Investigation of sorption characteristics of modified klinoptilolites by the method of infra-red energy and differential X-ray spectroscopy

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Abstract. The article presents investigations of adsorption of heavy metal ions Ni²⁺, Zn²⁺, Cu²⁺ by modified zeolites. As a modifier of zeolites of the Holinsky deposit, a sulfur polymer is proposed that is obtained from waste during the production of epichlorohydrin, the main components of which is 1,2,3-trichloropropane. The mechanisms of adsorption and the results of investigations by the methods of infra-red spectroscopy and energy differential X-ray spectroscopy of the initial samples of materials are described in detail. On the IR-spectres new absorption bands are considered. These bands reflect the nature of fixation of modifier on the surface of sorbent.

1. Introduction

Heavy metal ions and oil products are the main components of wastewater, which are formed at the enterprises of railway transport [1]. Adsorption as a method of wastewater treatment is the most effective, allowing to reach 98–99.5% of the degree of purification and, accordingly, the residual concentrations of pollutants in the treated wastewater to standard values [2, 3]. The sorption method allows removing pollutants of different origin, while avoiding the formation of secondary pollutants. The degree of purification reaches 97-99%, with the possible adsorption of pollutants of multicomponent mixtures [4]. In presented investigations, zeolites of the Holinsky deposit of Zabaykalsky region were considered [5].

Chelishchev N.F. and others [6], in the middle of the 20th century, revealed that zeolites have a large number of voids in their structure, caused by a framework in the form of [Al, Si]O₄ tetrahedra, which joined together. These voids are grouped into open channels in which cations are located [7]. At the same time, water molecules are relatively weakly bound to both cations and the skeleton. Thus, they can be removed and replaced with pollutant molecules. In this case there will be no destruction of the bonds of the crystal lattice [8]. Coordination-related exchange cations water can be removed by heating the zeolite.

IR-spectroscopy helps to assess the sorption activity and establish the mechanism of sorption. Analyzing the IR-spectra, it is possible to obtain the necessary information about the structure and other properties of zeolites, to identify what changes they undergo during a chemical reaction, taking into account various treatments. Analysis of the IR-spectra helps to describe which functional groups are present on the zeolite surface as a result of a particular modification.
2. Results and discussion

The method of IR-spectroscopy for investigations of zeolites of various crystal structures was first used in the works of P.N. Kiselev [9]. E.M. Flatilen with employees [10] conducted a more detailed systematic investigation of the frame structure of a number of synthetic zeolites by the method of IR-spectroscopy. Each zeolite has its own IR-spectrum. In the range from 200 to 1300 cm\(^{-1}\), the frequencies of fundamental vibrations of the TO\(_4\) tetrahedra (T = Si,Al) of the frameworks of all zeolites are displayed [8]. To obtain the IR-spectrum of the natural zeolite of the Holinsky deposit, the Fourier FTIR spectrometer was used at the Baikal Analytical Center for Collective Use of the SB RAS. Figure 1 shows the dependence of the transmission T (%) on the wave number V.

![IR-spectrum of zeolite tuff of Holinsk deposit of natural origin](image)

Analyzing the IR-spectrum (see Figure 1), it can be noted that the absorption bands at 610 cm\(^{-1}\) and 1220 cm\(^{-1}\) are related to the vibrations of the external tetrahedral Si–O–A1 bonds. At the same time, in the middle part of the IR-spectra, absorption bands are presented that characterize the main Al, Si–O\(_4\) (T–O\(_4\)) tetrahedra, which are the basis of the framework of natural zeolites of klinoptilolite type. The deformation vibrations of OH-bonds in the spectrum of natural zeolite appear at 1632,18 cm\(^{-1}\) (Fig. 1). Valence vibrations of OH-bonds are at 3436.38 cm\(^{-1}\). When zeolite is dehydrated, polyvalent cations become localized. Due to the presence of an electrostatic field associated with polyvalent cations, deformation may occur and even, perhaps, the dissociation of water molecules coordinated to these ions. In this case, cations of MeOH\(^+\) and H\(^+\) surface compounds are formed [11].

The absorption bands, related to vibrations along the external bonds of the Al,Si–O\(_4\)(T–O\(_4\)) tetrahedra, are characterized by absorption bands in the region of 750–820 cm\(^{-1}\) and 1050–1150 cm\(^{-1}\). The ratio of SiO\(_2\)/Al\(_2\)O\(_3\) in a zeolite affects the magnitude of the frequencies of the absorption bands in the region of skeletal vibrations, but not the general form and their number. In this case, the antisymmetric vibrations of Si-O-Si (Al), which are traced in the middle region of the IR-spectra with the absorption band at 1000-1100 cm\(^{-1}\), are most dependent on this ratio. The frequency of the maximum of this band increases with increasing SiO\(_2\)/Al\(_2\)O\(_3\) modulus. However, cases of deviation from this pattern are possible with a high sensitivity of vibrations of the Si-O-Si (Al), bonds, and taking into account the topology of the zeolite crystal structure [9].

![Figure 1. IR-spectrum of zeolite tuff of Holinsk deposit of natural origin](image)
For klinoptilolite, the frequency of the antisymmetric stretching vibrations of the Si-O-Si (Al) chains is traced as a function of SiO2/Al2O3 modulus. When the ratio of SiO2/Al2O3 = 8.3, the atomic fraction of silicon is 0.81, which is characterized by an absorption band of 1061.50 cm⁻¹. In the IR-spectra obtained, the stretching vibrations of the Si–O bonds are displayed as absorption band at 1061.50 cm⁻¹. At the same time there is a small shoulder at 1202 cm⁻¹. Analyzing Figure 1, we can note the fact that the deformation vibrations of the Si–O bonds are traced at 469.35 cm⁻¹ and 524.17 cm⁻¹. The silicon-oxygen tetrahedron of the zeolite lattice has Si-O-Si bonds, which are displayed in the IR-spectra as absorption bands at 795.04 cm⁻¹ and shoulders at 702 cm⁻¹. Si-O-Al bonds with deformation vibrations can be traced along absorption bands at 672.36 cm⁻¹ and 607.11 cm⁻¹.

We were [2] conducted investigations on the heat treatment of zeolite tuffs from the Holinsky deposit. IR-spectra were obtained reflecting changes in the structure in the case of processing at a temperature of 350-600 °C. It was found that the optimal calcination temperature of the zeolite is 350 °C, since this removes water, coordinated with exchange cations and oxygen scaffold. The sharp decrease in the sorption capacity of the initial sample in the case of calcination at 600 °C is explained by the destruction of the functional active centers in the structure of klinoptilolite. Taking into account the fact that the frequency of 1637.88 cm⁻¹ is characteristic of water molecules, coordinated with calcium cations [9], it can be concluded that the residual H2O molecules in the zeolite, which are most strongly associated with it, are retained by calcium cations.

As a result of joint research [1,12,13,14] hydrophobization of the zeolite surface occurs in the case, when high silicon organics, hexamethyldisilazane [(CH₃)₃Si-]₂NH (HMDS) and tetraethoxysilane (C₂H₅O)₄Si (TEOS), is using as a surface modifiers of natural zeolite of Holinsky deposit. It is recommended that the preliminary heat treatment of the sorbent at 350 °C. This contributes to a significant increase in the adsorption capacity of the investigating samples with respect to Ni²⁺, Zn²⁺ and oil products. To prove the nature of the fixation of modifiers on the surface of zeolites and to explain the sorption process, the IR-spectra of samples of modified zeolites were measured and investigated in detail before and after sorption.

Next, we [13, 14] investigated the energy-dispersive X-ray spectra of the investigated samples of zeolites, modified by HMDS and TEOS after sorption of heavy metal ions. The data obtained confirm the formation of Ni²⁺ and Zn²⁺ complexes on the zeolite surface. Analysis of the spectra confirms that the modified zeolites contain K, C, Ca, O, Al, Si. The fact of metal cations fixation of on the surface in the cavities of zeolites is confirmed by the presence of Ni²⁺ and Zn²⁺ peaks, respectively, 7.71% and 5.14%.

The next stage of our research was the investigation of sorption of heavy metal ions such as Ni²⁺, Zn²⁺ and Cu²⁺ on the natural zeolite of the Holinsky deposit of klinoptilolite type, modified by sulfur polymer, obtained from epichlorohydrin production waste [14]. The fixation of the modifier on the zeolite surface was confirmed by energy dispersive X-ray spectroscopy (see figure 2, table 1).

![Figure 2. Energy dispersive X-ray spectrum of natural zeolite, modified by sulfur polymer](image-url)
As can be seen from the presented spectrum, the modified zeolites contain O, S, C, Si, Al, Cl, K, Ca, Na, Mg. The fact of sorption, for example, of copper ions on the surface of modified zeolites, is characterized by the presence in the spectrum of the peak of this metal, the content of which is 1.3% by weight. After desorption, there are no peaks in the corresponding spectra characterizing metal ions, which confirms the destruction of the Me-O bonds. The nature of the IR-spectrum also indicates the change in the structure of the zeolite as a result of modification with a sulfur polymer (see Figure 3). The fixation of modifying substances on the surface of natural zeolite is characterized by the appearance of new absorption bands at 2954.89 cm\(^{-1}\) and 2903.08 cm\(^{-1}\) (C-H bonds from sulfur polymer) on the IR-spectra.

Table 1. Data of energy differential X-ray spectrum of a natural zeolite, modified by sulfur polymer

| Element      | AN | Series | norm. C [wt.%] | Atom. C [at.%] | Error [%] |
|--------------|----|--------|----------------|---------------|----------|
| Oxygen       | 8  | K-series | 38.32          | 45.00         | 4.6      |
| Sulfur       | 16 | K-series | 23.88          | 14.00         | 0.8      |
| Carbon       | 6  | K-series | 18.17          | 28.43         | 2.9      |
| Silicon      | 14 | K-series | 12.82          | 8.58          | 0.5      |
| Aluminium    | 13 | K-series | 2.74           | 1.91          | 0.1      |
| Chlorine     | 17 | K-series | 1.82           | 0.96          | 0.1      |
| Potassium    | 19 | K-series | 1.48           | 0.71          | 0.1      |
| Calcium      | 20 | K-series | 0.59           | 0.28          | 0.0      |
| Sodium       | 11 | K-series | 0.09           | 0.07          | 0.0      |
| Magnesium    | 12 | K-series | 0.08           | 0.06          | 0.0      |
| **Total:**   |    |         | 100.0          | 100.0         |          |

**Figure 3** IR-spectrum of natural zeolite, modified by sulfur polymer

The adsorption of metal ions Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\) forms stable complexes with sulfur-containing ligands on the surface of the sorbent [15]. To prove these interactions, we analyzed the IR-spectra of sorbent samples with an absorbed metal [16]. The absorption band at 1052.41 cm\(^{-1}\) of a natural zeolite, modified
by sulfur polymer, is shifted to the high-frequency region and appears at 1074.15 cm\(^{-1}\), 1077.16 cm\(^{-1}\), 1071.85 cm\(^{-1}\) in the spectra of the zeolite after sorption of metal ions copper, nickel and zinc, respectively. Thus, a donor – acceptor sorption mechanism can be assumed. During sorption of metal ions from wastewater, sorption of the water molecules themselves also takes place, which spectrally manifest as very weak oscillations of OH-groups at 3624 cm\(^{-1}\); 3624 cm\(^{-1}\); 3622.36 cm\(^{-1}\) after sorption of Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), respectively. As a result of the sorption process, the absorption band of 716.41 - 723.29 cm\(^{-1}\) for copper ions, 716.41 - 720.33 cm\(^{-1}\) for nickel ions, 716.41 - 720.33 cm\(^{-1}\) for zinc ions confirms the formation of sulfides.

3. Conclusion
As a result of experimental investigations on the extraction of Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\) from industrial wastewaters of railway transport enterprises, it has been proved in principle that zeolites from the Holinsky deposit of the Eastern Transbaikalia can be used. In order to improve the adsorption characteristics of the raw materials, we have proposed a modification of the natural zeolites of the sulfur polymer, obtained from waste in the production of epichlorohydrin. In this case, it is recommended to thermally pretreat the initial zeolite at a temperature of 350ºC. Using IR-spectroscopy and energy dispersive X-ray spectroscopy, the high adsorption capacity of the presented modified zeolites was proved. The obtained IR-spectra show the appearance of new absorption bands, which characterize the fixation of modifiers on the surface of the zeolite. In this case, after sorption of heavy metal ions, a shift in the absorption bands appears as evidence of the adsorption process.

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