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PURIFICATION OF SEWAGE FROM SALTS OF HEAVY METALS BY NATURAL ZEOLITE

It is investigated prospect of using of natural zeolite for purification of sewages from salts of heavy metals. It is well-proven that maintenance of heavy metals in purified sewage reply requirements of SNIP for drinking-water in Ukraine.

Key words: a zeolite, adsorption, sewage, heavy metals.

Досліджено перспективність використання природного цеоліту для очищення стічних вод від солей важких металів. Доведено, що вміст важких металів у очищеній стічній воді відповідає вимогам СНиП на питну воду в Україні.

Ключові слова: цеоліт, адсорбція, стічні води, важкі метали.

Raising of problem

Every year volumes of polluted natural water and sewage grows as a result of anthropogenic influence and need to search a new safe methods of their purification. Principal polluters of environment are heavy metals: iron, copper, molybdenum, cobalt, manganese, nickel, cadmium, lead, zinc, chrome etc. Most of them belong to the so-called oligoelements - chemical elements which are in alive creatures in low concentrations (thousandth particles of percent and below). These elements, as vitamins, are necessary for a human organism for its normal functioning. A lack of oligoelements in organism, especially of heavy metals, causes different diseases.

During process of evolutional development alive organisms produce the special mechanisms for the accumulation of heavy metals, as there were not enough of them in environment. When people began intensively pollute an environment, peculiarity to «accumulate» entailed the surplus piling up of heavy metals in human organism. The same «accumulate» peculiarity of human organism blockade taking out of surplus of heavy metals from him [1].

Heavy metals belongs to the priority polluters, looking after which is obligatory in all environments. A term “heavy metals”, that characterizes the wide group of polluters, during last time is wide used. As a criteria of belonging are used a lot of characteristics: atomic mass, density, toxicness, prevalence in natural environment, degree of involve in natural and technogenic cycles. In works, dedicated problems of natural environment pollution and ecological monitoring, nowadays to the heavy metals belongs more than 40 metals of the periodic system with atomic mass over 50 atomic units. According to N. Reymers’s classification to heavy belongs metals with density more than 8 g/sm^3. Thus, to heavy metals belongs Pb , Cu, Zn, Ni, Cd, Co, Sb, Sn, Bi, Hg.

Ions of metals are necessary components of natural reservoirs. Depending on conditions of environment (pH, oxidation and restoration potential, presence of ligands) they exist in different degrees of oxidization and composite various inorganic and metal organic connections, which can be a truly dissolved, colloid-dispersible or composite mineral and organic suspensions.

A lot of metals forms strong complexes with organic; these complexes are one of the principal forms of elements migration in natural waters. Most organic complexes are created according to khelathic cycles and are steadfast. Complexes, created by ground acids with salts of iron, aluminium, titan, uranium, vanadium, copper, molybdenum and other heavy metals, are relatively well soluble in the conditions of neutral, poorly sour and poorly alkali environments. Therefore metal organic complexes are able to migrate in natural waters on enough distances. It is especially important for poorly mineralized and superficial waters in which formation of other complexes are impossible [1].

For understanding of factors which regulate the concentration of metal in natural waters, its chemical reactionary ability, biological availability and toxicness, it is necessary to know not only gross maintenance but also particle of free and connected forms of metal.

The transition of metals in a water environment in metal complex form has three consequences:

- can be increase total concentration of ions of metal due to passing of him to solution from the ground deposits;
- membrane permeability of complex ions can substantially differ from permeability of the aquated ions;
- toxicness of metal as a result of complex forming can strongly change.

So, khelathic forms of Cu, Cd, Hg are less toxic, than free ions.

Pollution sources of waters by heavy metals are sewage of galvanic workshops, enterprises of mining, black and coloured metallurgy, machine-building plants. Heavy metals is component of fertilizers and pesticides and can get in reservoirs together with sewages from agricultural lands.

Increasing of concentration of heavy metals in natural waters is often related to other types of pollutions, for example, from protoxide. The falling of acid fallouts helps lowering of pH value and transition of metals from the occlusioned on mineral and organic matters state to free.

Existing chemical and physical and chemical methods of purification of polluted water (chlorinating, ozonization, osmose etc.) which include the active chemical operating or physical influence on water, allow to delete from it polluted components, by lowering physical and chemical properties of water and destruct natural balance of dissolved salts in it .

At the same time in nature exists safe methods of water purification with smoothing in it of salt balance during passing of water through surface and underground horizons of minerals which have enormous adsorption characteristics in relation to anthropogenic toxic matters (clays, aluminium silicates, zeolites etc.). Addition of such natural minerals-adsorbents during purification of sewage and pollution water on the stage of sedimentation not only will allow to release from dangerous anthropogenic pollution admixtures by adsorption without chemical reagents but also to improve a structure and mineralization of water [1].

Analysis of the last researches and publications

Harmful chemical elements and substances get in reservoirs, worsening them the sanitary state and causing the necessity of the special deep water purification before using of it for economic-drinkable and some industrial aims [1].

A lot of admixtures can't be removed from water mechanically or by traditional methods of water purification, as sedimentation, coagulation and flotation, not neutralized during bioscrubbing. It stipulates introduction to the complex technological scheme of water preparation of the stage of the sorption purification. As a rule, this stage is the final stage in the technological process of water purification [3].

Sorption method is the most effective method of purification of sewage which contain the admixtures of different origin and which enables to attain the deep purification to the norms of GDK. He allows to remove pollutions in a wide range, practically to the concentration more low from GDK regardless of their chemical firmness. Thus the second pollutions are absent. Hence it follows that it is perspective of developing of filtration and sorption apparatus, intended for local purification of drinking-water [2,3].

Nowadays it is possible to talk about that in Ukraine there enough sources of raw materials of zeolite rocks in Transkarphatian, Khmelnytsk and Rivne regions. However they differ between itself even in the beds of the same deposit as in color, by mechanical durability, % contents of zeolite, chemical composition and properties, and by biological effect. This natural mineral which has unusual ability to absorb, to retain and return different chemical and nourishing substances, toxins and ions, depending on necessities.

Sufficient technical durability of zeolite, firmness to the effect of high temperatures, aggressive environments and ionizing radiations, selectivity to large cations of alkaline, alkaline - grounded, rare, dissipated and some heavy metals, absorb ability and sieve effect is all of stipulates the wide use of mineral.

Zeolite as useful fossil has extraordinarily wide sphere of the use in industry and agriculture. Zeolites are successfully used in construction, petroleum chemistry, for deep drainage and purification of gas and liquid streams, separation of mixtures of hydrocarbons with different structure, purification of water streams from cations of heavy metals and absorption of radio nuclides in atomic energy, as catalysts of chemical reactions in the processes of cracking, during receipting motor oils etc.

To satisfy demands of production which is widely developed today, to find other ways of decisions of production tasks, are researching not popular rocks. Researching its quality we will be able more rationally uses rocks in the different spheres of industry.

Experimental researches

One of most widespread in Ukraine natural absorbents are zeolites, so-called molecular sieves. Zeolites are crystalline hydrogen aluminium silicates, have a porous structure, are well liquids and solutions absorbent. Interest of their using as active absorber, for example, for purification of sewage, grows [2].

Zeolites are a group of minerals of volcanic and sediment origin, framework aluminium silicates of alkaline and alkaline - grounded metals. More than 40 structural types of natural zeolites are known at present time. Common for all minerals of zeolites group is presence of three-dimensional aluminium-silicon-oxygen framework, which forms the systems of cavities and canals, in which are located alkaline, alkaline-grounded cations and molecules of water. Cations and molecules of water are poorly related to framework and can partly or fully involve (to retire) by an ionic exchange and un-hydration, thus without destruction of framework of zeolite. They are capable preferentially and quickly absorb salts which are dissolved in water, which extraction by other method usually is very difficult, for example, salts of lead, iron, cadmium, ions of copper, zinc, barium, cobalt, silver and other metals, radio-active ions of caesium, nitrates, selecting (trucking an ion for an ion – hence follows - ionic exchange) in the same solution other salts – preferably untoxic chlorides of sodium, magnesium and calcium [4].

Unaquatic zeolite is a microcellular crystalline «sponge», volume of pores makes up of 50% of volume of zeolite framework. Such «sponge» which has a diameter of ingates from 0,3 to 1 nm (depending on the type of zeolite) is a high-activity adsorbent.

Zeolites belongs to the group of framework, which framework makes by the tops of tetrahedrons of AlO_4 and SiO_4. Composition of zeolites is presented by empiric formula - $Me_{2/n}O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}y3H_2O$,

where x – always equally or more than 2, so as tetrahedrons of AlO_4 unite only with the tetrahedrons of SiO_4; n - is valency of cation, Me – Na, K, Ca, Mg; y - is a number of molecules of water.

We research chemical composition of zeolite from Sokirnick city of Transkarphation region, which belongs to microcellular framework aluminium-silicates in inner-crystallise space of which are accommodated exchange cations of alkaline metals and molecule of water, presented at table. 1. This work is dedicated to researching of adsorption properties of Sokirnick city zeolite in purification of sewages from salts of heavy metals.

Table 1

Chemical composition of zeolite of Sokirnick city of Transkarpation region

Composition of chemical elements	AI	Si	S	K	Ca	Ti	Mn	Fe	Sr	Cs	Ba
Mass particle %	4,810	60,738	0,249	8,497	17,096	0,671	0,167	6,933	0,177	0,100	0,335

Composition of tap water is taken for an analysis presented in table. 2

Table 2

Chemical composition of tap water

Composition of chemical elements	Mg	Si	S	Cl	Ca	Fe	Sr
Mass particle %	5,430	3,400	15,894	13,907	59,801	0,095	0,181

As objects for studding of processes of adsorption of Ni, Cu ions by a zeolite in the static mode were used different types of polluted water.

On the first stage of researches by x-ray photography fluorescence were determined component composition, and analysed selected samples of water.

Plenitude of exception of Sokirnick city zeolite of ions of metals, were investigated in static mode, to understand possibilities of using of this natural adsorbent for water purification on the stage of sedimentation. For this purpose in conical retorts which contained 1dm^3 water was added 0,5 ml of the probed solution with the concentration of Cu=1mg/sm^3 and concentration of Ni=1 mg/sm^3, that became equal GDK in sewages. After it were gathered the samples of water, which are presented in tables 4 and 6, and added 50 grammas of zeolite mass and abandoned on 1 day. A liquid in retorts were periodically mixed. Then gathered solutions and analysed their maintenance on the x-ray photography fluorescence analyzer «Expert 3L». Selective results of researches are presented in tables. 3—7.

Table 3

Composition of salts of heavy metals in water before and after its contact with Sokirnick city zeolite

Ions of metals	Concentration, g/m^3		
	Borne	Before contact with a zeolite	After contact with a zeolite
Cu	0,50	0,29	0,08
Ni	0,50	0,14	0,06

* Conditions of investigation: mass of absorbent- 50 grammas; volume of water — 1000 ml; time of contact — 1 day.

Table 4

Chemical composition of water with the concentration of Cu 0,5 g/m^3

Composition of chemical elements	Mg	Si	S	Cl	Cu	Ca	Fe	Sr
Mass particle %	7,328	3,919	11,576	3,111	0,290	73,624	0,092	0,062

Table 5

Chemical composition of water with the concentration of Cu 0,5 g/m^3 after a contact with a zeolite

Composition of chemical elements	Mg	Si	S	Cl	Cu	Ca	Fe	Sr
Mass particle %	5,568	3,081	14,947	9,339	0,089	66,065	0,059	-

Table 6

Chemical composition of water with the concentration of Ni 0,5 g/m^3

Composition of chemical elements	Mg	Si	S	Cl	Ni	Ca	Fe	Sr
Mass particle %	4,599	0,685	3,010	1,607	0,135	89,706	0,141	0,118

Table 7

Chemical composition of water with the concentration of Ni 0,5 g/m^3 after a contact with a zeolite

Composition of chemical elements	Mg	Si	S	Cl	Ni	Ca	Fe	Sr
Mass particle %	8,922	2,897	3,758	2,438	0,058	81,739	0,117	0,072

The conducted investigations prove that after the contact of even polluted sewage with Sokirnick city zeolite during the first day, maintenance in it of heavy metals reply GOST requirements for drinking-water in Ukraine.

Exceeded results certify that during the contact of this zeolite with water as a result of ionic exchange between hard and water phases happens enriching of water. Consequently, Sokirnick city zeolite can be used as cheap adsorption material already on the first stages of purification, including sedimentation. Application of zeolite in combination with chlorinating, ozonization, contact coagulation is considerably increase its efficiency. Offered approach is fully un waste, because of a hard phase of zeolite with the absorbed heavy toxic metals can be not utilized in the ground grave-diggers, but to use as a constituent at preparation of hard coverage of roads or in technological construction. It is predefined the irreversible absorption of zeolite of heavy metals and absence of their washing in soils.

Conclusions

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