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СОЗДАНИЕ НОВЫХ СОРБЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ ЦЕОЛИТОВ ВОСТОЧНОГО ЗАБАЙКАЛЬЯ И ИХ ТЕХНИКО-ЭКОНОМИЧЕСКАЯ ОЦЕНКА

М.В. Обуздина, Е.А. Руш

Марина Владимировна Обуздина (ORCID 0000-0002-4956-0063)*, Елена Анатольевна Руш

Кафедра техносферной безопасности, Иркутский государственный университет путей сообщения, ул. Чернышевского, 15, Иркутск, Российская Федерация, 664074
E-mail: obuzdina_mv@mail.ru *, lrush@mail.ru

Статья посвящена разработке полифункциональных сорбентов на основе модификации природных цеолитов для очистки сточных вод. В качестве исходного сырья рассмотрены цеолитсодержащие туфы клиноптилолитового типа Холинского месторождения Восточного Забайкалья. Выбор данного месторождения обосновывается его экономико-географическим положением, запасами сырья и его физико-химическими свойствами. Природные цеолиты обладают рядом уникальных свойств, среди которых адсорбционная способность по отношению к различных веществам, диаметр молекул которых соизмерим с размером входных окон. С целью улучшения адсорбционных свойств цеолитов была проведена модификация поверхности высококремнеорганическими соединениями – гексаметилдисилазаном [$(CH_3)_3Si-]_2NH$ (ГМДС) и тетраэтоксисиланом $C_2H_5O)4Si$ (ТЭОС), а также серным полимером, получаемым из отходов производства эпихлоргидрина, основным компонентом которого является 1,2,3-трихлорпропан При этом увеличение адсорбционной емкости по отношению к нефтепродуктам и ионам тяжелых металлов происходит за счет гидрофобизации поверхности. Для изучения природы взаимодействия предлагаемых модификаторов с поверхностью природных цеолитов были сняты ИК спектры. По появлению новых полос поглощения при 2852,03; 2921,60; 2960,75 $см^{-1}$ (С–Н из ГМДС) и 3625,57; 3702,58 $см^{-1}$ (ОН–группы из ТЭОС) доказана фиксация высококремнеорганических соединений на поверхности природного цеолита. Обоснованы механизмы протекающих процессов. Сорбция нефтепродуктов реализуется по смешанному механизму с преобладанием физической адсорбции. Сорбция ионов металлов протекает одновременно по ионообменному и донорно-акцепторному механизму. На стадии доочистки нами предлагается использовать адсорбер с неподвижным слоем адсорбента. В зависимости от того, какой тип загрязняющих веществ преобладает в сточных водах, в аппарате можно использовать загрузку слоев из разных модификаций природного цеолита. Представлены результаты расчета эколого-экономической эффективности исследуемых сорбционных материалов. Рассчитана величина предотвращенного экологического ущерба водным ресурсам.

Ключевые слова: цеолиты, сорбция, модификация, сточные воды, нефтепродукты, ионы тяжелых металлов, серный полимер, экономический эффект

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CREATION OF NEW SORPTION MATERIALS BASED ON ZEOLITES OF EASTERN TRANSBAIKALIA AND THEIR TECHNICAL AND ECONOMIC ASSESSMENT

M.V. Obuzdina, E.A. Rush

Marina V. Obuzdina (ORCID 0000-0002-4956-0063)*, Elena A. Rush

Department of Technosphere Safety, Irkutsk State Transport University, Chernishevskogo st., 15, Irkutsk, 664074, Russia

E-mail: obuzdina_mv@mail.ru *, lrush@mail.ru

The article is devoted to the development of polyfunctional sorbents based on the modification of natural zeolites for wastewater treatment. Zeolite-containing klinoptilolite-type tuffs of the Holinsky deposit in Eastern Transbaikalia are considered as feed materials. The choice of this deposit is based on its economic and geographical location, raw material reserves and its physicochemical properties. Natural zeolites have a number of unique properties, including the adsorption capacity in relation to various substances, the diameter of the molecules of which is commensurate with the size of the entrance windows. In order to improve the adsorption properties of zeolites, the modification of the surface was also carried out with highly silicon-organic compounds - hexamethyldisilazane $[(CH_3)_3Si-]_2NH$ (HMDS) and tetraethoxysilane $C_2H_5O)_4Si$ (TEOS), as well as a sulfur polymer obtained from epichlorohydrin production waste, the main component of which is 1,2,3-trichloropropane. In this case, an increase in the adsorption capacity in relation to oil products and heavy metal ions occurs due to the hydrophobization of the surface. The sorption activity of zeolite is maximum when it is heat treated at 350 °C. A schematic diagram of the production of sorption materials is considered, which can be implemented at the place of application in a complex of wastewater treatment facilities at the production sites of enterprises. To investigation the nature of the interaction of proposed modifiers with a surface of natural zeolites, IR spectra were recorded. By the appearance of new absorption bands at 2852.03; 2921.60; 2960.75 cm^{-1} (C-H from HMDS) and 3625.57; 3702.58 cm^{-1} (OH-groups from TEOS) fixation of highly organosilicon compounds on the surface of natural zeolite was proved. The mechanisms of running processes have been substantiated. Sorption of oil products is carried out according to a mixed mechanism with a predominance of physical adsorption. Sorption of metal ions proceeds simultaneously by ion exchange and donor-acceptor mechanisms. At the post-treatment stage, we propose to use an adsorber with a fixed bed of adsorbent. Depending on what type of pollutants prevails in the wastewater, the device can be loaded with layers from different modifications of natural zeolite. The results of calculating the ecological and economic efficiency of the investigating sorption materials are presented. The amount of prevented environmental damage to water resources is calculated.

Key words: zeolites, sorption, modification, waste water, oil products, ions of heavy metals, sulfurpolymer, economic effect

INTRODUCTION

Reducing the technogenic impact on water resources as a result of wastewater discharge from various enterprises is an important environmental and strategic task. The solution to this problem requires the use of reliable, modern methods of research and assessment of state of natural environment, levels of technogenic load, modern methodology for effectively predicting changes in the geological situation and development of technologies for treating wastewater from heavy metals and oil products, which are often the main components of wastewater from engineering enterprises, railway transport and other industries [1, 2].

Taking into account the fact that sorption methods of purification remain one of promising physicochemical methods, it is actual to search for new effective and economically profitable fillers for adsorption plants and filters that retain their properties under various conditions and modes of industrial wastewater treatment [3, 4].

Therefore, the presented work presents the results of investigation the possibility of obtaining new adsorption materials based on the modification of natural klinoptilolitive type zeolites of Holinsky deposit, and investigation the regularities of sorption extraction of heavy metals and oil products from industrial wastewater.

In the modern world, solving the problem of waste disposal is an important strategic task. Epichlorohydrin is the main monomer in the production of epoxy resins, as well as a raw material in the synthesis of glycerin and other organic synthesis products. Wastes from its production are represented by more than 40 different components, one of the main is 1,2,3-trichloropropane.

It is proposed to use wastes from the production of epichlorohydrin to create a sorbent effective in relation to heavy metal ions in wastewater treatment technologies. The adsorption treatment method is a promising and technologically controlled process and allows reaching residual concentrations of Ni^{2+}, Zn^{2+} and Cu^{2+} below the standard values for the quality of treated wastewater before being discharged into the city sewerage system [5].

Investigations of previous years have already studied the possibility of using sulfur-containing adsorbents in wastewater treatment technologies based on other starting materials. However, not all sulfur-containing polymers can be used as adsorbents. For example, polyarylene sulfides and thiokols cannot be used as adsorbents due to the peculiarities of their structure (steric shielding of sulfur atoms in polyarylene sulfides) and the rubbery state of thiokols [6].

There is a method [7] of obtaining a sulfur-containing adsorbent for purifying wastewater from Zn^{2+} by polycondensation of organochlorine wastes from epichlorohydrin production with sodium polysulfide on the surface of ash and slag particles of a thermal power plant in a water hydrazine-alkali system. Sodium polysulfide ((Na_2S_n, n = 3-4) is obtained from elemental sulfur and sodium hydroxide in aqueous solution in the presence of hydrazine hydrate as a reducing agent.

The authors [8, 9] proposed a method for producing an adsorbent obtained from epichlorohydrin production waste, in which the waste is fed to polycondensation with sodium polysulfide Na_2S_n (n = 3-4) in the presence of petcoke particles with a diameter of 0.15 mm or less.

A sulfur-containing adsorbent for purifying wastewater from heavy metal ions was obtained by polycondensation of organochlorine wastes from the production of epichlorohydrin and chlorinated lignin with sodium polysulfide obtained from elemental sulfur and alkali in an aqueous solution of hydrazine [10].

EXPERIMENTAL PART

The presence of large reserves of natural zeolites in Eastern Transbaikalia allowed us to investigate the processes of their modification in order to create sorption materials effective for the extraction of oil products and heavy metal ions from industrial wastewater.

Natural zeolites and zeolite-containing rocks, being a widespread and cheap mineral raw material, have a unique spectrum of physical, physicochemical, and adsorption properties [11].

The Holinsky deposit of zeolite-containing rocks (klinoptilolite type) is the largest and most profitable for industrial development within Eastern Siberia. The investigated zeolite-containing tuffs contain: klinoptilolite 60-66%; montmorillonite 3-5%; quartz 3-5%; microline 3-5%; cristobalite 10-12%; X-ray amorphous phase 10-12% [12].

The structure of natural zeolites is based on a framework of alumino-silicon-oxygen tetrahedral inits [Al, Si]O_4, in which each of the four oxygen atoms is located at the vertices of the tetrahedron. Silicon and aluminum atoms are located at the centers of tetrahedral init. The main feature of the structure of zeolites is the presence of large voids in the framework, which are combined into open channels. The channels contain cations that balance the negative charge of [Al, Si]O_4 tetrahedral units, and water molecules that are weakly bound to the framework and cations and can be removed and replaced without destroying the framework bonds. Zeolites belong to the category of microporous sorbents with a micropore size of 0.5-1.5 nm. Pore diameters do not exceed 10 Å [13].

Zeolites as sorbents are characterized by such physical parameters as true and apparent density, bulk density and porosity; they are microporous sorbents with micropore sizes of 0.5-1.5 nm.

We have proposed methods for modifying natural zeolites of the Holinsky deposit with highly organosilicon compounds HMDS $[(CH_3)_3Si-]_2NH$ and TEOS $(C_2H_5O)_4Si$, as well as a sulfur polymer obtained from epichlorohydrin production waste, the main component of which is 1,2,3-trichloropropane. The results of experimental and theoretical investigations are confirmed by patents and considered in our previous scientific efforts [14, 15].

As an example of obtaining a zeolite modified by a sulfur polymer, consider the following method: Into a mixture of hydrazine hydrate (weight 10.5 g or 0.21 mol) and monoethanolamine (weight 1.28 g or 0.021 mol) was introduced powdered sulfur (weight 4.0 g or 0.125 mol). At a temperature of 60-65 °C, the mixture was thoroughly stirred for 3.5 h, then cooled to room temperature and sprinkled with 20 g of natural zeolite with an average particle size of 5 mm. While stirring, 21 g of hydrazine hydrate was introduced and 6.2 g (0.042 mol) of 1,2,3-trichloropropane were added dropwise.

Subsequently, for another 3 hours, the reaction mixture was stirred in a shaker at room temperature. The precipitate was filtered, washed with water, then with acetone, and dried under vacuum. Due to the presence of sulfur in the proposed sorbent, it was possible to increase the degree of extraction of heavy metal ions to 99-100%, due to the fact that heavy metals form sulfides with sulfur, which are practically insoluble in water.

The process of adsorption of Ni^{2+}, Zn^{2+} and Cu^{2+} from wastewater by a zeolite modified with a sulfur polymer, investigated when assessing the influence of various factors – the time of contact of the sorbent with the solution, pH of medium, temperature. The highest adsorption capacity is achieved at pH = 7 (Fig. 1). The curves at higher temperatures are located higher, which indicates that the adsorption process is activated.

In the process of organizing technological processes, wastewater of different composition and flow rate is formed. Thus, when developing technological schemes for wastewater treatment at industrial sites of enterprises, various layout solutions and instrumentation of the processes are adopted, which often include the stage of mechanical cleaning in a sump or oil trap, followed by a physical and chemical treatment unit – a flotation device. Further, the scheme provides for a post-treatment unit – a filter with a sandy load of quartz sand or activated carbon. It is proposed to install an adsorber with fixed three layers of adsorbent instead of the filter. The sorbent consumption is 3120 kg/year.

It is proposed to regenerate the loading once every 10 days, and replace the filtering loading once every 2 months. At the same time, zeolite modified with TEOS possesses the highest adsorption capacity with respect to oil products, with respect to Ni^{2+} and Zn^{2+} – it is zeolite modified with HMDS, and when extracting Cu^2, it is recommended to use a zeolite, modified with sulfur polymer. At the end of the filtration cycle, the spent sorbent can be used in the production of various building materials [16, 17].

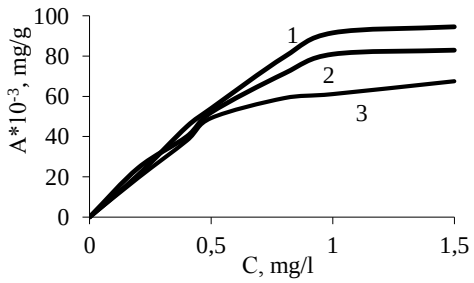

Fig. 1. Isotherms of adsorption of Zn^{2+} on the zeolite modified with a sulfur polymer at the following temperatures: 1-333 °K; 2- 313 °K; 3- 293 °K

Рис. 1. Изотермы адсорбции Zn^{2+} на цеолите, модифицированном серным полимером, при следующих температурах: 1- 333 °К; 2- 313 °К; 3- 293 °К

RESULTS AND THEIR DISCUSSION

Based on the results of complex physical and chemical investigations with using IR spectroscopy methods, the high adsorption activity of the proposed materials in relation to oil products and heavy metal ions has been proven.

The presence of functional groups on the surface of sorbents, which would determine the formation of active sites for adsorption, was determined by IR spectroscopy [18]. Infrareds spectrums were obtained using a Vertex70 IR Fourier spectrometer at the Baikal Analytical Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences. As a result of investigations of infrared spectrums, dependences of transmission T (%) on the wave number V were obtained. The presence of functional groups on the sorbent surface indicates the formation of active adsorption centers

To assess the sorption activity, we determined the presence of functional groups on the surface of the sorbent, which are responsible for the formation of active adsorption centers. Fig. 2 shows the infrared spectrums of zeolite of Holinsky deposit of natural origin and modified HMDS and TEOS. The characteristic absorption bands in infrared spectrums appear at wave numbers of 610 cm^{-1} and 1220 cm^{-1}, which characterizes the vibrations of external tetrahedral Si–O–A1 bonds.

The absorption bands of the main tetrahedral units Al,Si–O_4(T–O_4) of the aluminosilicate framework of zeolites are in the middle region of infrared spectrums. In the infrared spectrum of unmodified natural zeolite of the Holinsky deposit, stretching vibrations of OH bonds appear at 3436.38 cm^{-1} and bending vibrations of OH bonds appear at 1632.18 cm^{-1} (Fig. 2). The rest of absorption bands attributed to vibrations in the external bonds of the tetrahedral units are located in the range 750-820 cm^{-1} and 1050-1150 cm^{-1} [19].

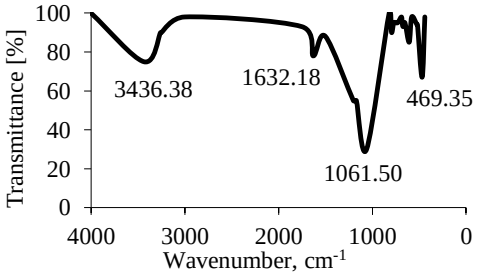

Fig. 2. IR srectrum of natural zeolite of the Holisky deposit

Рис. 2. ИК спектр природного цеолита Холинского месторождения

The sorption capacity of zeolite is maximum when it is pre-fired at 350 ° C (Fig. 2), and when the

firing temperature is increased to 600 °C, it decreases. The most sensitive to thermal destruction are the bands of intertetrahedral vibrations with frequencies in the range of 520-650 and 1200 cm^{-1}, associated with secondary structural units. As a result, during the heat treatment of the zeolite, the band at 524.17 cm^{-1} disappears. At the same time, intra-tetrahedral vibrations with frequencies near 450 and 1050 cm^{-1} react less to heating.

When zeolite is modified with highly organosilicon compounds HMDS and TEOS, the surface of the sorbent is hydrophobized and its adsorption capacity increases. Infrared spectrums of natural zeolite are characterized by absorption bands at 469.35 (Si–O), 795.04 (OH–groups) 1061.50 (Si–O–Si) and 3436.38 cm^{-1} (adsorbed water). The fixation of modifying substances on the surface of natural zeolite is characterized in the infrared spectrums by the appearance of new absorption bands at 2852.03; 2921.60; 2960.75 cm^{-1} (C–H from HMDS) and 3625.57; 3702.58 cm^{-1} (OH-groups from TEOS) (see Fig. 3, 4) Shift of the absorption band of the outer tetrahedral Si–O bond 1055.28-1073.69 cm^{-1} for zeolite modified with TEOS, and 1058.18-1077.34 cm^{-1} for zeolite modified with HMDS is evidence of sorption of oil products.

The evidence of sorption of oil products is the shift of absorption bands: 1055.28-1073.69 cm^{-1} in case of modification of TEOS zeolite; 1058.18-1077.34 cm^{-1} for zeolite modified with HMDS and 1061.50-1088 cm^{-1} for sorption of Ni^{2+} and Zn^{2+} [20].

Further, we carried out investigations of kinetic and thermodynamic features of adsorptive extraction of oil products and heavy metal ions by modified zeolites. Sorption of oil products on zeolite modified by TEOS proceeds according to a mixed mechanism with a predominance of physical adsorption. And the adsorption of nickel and zinc ions on a zeolite modified with HMDS is realized simultaneously by the ion-exchange and donor-acceptor mechanisms.

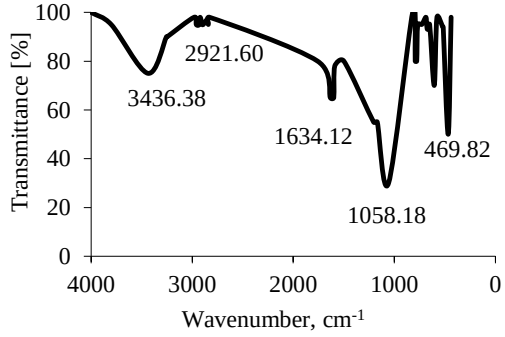

Fig. 3. IR spectrum of natural zeolite, modified with HMDS
Рис.3. ИК спектр природного цеолита, модифицированного ГМДС

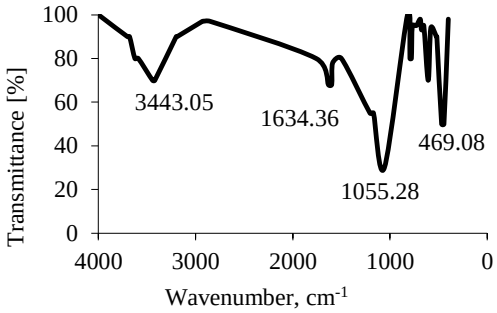

Fig. 4. IR spectrum of natural zeolite, modified with TEOS
Рис.4. ИК спектр природного цеолита, модифицированного ТЭОС

Calculation of the cost of the proposed sorption materials based on natural klinoptilolitive type zeolites modified with HMDS, TEOS and sulfur polymer makes it possible to compare the economic indicators of the obtained sorbents with analogues available on the market (see Table 1). The production assumes the repeated use of solvents, which is taken into account when calculating the cost of the obtained sorbents. A preliminary assessment with sorption materials available on the market made it possible to establish the competitiveness of the proposed sorbents. The total volume of the sorbent market is more than 160 items.

The ecological efficiency of using a zeolite-containing sorbent for the post-treatment of industrial wastewater on the example of one of the railway transport enterprises is due to achievement of quality standards for treated wastewater before being discharged into the city sewage system.

In this case, the main factors affecting the amount of prevented environmental damage include the mass of pollutants that are not allowed to be discharged into water bodies as a result of environmental protection measures.

The assessment of the amount of prevented environmental damage from pollution of water resources is carried out on the basis of regional indicators of specific damage (Irkutsk region), which are specific cost estimates of damage per 1 conventional ton of pollutants. The calculation of the amount of prevented environmental damage is made according to the formula:

$$У_{пр}^{В} = \sum_{j=1}^{n} У_{уд}^{В} \cdot \Delta M \cdot К_{Э}^{В} \cdot J_{Д} \qquad (1)$$

Where $У_{пр}{}^{В}$ is a prevented environmental damage to water resources in the considered r – th region, as a result of the implementation of the n-th direction of environmental protection, thousand rubles; $У_{пр}{}^{В}$ is an indicator of specific damage to water resources caused by the conditional ton mass of pollutants at the end of the reporting period for the j-th water body, rubles/conditional ton.

Table 1

Comparison by cost of sorbents

Таблица 1. **Сравнение по стоимости сорбентов**

Sorption material	Appearance	Cost rubles/kg
zeolite modified by TEOS	granules	114.92
zeolite modified by HMDS	granules	116.6
zeolite modified by sulfur polymer	granules	190.5
Activated sinter carbon of rank AHPV	powder	355
Activated sinter carbon of rank AHPW-PromKarb	powder	340
Activated carbon of rank AG-3	granules	203
Activated sinter carbon of Rank BAU	granules	150
Ekvosorb-L	chippings	320

Reduced mass of pollutants not allowed to be discharged into the j-th water source as a result of the implementation of the n-th direction is calculated by the formula:

$$\Delta M = M_{j1} - M_{j2} \quad (2)$$

Where M_{j1},M_{j2} are the masses of the j-th pollutant before and after the environmental protection measure; *j* is the number of pollutants or a group of substances; *n* is the number of pollutants or a group of substances taken into account; $K_{Э}^{B}$ is a coefficient of ecological situation and ecological significance of the state of water bodies; $J_{Д}$ is a deflator index.

The reduced mass of pollutants for a specific object is calculated using the following formula:

$$M = \sum_{i=1}^{n} m_i \cdot A_i \quad (3)$$

Where Ai is an indicator of the relative hazard of the i-th pollutant to water bodies, conventional ton/ton; *i* is a type of pollutant; *n* is the number of pollutants taken into account.

The total mass of the annual discharge of the i-th pollutant by the source under consideration is calculated by the formula:

$$m_i = C_i \cdot V_i \quad (4)$$

Where *Ci* is the actual concentration of the i-th pollutant in wastewater, g/m^3; *Vi* is the volume of annual wastewater discharge from the source under consideration, m^3/year.

As a basis for calculating the reduced mass of contaminants, the approved values of the maximum permissible concentrations (MPC) of pollutants in the water of reservoirs of fishery significance are used. Using the MPC, the coefficients of the ecological and economic hazard of pollutants are determined, as the inverse of the MPC. The coefficients are grouped according to hazard classes and the sign of close values of MPC of fishery significance. The total prevented environmental damage resulting from environmental protection measures at the railway transport enterprise amounted to 19.571 million rubles/year.

Table 2

Costs for the reconstruction of purification plants

Таблица 2. **Затраты на реконструкцию очистных сооружений**

Characteristics	Quantity	Cost, rubles	
		unit	tottal
Collection and cooling bins	5 items	10000	50000
Flint mill	1 item	55000	55000
Coarse screen	1 item	90000	90000
Mixer with heating jacket and stirrer	1 item	550000	500 000
Dry chamber	1 item	6 000	62000
Muffle furnace	1 item	570000	57000
Dosing tanks	4 items	11000	44000
Totak			1371000
Projects works	7%		95970
Delivery of zeolite from the deposit	2%		27420
Equipment delivery	5%		68550
Mechanical and commissioning works	25%		342750
Unanticipated needs	3%		41130
Total cost of inputs			1946820

Table 3

Calculating the economic efficiency of the use of sorbents

Таблица 3. **Расчет экономической эффективности применения сорбентов**

Characteristics	Indicators
The cost of reconstruction of waste water treatment plans	1.947 million rubles
Value of operating costs	1.156 million rubles/year
Performance of waste water treatment plans	300 m^3/day
The productivity of waste water treatment plans per year	109500 m^3/year
Discharge cost 1 m^3 treated waste water to the city sewer	12.62 rubles/m^3
The cost of 1 m^3 of tap water received from the city water supply	14.45 rubles /m^3
Annual savings by canceling the purchase of water for technological needs	1.588 million rubles/year
Savings due to lack of discharge to city sewer:	1.382 million rubles/year
Total savings:	2.97 million rubles/year
Overall economic effect:	22.541 million rubles/year
Reduced costs:	1.389 million rubles/year
Neat economic benefit:	21.152 million rubles/year

The ecological efficiency of using modified zeolite for post-treatment of industrial wastewater can be calculated based on the condition of achieving the standards used for the circulating water use system. The costs for the reconstruction of the treatment facilities are presented in Table 2, taking into account the fact that it is necessary to replace the load in the already existing adsorbers, which previously used activated carbon, as well as to purchase equipment for modifying the zeolite. The calculation of the economic efficiency of the proposed technology is presented in Table 3.

CONCLUSIONS

As a result of our investigations of modification of natural klinoptilolite-type zeolites of the Holinsky deposit in Eastern Transbaikalia, the possibility of increasing their adsorption capacity in relation to oil products and heavy metal ions was proved due to the hydrophobization of the surface.

Highly organosilicon compounds (hexamethyldisilazane and tetraethoxysilan) and a sulfur polymer obtained from epichlorohydrin production waste, the main component of which is 1,2,3-trichloropropane have been proposed as modifiers.

Sulfur-containing polymeric materials, like low-molecular-weight organosulfur compounds, are capable of complexation with heavy metal ions; therefore, sorbents effective with respect to heavy metal ions were obtained on their basis.

Preliminary heat treatment of the initial zeolite at a temperature of 350 °C is recommended. The fixation of modifying substances on the surface of natural zeolite was proved by infrared spectroscopy, as evidenced by the appearance of new absorption bands. In this case, after the extraction of oil products and heavy metal ions, a shift of certain absorption bands occurs as the main proof of the presence of an adsorption process.

The expected environmental and economic effect due to the reduction of over-limit payments from the introduction of the proposed technology for additional wastewater treatment will amount to 21.152 million rubles/year. The total prevented environmental damage to water resources from pollution of water reservoir, obtained as a result of environmental protection measures at the railway transport enterprise, amounted to 19.571 million rubles/year.

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