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SORPTION POSSIBILITIES OF NATURAL ADSORBENTS ZEOLITE AND BENTONITE

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The main objective of our study is to obtain a complex compound from natural adsorbents to purify wastewater with simultaneous sorption of chemical and microbiological substances contained therein, which contribute to disinfection and softening of water, increasing the degree of treated water saturation with calcium, magnesium salts and trace elements, while not requiring the use of sophisticated equipment. The technical result is to create a complex of adsorbents with the sorbing ability of chemical and microbiological pollution, disinfecting and softening water, enriching it with calcium ions, magnesium, sodium, potassium, as well as trace elements.
Keywords: *water, purification, sorption, natural adsorbents, aluminosilicates, heavy metals.*

Біздің зерттеуіміздің негізгі мақсаты суды зарарсыздандыруға және жұмсартуға, тазартылған судың кальций, магний тұздарымен және микроэлементтермен қанығу дәрежесін арттыруға ықпал ететін химиялық және микробиологиялық заттарды бір мезгілде сіңіре отырып, ағынды суларды тазарту үшін табиғи адсорбенттерден күрделі қосылыс алу болып табылады, күрделі жабдықты қолдануды қажет етпей-ақ. Техникалық нәтиже химиялық және микробиологиялық ластанудың сіңіру қабілеті бар, суды зарарсыздандыратын және жұмсартатын, оны кальций, магний, натрий, калий иондарымен, сондай-ақ микроэлементтермен байытатын адсорбенттер кешенін құру болып табылады.
Тірек сөздер: *су, тазарту, сорбция, табиғи адсорбенттер, алюмосиликаттар, ауыр металдар.*

Основной целью нашего исследования является получение комплексного соединения из природных адсорбентов для очистки сточных вод с одновременной сорбцией содержащихся в них химических и микробиологических веществ, которые способствуют обеззараживанию и умягчению воды, повышению степени насыщения очищаемой воды солями кальция, магния и микроэлементами, при этом не требуя применения сложное оборудование. Техническим результатом является создание комплекса адсорбентов, обладающих сорбирующей способностью химических и микробиологических загрязнений, обеззараживающих и умягчающих воду, обогащающих ее ионами кальция, магния, натрия, калия, а также микроэлементами.
Ключевые слова*: вода, очистка, сорбция, природные адсорбенты, алюмосиликаты, тяжелые металлы.*

Currently, water purification is becoming one of the most common technological processes in the world, including Kazakhstan. This determines the particular relevance of the issue of reducing the cost of cleaning drinking water, and sewage. In this regard, a very promising seems the application of natural sorbents, deposits of which are available in Kazakhstan. In the literature appears more and more with about the effectiveness of natural sorbents for disperse impurities, heavy metals, oil and oil products, surface active agents, dyes, radioactive contaminants and others.

The study was intended to determine the methods a promising approach, the creation of new types of modified complex sorbents and an experimental evaluation of the effective the use of a modified complex of natural mineral sorbents, based on zeolite and bentonite, for the purification and conditioning of drinking water and the purification of wastewater.

Technical characteristics of the studied adsorbents:

Bentonite (Mukrynskoye fieldof Almaty region) - natural clay mineral, hydroaluminosilicate, has the property of swelling during hydration (14-16 times). In a confined space for free swelling in the presence of water , a dense gel is formed that prevents further penetration of moisture. This property, as well as non-toxicity and chemical resistance, makes it indispensable in industrial production, construction and many other fields of application.

Natural bedding bentonites usually have a pH of 6-9.5 (for 5% aqueous suspension after settling for 1 hour) and contain less than 2% sodium carbonate ; the total content of interchangeable sodium and calcium does not exceed 80 me/100. There are two types of bentonites:

- Calcium, with a low degree of swelling;
- sodium, with a high degree of swelling (swelling rate less than 7 ml/g or more than 12 ml/g).

Chemical formula: $AI_2 [Si_4O_{10}] (OH)_2 \cdot nH_2O$

Chemical composition: SiO_2 -58.25%; AI_2O_3 -14.27%; Fe_2O_3 -4.37%; FeO-0.5%; Ti_2O -0.36%; CaO-2.07%; MgO-3.67%; P_2O_5 -0.18%; S-0.14%; K_2O-1.2%; Na_2O - 2.25%; PPP-12.19%

Zeolites (Maytobinskoye deposit of Almaty region) - a large group of minerals with similar composition and properties ; aqueous calcium and sodium aluminosilicates of the subclass of frame silicates , with glass or pearlescent gloss , known for their ability to give and reabsorb water depending on temperature and humidity. The most common representatives of the group of zeolites - natrolit, shabazit, geylandit, stilbite (desmin), mordenite, thomsonite, lomontite.

The crystal structure of natural zeolites is formed by the tetrahedral groups $SiO_{2/4}$ and $AlO_{2/4}$, united by common vertices in a three-dimensional framework, permeated with cavities and channels (windows) of 2-15 angstroms . The open frame-cavity structure of zeolites $[AlSi] O_4^-$ has a negative charge, compensated by counterions (metal cations, ammonium, alkyl ammonium and other ions, introduced by the mechanism of ion exchange) and easily dehydrating water molecules.

Chemical formula: Zeolite-clinoptilolite, described by the idealized formula $(KNa,)_4 CaAl_6Si_{30}O_{72} \cdot 24H_2O$ - is a crystalline aqueous aluminosilicate.

Chemical composition: AI_2O_3 - 12.9-13.2%; K_2O - 4.0-4.8%; CaO 1.8-2.4%; V-0.001%; Cu-0.001%; Rb - 0.001%; SiO_2 - 66.2-78.3%; Na_2O - 1.8-2.2%; Fe_2O_3 - 0.8-1.2%; Mn-0.001%; Be-0.001%; As-0.03%.

Materials and research methods

A sorbent based on zeolites modified by ion exchange of silver ions is known for absorption of radioiodine and / or radiocaesium . After ion-exchange modification, the sorbent is additionally treated with acetylene in a gaseous or liquid medium so that its carbon content in carbon is 0.4 - 2, 0 wt. The sorbent is designed specifically for purifying water from strong contamination with radionucleotides , it is effective to purify drinking water, but it does not enrich water with calcium, magnesium salts, as well as with trace amounts of elements from side groups of the Periodic System.

The technical result is achieved by the fact that the proposed sorbent of the following composition, chemical formula: Zeolite-clinoptilolite, chemical formula: $(KNa,)_4 CaAl_6Si_{30}O_{72} \cdot 24H_2O$ is a crystalline aqueous aluminosilicate, chemical composition: AI_2O_3 -12.9-13.2%; K_2O-4.0-4.8%; CaO-1.8-2.4%; V-0.001%; Cu-0.001%; Rb - 0.001%; SiO_2 - 66.2-78.3%; Na_2O-1.8-2.2%; Fe_2O_3 -0.8-1.2%; Mn-0.001%; Be-0.001%; As-0.03% and Bentonite - hydroalumino silicate, chemical formula: $AI_2[Si_4O_{10}] (OH)_2 \cdot nH_2O$, the chemical composition: SiO_2 -58.25%; AI_2O_3-14.27%; Fe_2O_3 -4.37%; FeO-0.5%; Ti_2O-0.36%; CaO-2.07%; MgO-3.67%; P_2O_5 -0.18%; S-0.14%; K_2O-1.2%; Na_2O - 2.25%; PPP-12.19% .

To test the effectiveness of the complex, natural adsorbents were taken in different percentages, agglomerate was obtained: 1) zeolite (60%) and bentonite (40%), 2) zeolite (50%) and bentonite (50%), 3) zeolite (40%) and bentonite (60%). Subsequently, capsules 10 mm wide, 15 mm long were made from the mixture obtained, acid activation was performed using 15 % H_2SO_4 taken in an amount of 50 % of the air-dry sample, the duration of treatment was 4 hours. In a muffle furnace at a temperature of 400 degrees, heat treatment was carried out to increase the total porosity.

Determination of the sorbent porosity

One of the most important characteristics of the adsorbent is the determination of its porosity, which in general depends on its deposit. It is characterized by the total volume of all voids (pores) in the rock.

The samples were boiled in a glass with distilled water for 1.5–2.0 hours and then weighed.

Sample density, water absorption and porosity were calculated according to Table 1, where: m_0 - the mass of the samples with suspension in water, g; m_1 - weight of wet samples, g; m_2 - weight of dry samples g; m_3 - suspension weight year

Table 1

Incoming data for calculation (modified complex of bentonite and zeolite)

No experience	Material name	m_0, g	m_1, g	m_2, g	m_3, g
1	Zeolite complex (60%) and bentonite (40%)	10,0018	31.4312	19.0645	0.5923
2	Complex zeolite (50%) and bentonite (50%)	9.6453	29.2576	16.7312	0.4627
3	Zeolite complex (40%) and bentonite (60%)	9,9459	31.2057	18,1124	0.4134

The results of the laboratory research on change of heavy metals in wastewater by modified complex of natural adsorbents consisting of bentonite, zeolite in different percentages.

The limits of the relative total error of result, which is admitted, is equal to 2.0; at confidence probability is 0,95. The results of the research are given in Table 2.

Table 2

Determination of porosity of bentonite and zeolite complex

Sample number	The name of material	Sample weight, g	Water adsorption, %	Density, %	Porosity, %
1	Zeolite (60%) and bentonite (40%) complex	21,2145	76.0690	43.8490	73.45
2	Zeolite (50%) and bentonite (50%) complex	20,7124	77.7860	44,7296	73.91
3	Zeolite (40%) and bentonite (60%) complex	19,9437	82,3320	45.6125	80,51

Determination of adsorption capacity according to methyl orange and iodine.

To determine the adsorption according to methyl orange we have chosen the method, introduced at State Standard 4453–74.

For this purpose, the sample of coal was placed in a conical flask with capacity of 100 cm^3, added 25 cm^3 of methyl orange solution. After that, optical density was determined using a photoelectric colorimeter.

As a control solution we used distilled water. From the received optical densities on the base of calibrating graph we determined residual concentration of the pigment.

Adsorption activity was calculated by the formula 1:

$$X = \frac{(C_1 - C_2 K) \cdot 0.025}{m} \quad (1)$$

where C_1 - concentration of the original dye solution, mg/dm^3 ; C_2 - concentration of the dye solution after interacting with tripoli powder, mg/dm^3 ; K - dilution factor; m - weight of the coal sample, g; 0.025 - the volume of methyl orange solution, dm^3 .

The results of the research of the adsorption capacity are given in Table 3.

Table 3

The results of the experiment to determine the adsorption capacity according to methyl orange

Sample	Adsorption capacity according to MO			
	Weight of the sample, g	Concentration, mg / dm ^{3}		Adsorption capacity according to MO, mmol / g
		Original	Residual	
1. Zeolite (60%) and bentonite (40%) complex	0.1	1500	0,600	0.6880
2 Zeolite (50%) and bentonite (50%) complex	0.1	1500	0,800	0.5351
3. Zeolite (40%) and bentonite (60%) complex	0.1	1500	0.750	0.6291

Determination of the adsorption capacity of tripoli by iodine was realized in accordance with the State Standard 4453–74. Iodine number is an approximate measure of the ability of a substance to adsorb small molecules, which depends on the size of the surface area. The processing of the result was carried out according to formula 2:

$$X = \frac{(V_1 - V_2) \cdot 0.0127 \cdot 100 \cdot 1000}{10 \cdot m} \quad (2)$$

where V_1 - the volume of sodium thiosulfate solution (0.1 n), which was used for titration of 10 cm^3 of iodine solution in potassium iodide, cm^3 ; V_2 - the volume of sodium thiosulfate solution (0.1 n), which was used for titration of 10 cm^3 of iodine solution in potassium iodide, after processing it with bentonite and zeolite complex, cm^3 ; 0,0127 - the mass of iodine, which corresponds to 1 cm^3 of sodium thiosulfate solution, g; 100 - the volume of iodine solution in potassium iodide, which is needed for bentonite and zeolite complex, cm^3 ; m - the mass of the sample of bentonite and zeolite complex, 1.00 g.

Table 4

The results of the experiment to determine the iodine number of the bentonite and zeolite complex

Sample	Iodine adsorption capacity			
	Weight of the sample, g	The amount of thiosulfate for titration, cm^3		Iodine adsorption capacity, mmol/g
		Iodine	Bentonite and zeolite complex	
1. Zeolite (60%) and bentonite (40%) complex	0.5	16,10	12.60	10.16
2. Zeolite (50%) and bentonite (50%) complex	0.5	16,10	12.40	12.70
3. Zeolite (40%) and bentonite (60%) complex	0.5	16,10	12.52	11.80

Since bacterial spores are much more resistant to disinfecting agents than E.coli cells, the absence of the latter in water does not guarantee absence of the spores. The indicator, showing presence of bacterial spores in water was anaerobic spore-forming organism C. perfringens and aerobic spore-forming bacterium B. subtilis. These bacteria differ in location of spores in a cell. Since their spores are able to exist in water for much longer than coliform bacteria, they are resistant to disinfection and therefore serve as indicators of long-term contamination and defects in filtering techniques at waterworks.

Tables 5 ÷ 7 show the results of studying the effectiveness of NMS (natural mineral sorbents) regarding removal of E. coli cells from water, as well as B. subtilis and C.perfringens spores.

The results shown in Tables 5÷7 indicate that NMS effectively remove microbial contamination from water at the concentration of bacterial suspension (1.2 ÷ 3.5) x10^3 cells/ml.

At increasing the concentration of the bacterial suspension significantly [up to (3.1 ÷ 3.2) x10^4 cells/ml] in the filtrate inoculations you can find bacteria colonies. At the same time, their number decreases in comparison with the initial by (4 ÷ 5) x10^3 times - for the filter. The effectiveness of reducing microbial contamination with zeolite is significantly lower than in control, and is (2 ÷ 2.8) x10^3 times.

Table 5

The number of microorganisms E.coli (X ± x) in water before and after filtration through filters (n = 5)

The number of microorganisms, cells/ml			
Initial	Filter type		
	Coal filter	Zeolite filter	Filter - zeolite, bentonite complex
(1.2 ± 0.1) x10^3	0	0	0
(3,5 ± 0,2)) x10^3	0	0	0
(3.2 ± 0.2) x10^3	(1.5 ± 0.3) x10^3	(0.7 ± 0.05) x10^3	(0.6 ± 0.03) x10^3

Table 6

The number of microorganisms B. subtilis (X ± x) in water before and after filtration through filters (n = 5)

The number of microorganisms, cells / ml		
Initial	Filter type	
	Carbon filter	Filter - zeolite, bentonite complex
(1.5 ± 0.1) x10^3	*(1.5 ± 0.1) * x10^1*	(0.7 ± 0.02) x10^1
(3.4 ± 0.2) x x10^3	*(1, 8 ± 0.1) * x10^2*	(1 , 1 ± 0.02) x10^2
(3.2 ± 0.1) x10^4	*(4 , 5 ± 0.1) * x10^2*	(2 , 3 ± 0.02) x10^2

It should be noted that in practice in distribution networks, as well as at water withdrawal from a natural water source, we face less severe microbiological pollution. Installations designed for water disinfection in the field and built on the principle of ultraviolet bactericide irradiation are designed for coli index of not more than 5 × 10^3 cells/l.

Determination of toxicity of water samples containing chemical toxicants (phenol, copper sulphate) before and after passing through NMS filters was performed using Daphnia magna and microalgae Chlorella vulgaris.

The data in Table 7 show that water before passing through NMS filters had a toxic effect on the Daphnia magna (the percentage of daphnia death in both cases exceeded 50%). After passing water through NMS filters there was no toxic effect on daphnia in all cases, and the percentage of their deaths hardly differed from the control one, except for the variant with bentonite at concentration of 1.5 mg/l, when the percentage death was 11%.

Table 7

The effect of NMS on the death of Daphnia magna (% to the control one) in water samples containing toxicants (n = 5)

Toxicant content mg/l	Original water	Zeolite	Bentonite
10.0 $CuSO_4$	85.5 ± 5.0	4.0 ± 0.2	3.0 ± 0.2
5.0	59.0 ± 3.0	3.0 ± 0.1	3.0 ± 0.2
1.5	73.0 ± 2.5	11.0 ± 0.5	4.0 ± 0.3
0.05	57.0 ± 1.5	3.0 ± 0.2	3.0 ± 0.1

The received results testify that after passing tap water through the filter zeolite and bentonite complex the composition of water had significant changes. Its organoleptic characteristics significantly improved, in particular, they began to comply with the Sanitary Regulations and Standards in smell and taste of water.

The iron content in water decreased by 9.5 times and began to comply with the Sanitary Regulations and Standards requirements.

In the filtered water pH, the content of calcium, magnesium, silicon, hydrocarbonate ions, as well as the total hardness and dry residue increased. This fact should be assessed positively, since it is known that tap water is distinguished by low content of these essential elements, increased softness and total low salt content.

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DEVELOPMENT OF A METHOD FOR DESIGNING INFORMATION SY STEMS FOR ENERGY COMPANIES

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The creation of information models requires the use of known methods and the development of new methods of formalizing the pre-design research process. The modeling process consists of four stages: data collection on the object of management - pre-project research; creation of a graphical model of business processes taking place in the enterprise; development of a formal model of business processes; business research by optimizing the formal model.

To support the creation of workflow management services and systems, the complex offers methodologies, standards and specialized software that make up the developer's tools.

Key words: *information systems, management information systems (MIS), integrated databases, sadt methodology.*

Ақпараттық модельдерді құру белгілі әдістерді қолдануды және жобалау алдындағы зерттеу процесін формализациялаудың жаңа әдістерін әзірлеуді талап етеді. Модельдеу процесі төрт кезеңнен тұрады: басқару объектісі туралы деректерді жинау – жоба алдындағы зерттеу; кәсіпорында болып жатқан бизнес үдерістерінің графикалық моделін құру; бизнес үдерістердің формальды моделін әзірлеу; формальды модельді оңтайландыру жолымен бизнесті зерттеу.

Жұмыс ағындарын басқару қызметтері мен жүйелерін құруды қолдау үшін кешенде әзірлеушінің құрал-саймандық құралдарын құрайтын әдіснамалар, стандарттар және мамандандырылған бағдарламалық қамтамасыз ету ұсынылады.

Тірек сөздер: *ақпараттық жүйелер, басқарудың ақпараттық жүйелерін (БАЖ), интегралдық деректер базасы, sadt әдістемесі.*