Bactericidal Properties of Modified Zeolites

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Abstract. Bactericidal properties of modified zeolites are investigated. N,N’-bis(3-trietoxysililpropyl) thiocarbamide (BTM) and hydrochloric acid was chosen as a modifier of natural zeolites from the Kholinskoe deposit (Trans-Baikal, Russia). Thanks to the presence of the structure of sizing of chemically active thiocarbamide groups adsorption in this case is accompanied by the formation on the surface of the material of stable coordination compounds, which stipulates high efficiency of such materials. It is established the improvement of bactericidal properties and an increase of the degree of water disinfection to 89–97% in the case of modified sorbents. For all water samples taken in surface water bodies the most efficient results in the decrease of the total microbial number were shown by zeolites modified by hydrochloric acid. Their practical use makes it possible to reduce TMN to standards of drinking water (50 CFU/cm³).

1. Introduction
Safety of drinking water in epidemiological respect is determined by its correspondence to standards in terms of microbiological and parasitological indicators.

Modern methods of water disinfection may include treatment by ultraviolet (UV) rays and ultrasound. It is known that UV rays produce destructive effect on vegetative forms of bacteria, spores, protozoa and viruses [1]. The efficiency of the effect of UV rays depends on the amount of the given bactericidal energy, the presence of suspension, number of microorganisms and their morphological and physiological features, etc.

Tazieva et al. [2] investigated the influence of low-frequency ultrasound on the efficiency of disinfection of waters of cultural and domestic purpose of E. coli. Obtained equation of regression adequately describing disinfection effect of ultrasound depending on three parameters: intensity, duration of ultrasound disinfection and also initial contamination of water samples.

For disinfection of water ozonization and oligodynamics are used on a wide scale. Bactericidal action of ozone with its high oxidation potential and easiness of diffusion through cellular cells of microbes [3]. It oxidizes organic substances of the microbial cell and results in its demise.

Oligodynamics (disinfection of water by silver ions) is based on bactericidal action of silver. As a rule, silver ions in interaction with enzymes of bacteria disturb the exchange of bacterial cells with the ambient medium, which results in the death of the cell. Silver produces the bactericidal and bacteriostatic effect with respect to more than 500 species of bacteria [4].
In Russia more often than not treatment by chlorine and chlorine containing substances are used. The essence of disinfection effect of chlorine lies in oxidizing-reduction processes taking place with interaction of chlorine and its compounds with organic substances of the microbial cell [5, 6]. As is known that annihilation of spore-containing bacteria and viruses require increased doses of chlorine and a prolonged contact [6]. However, high contact of chlorine in purified water worsens its tasty qualities and makes it unlikely palatable and even dangerous for drinking water supply. In this connection it is will be necessary to conduct the search for alternative inexpensive and effective methods of disinfection of water making it possible to preserve gustatory qualities after its purification. The objective of the present article is investigation of bactericidal properties of modified zeolites.

2. Experimental

\( N_N'-\text{bis (3-trietoxysililpropyl) thiocarbamide (BTM)} \) was chosen as a modifier of natural zeolites of Zabaikalie deposit. Thanks to the presence of the structure of sizing of chemically active thiocarbamide groups adsorption in this case is accompanied by the formation on the surface of the material of stable coordination compounds, which stipulates high efficiency of such materials.

Modification is done in the following way: 10 g of zeolite was in contact during stirring with 100 g of a 30\% solution of BTM in hexane [7]. Stirring was carried out for three hours at 50°C. Upon the expiry of the indicated time the zeolite was separated from the solution dried in the air and was held in a drying cabinet for one hour at 110°C. The resultant product was cooled in the vacuum-desiccator and determined the change of the weight in the course of modification. In this case the increment of the weight constituted 39.4%.

Practical use of zeolites modified by organic compounds in technologies of purification of wastewaters have an essential limitations. These zeolites fail to be used repeatedly since it is difficult and sometime even impossible to regenerate [8]. Therefore preference should be given to mineral modifiers (salts and oxides of active metals, alkali, mineral acids, etc.) in the case of which the possibility of repeated use of sorbents is increased greatly [9].

For obtaining zeolites modified by HCl the following technique was used: 100 g of zeolites dried out to constant weight a 120\% solution of HCl in water. Then suspension was filtered and washed with distilled water to neural reaction. The resultant modified zeolites were dried out to the constant weight and was analyzed for the content of main elements. In this case an increase of the weight of zeolites constituted 20%.

The X-ray analysis was carried out on an automatic X-ray diffractor D8 Advance fitted by the Gebel mirror and a detector Vantec1 PSD. The calculation of X-ray photographs was fulfilled by means of the software of the diffractometer. For identification of phases one used the basis of powder diffractograms PDF2. The content of mineral components in the samples was calculated by the Topaz program.

IR spectral research was conducted on a device Bruker Tensor 27. Attribution of absorption bands was done in accordance with atlases of IR spectral data.

Porosity and the specific surface were determined on devices of the series Sorbtometr M and Thermosorb designed for investigation of textural characteristics of substances and materials.

Bactericidal properties of zeolites were investigated in static conditions, the S : L ratio constituted 1 : 100.

Water samples were taken in surface water bodies near the city of Irkutsk, in the spring period of the current year (these are rivers Angara, Irkut, Olkha, Kaya and Ushakovka; Siberian region of Russia).

3. Results and discussion

The efficiency of disinfection of sampled samples (E, \%) was determined by the formula:
where $C_{\text{ini}}$ – TMN in initial samples of water, $C_{\text{fin}}$ – the same in purified water samples, CFU/cm³.

On the basis of the data obtained histograms of efficiency of disinfection of taken water samples were built (Figs. 1a–1c) from which it follows that the degree of water disinfection in the case of zeolites modified by BTM increased from $79 \pm 10$ to $85 \pm 5\%$.

For zeolites modified by HCl disinfection was achieved from $89 \pm 7$ to $92 \pm 8\%$. If one compares obtained results with similar ones for natural analogues (AS) then in the given case the degree of disinfection increased from $50 \pm 11$ to $64 \pm 18\%$. Thus, for all water samples being studied the most efficient results in decreasing TMN were shown by zeolites modified by HCl.

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E = \frac{C_{\text{ini}} - C_{\text{fin}}}{C_{\text{ini}}} \times 100, 
\]

As is known bacterial action of chlorine is connected with its high oxidation potential ($1.36$ V) [5]. Chlorine when dissolved in water forms two acids – hydrochloric and hypochlorous acids. Dissociation of a very weak hypochlorous acid depends on active reaction of the medium. The lower the value of $pH$ of the system, the higher the content of hypochlorous acid ensuring water disinfection. Therefore water disinfection by chlorine and chlorine containing substances is advisable to be carried out before the introduction into it of alkaline reagents.

In our case when investigating antibacterial properties of initial water samples the $pH$ of the medium constituted $7.5$–$8.2$. The highest water acidification was noted at interaction with the taken samples of zeolites modified by HCl. Noted was a decrease of the $pH$ to $3.1$–$4$, which was affected bis(3rietoxysilpropyl) thiocarbamide allows us substantially lower down the concentration of ions of heavy metals in diluted solutions [7]. Thanks to the presence in the structure of the finishing agent of chemically active thiocarbamide groups adsorption in this case is accompanied by the formation on the surface of the material. The structure of the modified adsorbent is confirmed by the presence in its IR spectrum of the intensive band of valence oscillations of siloxane connection ($1050$ cm$^{-1}$), the bands of deformation oscillations of amino groups ($1634$ cm$^{-1}$) and the set of bands of thiocarbonyl groups ($1558$–$1345$ cm$^{-1}$) (Fig. 2).

The presence in the silicon-organic finish of thiocarbamide groups determines the possibility of the formation on the surface of the modified adsorbent of ionic coordination complexes of ions of metals with donor atoms of nitrogen and sulfur in accordance with the Kuznetsov theory analogies [11].

The content of main components in the samples being studied was determined by means of X-ray analysis. Based on the data obtained it was established that at modification of zeolites by HCl there occurs destruction of the main component of the heulandite, its concentration decreases from $64.3$ to...
42.9%. However, temperature treatment at modification is conducive to compaction of the sanidine structure $\text{KAlSi}_3\text{O}_8$ almost twice, which should tell on the adsorption properties of modified sorbents. Whereas adsorption characteristics of natural analogues remain much lower than of modified zeolites [12]. The change in the structure of modified zeolites was also confirmed when studying their texture characteristics by the method of low temperature adsorption-desorption of nitrogen (Table).

![IR spectrum of zeolites modified by BTM](image)

Fig. 2. IR spectrum of zeolites modified by BTM

| Characteristics                  | AS   | HCl  |
|----------------------------------|------|------|
| Specific surface, m$^2$/g         | 33   | 75   |
| Specific volume of pores, cm$^3$/g| 0.015| 0.036|
| Average size of pores, nm        | 1.8  | 1.6  |

It should be noted that at modification of zeolites by HCl their specific surface and specific volume of pores increases by more than twice. The average size of pores reduces from 1.8 to 1.6 nm. The research conducted showed the change of the structure and construction of modified zeolites promoting their physicochemical characteristic including adsorption ones. In investigating a bactericidal properties of modified zeolites one discovered improvement of their microbial indicators. For all studied water samples taken in surface water, the most effective results on the decrease of TMN were shown by alumosilicates modified by HCl. Their practical use allows one to reduce TMN to standards of drinking water (50 CFU/cm$^3$) [13-15].

4. Summary

It has been established that in case of zeolites modified by BTM the degree of water disinfection constituted 79-85%, while for zeolites modified by HCl – 89-92%. The best results on reducing the total microbial number were showed by zeolites modified by HCl. Their practical use makes it possible to reduce TMN to standards of drinking water (50 CFU/cm$^3$).

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