Theoretical Objectives and Development of Methods to Protect the Water Resources of the Angara Region from Heavy Metals Pollution

M V Obuzdina¹, E A Rush¹

¹Technosphere Safety, Federal Agency of Railway Transport, Irkutsk State Transport University (ISTU), Chernishevskogo str. 15, Irkutsk 664074, Russia

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

Abstract. This paper presents the results of investigations on the possibility of obtaining new sorption materials based on modifying the natural zeolites of the Eastern Transbaikalia deposit, investigating the laws of sorption extraction of heavy metals and oil products from industrial wastewater of railway transport enterprises with a new sorbents. It is shown that chemical modification of natural zeolites allows obtaining sorbents with a more ordered structure compared to natural layered silicates, an increased surface area and a transient nature of porosity, which ensures their high sorption activity and, therefore, the perspectivity of application in the sorption technology of wastewater treatment.

1. Introduction
The global nature and complex processes of anthropogenic environmental change in the Angara region led to the exacerbation of the problem of pollution of natural objects and, first of all, of water resources. Enterprises of the chemical and petrochemical industries, railway transport, machine-building and metallurgical complexes put the greatest pressure on water resources, dump significant amounts of insufficiently treated wastewater containing heavy metals and oil products in the Angara water basin. The distribution and dispersion of heavy metals in environmental objects led to the formation of areas with abnormally high concentrations of pollutants on the territory of the Upper Angara region, which, accordingly, creates an unfavorable geo-ecological situation and adversely affects the health of the population.

Reducing the level of anthropogenic impact on the aquatic environment of the Angara basin, the main source of drinking and household water supply for most cities and industrial centers of the Irkutsk Region, is one of the priority tasks of ensuring environmental safety. The solution of this task requires the use of reliable, modern methods of research and assessment of the state of the natural environment, levels of technogenic load, modern methodology for effectively predicting changes in the geoecological situation and the development of wastewater treatment technologies for heavy metals and oil products [1].

For the treatment of industrial wastewater from heavy metals and oil products, it seems perspective to use a sorption method that provides ease of operation, the ability to automate the process and achieve the standard quality of treated water while involving sorbents of various chemical nature into the cleaning process [2]. Therefore, the presented article presents the results of investigation of the...
possibility of obtaining new sorption materials based on the modification of natural zeolites, and researches the laws of sorption extraction of heavy metals and oil products from industrial wastewater of railway transport enterprises with a new sorbents.

2. Experimental investigations. Results and discussion
As a source of raw materials for the creation of new sorbents that are effective in relation to the extraction of heavy metals from industrial wastewater, we investigated the zeolite tuffs in Eastern Transbaikalia. The deposits of these minerals are geographically located near industrial objects of the East-Siberian railway, which determined the feasibility of their involvement in processing [3].

Dates of mineralogical, phase-radiographic, chemical analyses and infrared spectroscopy are showed that investigated zeolite tuffs of Holinsky deposit contain 60-66% klinoptilolite, 3-5% montmorillonite, 3-5% quartz, 3-5% microcline, 10-12% cristobalite, 10-12% amorphous-oxygen framework phase. Bulk density of zeolite tuffs for the mass of rocks is 1.007 – 0.7789*10^3 kg/m^3, wear vibration index is 0.73-2.59, which meets the requirements of the standards. Water resistance in water at room temperature is 89-100%, in boiling water - 76.0-99.7%. The loss of mass of the substance during washing of the fraction 0.25-1 mm varies from 3 to 80%, more often is 30-50%, which indicates a considerable heterogeneity of the mechanical composition of zeolite tuffs. Thus, the presented characteristics of the initial zeolite feedstock allow us to conclude about the fundamental possibility of its use in the technology of sorbents for wastewater treatment [4].

Klinoptilolite is the basis of zeolites of Holinsky deposit. In terms of chemical composition, clinoptilolite is a highly siliceous member of the structure of the Heylandite group, which contains more monovalent than divalent cations. It has the following properties: large specific surface, molecular sieve action, high selectivity to polar molecules, ability to sorption and ion exchange. The high selectivity of klinoptilolite with respect to monovalent cations of large dimensions is due to their localization in eight-membered silicon-oxygen rings in the structure [5].

Zeolites, as sorbents, have two main features: molecular sieve action and high selectivity to molecules capable of specific interaction. Both these factors have a decisive influence on the sorption kinetics. Unlike other sorbents, natural zeolite tuffs have a lower density (about 2 g/cm^3), greater porosity and developed specific surface (compared, for example, with activated carbons) [6].

Zeolites are crystalline aqueous aluminosilicates having a three-dimensional framework structure. The crystal structure of zeolites is formed by tetrahedrons SiO₄ and AlO₄. They are arranged in such a way that voids are afforded in space in the form of channels in which metal cations and water molecules are loosely connected with the rest lattice. Cations compensate the excess negative charge of anionic part of aluminosilicate zeolite skeleton. A feature of zeolite skeletons structure is the presence in them of a system of regular channels and communicating cavities with dimensions comparable to the dimensions of molecules [7]. These adsorbents have a well developed internal surface, which is available for adsorbed molecules. In this case, the proportion of the external surface of zeolites constitutes only a very small part of the total surface.

A characteristic feature of zeolites is that Al in the framework is in the tetrahedral position, therefore the skeleton of zeolites carries an excess negative charge. To ensure electroneutrality, the structure of zeolites requires the presence of cations of various metals, which are not long in the voids of crystal lattice. Under certain conditions, these cations have the ability to exchange with other cations[8].

Molecular-sieve properties of porous crystals of zeolites are determined not only by the geometry features of their silicon-oxygen frameworks, but also by their nature and the number of cations that compensate for negative charge of polymeric aluminosilicate anion. The chemical composition of zeolites determines the thermal stability of their scale, chemical stability in acid media, adsorption capacity, etc. When the zeolites are heated, water is evolved from them and adsorption cavities are formed. These cavities connect with each other and with the external space of the entrances - windows of small dimensions (0.4-1.1 nm). For this reason, zeolites sorb only molecules of substances, the critical size of which is smaller than diameter of entrance window.
One way to improve the activity of layered silicates, giving them an affinity for organic substances (in particular aromatic carbons) is the modification of the structure by organic substances [9]. Modification of the surface by organic substances leads, as a rule, to substitution of hydroxyl group surfaces with organic radicals. GMDS - hexamethyldisilazane [(CH₃)₃Si]₂NH and TEOS - tetraethoxysilane (C₂H₅O)₄Si were chosen as modifiers of the surface of the natural zeolite [10,11].

Hexamethyldisilazane [(CH₃)₃Si]₂NH is a transparent colorless liquid with a strong odor. HMDS is hydrolyzed by the moisture of the air, is very soluble in inert organic solvents, reacts with water, alcohols, acids. The following types of bonds are present in HMDS: Si-N, Si-O, S-O-Si, Si-N-Si. Tetraethoxysilane (C₂H₅O)₄Si is an ether of orthosilicate acid. In TEOS there are the following types of bonds: Si-H, Si-OH, Si-ONa, Si-OR (R = CH₃–CH₂).

Experimental investigations have shown that the maximum adsorption capacity for zeolites modified by HMDS or TEOS was observed for 4 hours and 3.5 hours, respectively. When the modification occurs, the surface of the sorbent is hydrophobized and its adsorption capacity increases with respect to oil products [12]. An important proof of the interaction of modifiers with the surface of natural zeolites is the results of research conducted by IR spectroscopy [13]. Figure 1 shows the infrared – spectrums of zeolite modified with HMDS. Experimental investigations of oil products sorption by zeolite modified with TEOS were carried out in a similar method.

![Figure 1. IR spectrum of natural zeolite, modified with HMDS.](image)

Infra-red spectrums of non-modified natural zeolite is characterized by absorption bands at 470 (Si-O), 820 (OH-groups) 1000-1200 (Si-O-Si) and 3400-3600 (adsorption water) cm⁻¹. Fixing of modifying substances on the surface of the natural zeolite is characterized on the Infra-red spectrums by appearance of new absorption bands at 3600-3700 cm⁻¹ (OH-groups of TEOS) and 2500-2900 cm⁻¹ (C-H of GMDS).

The nature of the fixation of oil products on zeolite surface can be traced on the infra-red spectrum, which is presented in the figure 2. The displacement of the absorption band of texturally-bound hydroxyl groups by 20 cm⁻¹ serve as evidence of interaction of zeolite with introduced modifier. The displacement of the absorption band of the outer-tetrahedral Si-O-Al bond 1055.28– 1073.69 cm⁻¹ for
modified by TEOS zeolite and 1058.18-1077.34 cm\(^{-1}\) for modified by HMDS zeolite serve as evidence of oil products sorption on the zeolite [14, 15].

\[ \text{Figure 2. IR-spectrum of natural zeolite, modified with HMDS after sorption of oil products with concentration of 114 mg/l within 6 hours.} \]

The proposed results of researches have allowed to make the assumption that at extraction of oil product by modified zeolite carries out the process proceeding on three-stage mechanism: a stage of input of substance to grain of an adsorbent; the external diffusion stage of mass transfer kinetics; the stage of movement of matter inside the grain [16]. The maximum static sorption capacity of natural zeolites in relation to oil products is observed in the pH range of 6-8. It was experimentally determined that the modification of TEOS promotes to an increase in the oil capacity of a new sorbent by 1.2 times under static conditions, as compared with the natural zeolite, i.e. it has the maximum adsorption capacity with respect to recoverable oil products, which, in turn, allowed it to be recommended for practical use in wastewater treatment technology.

Investigation have established that zeolites modified with HMDS and TEOS have high sorption activity with respect to not only oil products, but also heavy metal ions. Figures 3-4 show the kinetic dependences of the sorption of nickel (II) and zinc (II) ions by natural zeolite modified by HMDS.

The speed of the sorption process depends on concentration, nature and structure of the dissolved substances, solution temperature, the type and properties of sorbent. Investigation of heavy metal ions exchange on modified zeolites showed that the rate is high in the initial period. Then the slowed-down sorption stage follows. This stage corresponds to the exchange, which takes place on the surface of the sorbent particles. The third stage is connected with the penetration of counterions into the depth of particles, i.e. with ions diffusion inside of material. Kinetic investigations have shown that the sorption interaction proceeds quite intensively. The time of sorption equilibrium is 1 to 3 hours, depending on the ratio "sorbent mass-solution."
Experimental investigations of nickel (II) sorption by modified TEOS zeolite realized in a method, which analogous to the method of investigation of nickel (II) sorption on zeolite, modified by HMDS. Temperature is an important factor, which determining the sorption equilibrium. It is established that the limiting sorption capacity increases with increasing temperature. The maximum sorption is achieved at a temperature of $333^\circ K$ [17].

The optimum pH value for nickel ions at which the zeolite modified by HMDS has the highest sorption capacity conform to a pH value of 5.2-5.5, for zinc ions, pH = 5. Optimal ranges of pH values under static conditions: for sorption of nickel (II) by zeolite, modified TEOS, pH = 5.2 - 5.5; for the sorption of zinc pH = 3.

Heavy metals have a high affinity for sulfur atoms, forming stable insoluble sulphides and complex compounds with organo-sulfur ligands. Thus, creation of sorbents based on organosulfur polymers is a perspective research direction. The important property of organosulfur compounds is their ability to form strong complex compounds with heavy metal ions. The possibility of such interaction is determined by the Pearson principle of hard and soft acids, according to which soft acids (heavy metal cations) preferably coordinate with soft bases (sulfur atoms). Low-molecular organosulfur compounds form complexes with many transition metals [18].

We propose a method for obtaining solid granular sulfur-containing sorbents using waste products of epichlorohydrin, the main component of which is 1,2,3-trichloropropane. Sorbents were investigated for the ability to extract nickel (II), zinc (II) and copper (II) ions from model solutions when assessing the effect of sorbent contact time with the solution. Due to the presence of sulfur, it was possible to increase the recovery ratio of heavy metal ions to 99-100%, because heavy metals form sulphides with sulfur. These sulphides are practically insoluble in water. As a result of the research, it was found that the optimal sorption time of nickel (II), zinc (II) and copper (II) ions averages 30 minutes (Figure 5-6) [19, 20].

The adsorption process of nickel (II), zinc (II) and copper (II) ions from wastewater with chemically modified zeolites was also investigated taking into account the influence of model solution temperature. It is established that the optimal temperature range is within 300-310 °K. The maximum sorption capacity with respect to recoverable heavy metals for modified zeolites is observed at pH = 7.

3. Conclusion
The main scientific and practical results of the research are as follows: for the first time, the possibility of using chemically modified zeolites of the Holinsky deposit in Eastern Transbaikalia as oil products and heavy metal ions as sorbents was proved; changes in the sorption characteristics of natural zeolites in contact with modifiers − hexamethyldisilazane [(CH$_3$)$_3$Si]$_2$NH (HMDS), and tetraethoxysilane (C$_2$H$_5$O)$_4$Si (TEOS) and sulfuric polymer obtained from waste products of epichlorohydrin in relation to the recoverable pollutant components of industrial wastewater of railway transport enterprises are established. It was proved that chemical modification of natural zeolites allows to obtain sorbents with a more ordered, compared to natural layered silicates structure, increased surface area and transient
nature of porosity, which ensures their high sorption activity and, therefore, the promise of application in the sorption technology of wastewater treatment.

Figure 5. Kinetic curves of nickel ions (II) sorption of zeolite.

Figure 6. Kinetic curves of zinc ions (II) sorption of zeolite.

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