydrophilic and hydrophobic balance of the natural layered silicates surface. Thus, due to the freeze-drying of the clay mineral surface it is possible to extract the diverse organic pollutants from waters [14].

For the environmental purposes of removing the heavy metals and radionuclides it is widely used the sorbents on the basis of clinoptilolite, mordenite, gybsite, diatomite, etc. with a rather high cation exchange capacity [15, 16]. However, the efficiency of sorption extraction of uranium compounds (VI) by natural minerals is not complete because this element can be in natural waters both in the cationic and anionic and neutrally charged forms; and the probability of the anionic form evolution increases significantly in the underground waters which migrate through the carbonate rocks [17]. The authors [4, 13] carried out a study of the sorption process characteristics of the anionic and cationic forms of uranium (VI) and its carbonate complexes on the clay mineral layered structure (montmorillonite) depending on the degree of its modification by the cationic SAS. Modifying of the layered silicates by the cationic SAS allows to regulate the hydrophilic and hydrophobic balance of the silicate surface in a wide range and contributes to a significant increase of the clay mineral absorption capacity with respect to such dangerous toxins as the uranium compounds by sorption of its cationic and anionic forms [4, 13, 18].

Conclusions

The use of domestic natural silicate materials and their modified forms for sewage sorption treatment from heavy metals and radionuclides should take the first place in eco-technologies today. It is confirmed by the numerous experimental data. However, the mechanisms of sorption, ion exchange, adsorption materials efficiency and their partial selectivity to certain ions in the certain conditions are quite individual in each case. Therefore, the use of a certain type of sorption mineral needs the preliminary ecological characteristics of the water bodies or sewage discharges for the selection of the most effective sorbent material.

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