Wastewater treatment of industrial enterprises via adsorption method

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Abstract. The publication justifies the feasibility of adsorption method of industrial wastewater treatment from aromatic compounds. Objects and methods of research are described. Studies of adsorption mechanisms of aromatic compounds on bentonites of various modifications made it possible to establish the most effective sorption rock clay-based materials, as well as filter compositions. Bentonite modified with carbon nanotubes after heat treatment 550 °C proved to be the most effective with respect to the studied aromatic compounds. The principle of combining sorbents in a single filtering system, based on the sorbent selection for various groups of organic pollutants according to their ability to be ionized in an aqueous medium, has been proposed and investigated. Three most effective multicomponent adsorption filter compositions for sewage treatment from nitro and amino compounds were established. The proposed approach is aimed at designing local water treatment stations for industrial enterprises to deal with aromatic compounds via use of multicomponent adsorption filter compositions.

1. Introduction

The development of improved wastewater treatment methods in sewage systems is a priority area of modern industrial ecology. This procedure is associated with designing highly efficient filtering systems that can provide wastewater treatment for various industries. The most harmful wastewater is produced in the course of industrial production of dyes, chemicals and medicines. Cleaning the effluent of these industries from organic pollutants is especially difficult [1-3]. It has been established [4] that use of adsorption filtering systems is most appropriate for wastewater treatment from organic contaminants. Therefore, the improvement of adsorption technologies and sorbent compositions through their chemical modification plays an important role in creating new, more efficient wastewater treatment methods for enterprises in the field of chemical industry [5].

Development of new methods for adsorption treatment of polluted waters has been conducted at the Department of Ecology, Yuri Gagarin State Technical University of Saratov (SSTU), since 2011 [6-8]. Department scientists focused their efforts on using inexpensive and readily available natural clay materials, primarily bentonites, as sorbents [9-12]. Bentonites are multi-mineral formations consisting predominantly of silicates. Clay rocks are usually highly ion-exchangeable. This property is typical for the minerals with a so-called “sliding” crystal lattice, such as montmorillonite. When this mineral interacts with water, a water molecule is able to enter the gaps between the layers of montmorillonite.
crystal lattice and push them apart. It is this property of the mineral that explains its high adsorption capacity.

SSTU Department of Ecology scientists developed complex sorbent compositions of a new generation for efficient removal of toxic organic substances, heavy metals and oil refining by-products from industrial wastewater. These compositions were also found effective for water disinfection.

Multi-layer filter compositions are of particular interest, since they provide comprehensive treatment of polluted water from several pollutants simultaneously. Current experimental studies conducted at SSTU Department of Ecology are directed at creating filter compositions for treating wastewater containing various organic toxicants. Special attention is paid to the extraction from the water of benzene (aromatic) compounds that penetrate into natural water bodies with sewage of dye, chemical, pharmaceutical, light, and other types of industry [13]. Benzene compounds are the most toxic and biologically steady pollutants [14, 15].

2. Objects and methods of research

The object of our study was wastewater from industrial enterprises. To solve the problem of wastewater treatment, we proposed various structural modifications of the bentonites: by high-temperature heat treatment (HTHT) at different regimes (with preliminary or direct calcination at a given temperature) and by organic components - carbon nanotubes (CNT) and glycerol, both individually and in combination with each other. Modification of bentonites was carried out jointly with our collaborators from scientific and production enterprise "LISSKON".

Major employed research methods were spot test analysis [16], photometry, titration, etc.

We selected nitro and amino compounds - o-toluidine, o-phenylenediamine and p-dinitrobenzene - as model pollutants for our laboratory studies. Concentrations of these chemical compounds, exceeding MAC, were found in wastewater of textile production in Saratov region [17].

Laboratory studies of various filter compositions using modified bentonites included the following:
1. The study of the bentonite adsorption capacity with respect to aromatic organic compounds for different variants of bentonite modification.
2. The study of multicomponent adsorption filter compositions for water treatment from nitro and amino compounds.
3. Selection of the most effective filter compositions for adsorption filtering systems used for wastewater treatment of industrial enterprises from a complex of organic pollutants. The model water solution to be filtered included the following pollutants: p-dinitrobenzene, m-aminophenol, o-phenylenediamine, p-nitroaniline and o-toluidine. 200 ml of the model solution were filtered through each filter composition.

3. Results and Discussion

The results of our studies on the adsorption capacity of modified bentonites with respect to selected organic pollutants (o-phenylenediamine, o-toluidine and p-dinitrobenzene) revealed that all four modifications of the sorbents selected for research have different adsorption capacity. The highest adsorption capacity was manifested for the bentonite modified with CNT at a firing temperature of 550 °C (direct calcination); somewhat lower adsorption capacity was shown for the bentonite modified with glycerol and CNT at a firing temperature of 550 °C (direct calcination); still lower adsorption capacity was found for the bentonite modified with glycerol and CNT at a firing temperature of 550 °C (calcination with preheating for 30 minutes); finally, the lowest adsorption capacity was discovered for the bentonite without modifiers (direct calcination at a temperature of 550 °C). Such pattern was observed for all studied pollutants.

Established parameters for o-phenylenediamine, o-toluidine and p-dinitrobenzene adsorption on investigated sorbents in dynamic conditions are included in Table 1.
Table 1 – Adsorption effectiveness parameters of organic substances on investigated sorbents

| Organic substance | Bentonite modification | DEC, mg/g | \(K_d\), mg/dm³ | S, %       |
|-------------------|------------------------|-----------|-----------------|------------|
|                   | unmodified             | 3,089±0,011 | 1,907±0,030     | 94,600±0,060 |
|                   | CNT                    | 3,935±0,049 | 2,623±0,030     | 95,000±0,110 |
| glycerol          |                        | 3,645±0,051 | 2,433±0,020     | 94,801±0,100 |
| glycerol and CNT  |                        | 3,499±0,010 | 2,187±0,04      | 94,667±0,360 |
| unmodified        |                        | 2,066±0,013 | 1,878±0,017     | 94,500±0,140 |
|                   | CNT                    | 2,872±0,021 | 2,872±0,011     | 95,000±0,350 |
| glycerol          |                        | 2,521±0,041 | 2,480±0,031     | 94,950±0,250 |
| glycerol and CNT  |                        | 2,341±0,014 | 2,209±0,039     | 94,700±0,300 |
| unmodified        |                        | 1,012±0,051 | 1,177±0,060     | 94,267±0,990 |
|                   | CNT                    | 1,322±0,036 | 1,762±0,080     | 95,000±0,430 |
| glycerol          |                        | 1,173±0,062 | 1,563±0,033     | 95,000±0,120 |
| glycerol and CNT  |                        | 1,023±0,010 | 1,421±0,050     | 95,200±0,510 |

DEC – dynamic exchange capacity, \(K_d\) – interfacial partition coefficient, S – adsorption rate

In the study of multicomponent adsorption filter compositions, it was established experimentally that the most effective compositions with respect to complex pollution with organic substances were the compositions [18, 19], containing the following sorbents:

1. Bentonite modified with CNT, thermally treated at 550 °C; AB-17-8 anion exchange resin; ASKG silica gel.
2. Peat; zeolite; organobentonite TS 952752-2000; bentonite modified with heat treatment at 550 °C; bentonite modified with glycerol after heat treatment at 550 °C.
3. Zeolite; organobentonite TS 952752-2000; bentonite modified with heat treatment at 650 °C; bentonite modified with glycerol after heat treatment at 650 °C.

Figure 1 presents the results of comparative analysis of filter compositions.

The effectiveness of water treatment from amino and nitro compounds for each of three listed filter compositions exceeded 95% [20].

4. Conclusions

Studies of the adsorption capacity of modified bentonites with respect to o-phenylenediamine, o-toluidine and p-dinitrobenzene established that model solutions filtered through bentonite modified with CNT (direct calcination at 550 °C) stably reached a negative reaction faster than in case of other sorbents. It was also found that the highest efficiency of water treatment from the listed pollutants was observed for the bentonite modified with CNT (direct calcination at 550 °C, no preheating).
The principle of combining different sorbents in the structure of a single filtering system, based on sorbent selection for various groups of organic substances according to their ability to be ionized in an aqueous medium, has been proposed and investigated. In relation to the amino and nitro compounds, the most effective filter composition contained the following sorbents: bentonite modified with CNT, thermally treated at a temperature of 550 °C (direct calcination); AB-17-8 anion exchange resin; ASKG silica gel.

5. Acknowledgements and Conflict of Interests
The authors are grateful to the scientific-industrial enterprise LISSKON located in the city of Saratov, Russia, for using their laboratory space and equipment for conducting the research. The study was supported by the grant No. 5.3922.2017/PCh from the Russian Federation Ministry of Education. The authors state no conflict of interests involved.

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