Innovative technologies for industrial wastewater treatment

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Abstract. We justified the need to purify wastewater, coming from industrial enterprises, from aromatic compounds using sorption technologies. The objects and methods of our research are described in this paper. In the process of studying adsorption mechanisms of aromatic compounds on bentonites of various modifications in static and dynamic conditions, the basic characteristics of adsorption processes were established. Bentonite, modified by carbon nanotubes after thermal treatment, proved to be the most effective with respect to organic compounds. Three most effective compositions of multicomponent adsorption filter for wastewater treatment from nitro and amino compounds are described. We developed the technological design of a local water treatment plant designed for purifying the wastewater, coming from industrial plants, from aromatic compounds. Multicomponent adsorption filters for wastewater treatment have been developed and patented.

Key words: adsorption, bentonite, aromatic amine compounds, hydrodynamic conditions

Introduction

Modern production of paint, varnish, textile, rubber, etc., is a potential cause for pollution of surface water bodies and groundwater, since wastewaters of those industries are characterized by increased content of organic impurities, including toxic content [1]. At present, studies of wastewater treatment from pollutants represented by aromatic compounds acquire particular urgency.

Complete removal of organic matter from wastewater is a difficult task [1], despite the fact that, at present, there is a wide range of biological, physicochemical and other methods for water purification. Each of these methods has its drawbacks, which substantially narrows the limits of their applicability.

Adsorption methods have a number of advantages over other existing methods of water treatment. The main advantages of these methods include simplicity of instrumentation, the ability to extract many organic substances from water, including biologically stable ones, which cannot be removed by other methods [2]. Another significant advantage is an absence of secondary impurities [2-3].

Modern problems of industrial ecology in the field of cleaning contaminated waters in both water supply and wastewater systems include the need to develop approaches to improving adsorption technologies and the composition of sorbents by means of their chemical modification [4]. Currently, the Scientific and Educational Center "Industrial Ecology" at Yuri Gagarin State Technical University of Saratov (SSTU) works on developing innovative technologies for wastewater treatment from nitro and amino compounds within the framework of the State Task of the Russian Federation Ministry of
Education and Science, grant No. 5.3922.2017/PCh: "Development of environmentally friendly energy-saving technologies for the integrated treatment of water contaminated as a result of natural and man-made emergencies for local water treatment plants in problem regions of the Russian Federation".

**Objects and methods of research**

The objects of investigation were bentonites modified by various methods, including high-temperature heat treatment under various modes (with preheating or burning directly at a given temperature); modification of the bentonite structure by organic components - carbon nanotubes (CNT) and glycerol, either individually or in combination with each other. Bentonite modification was carried out in collaboration with our partners from scientific-industrial enterprise "LISSKON".

Studies on adsorption efficiency were conducted both for individual modifications of bentonites and for multicomponent adsorption filtering loads, including various modifications of bentonite and other sorbents (AN-17-8 anion exchange resin, ASKG silica gel, zeolite, etc.). In our experiments, the control was represented by BAU-A activated carbon. The major methods of our study included spot test reactions, photometry, titration, electron microscopy, and statistical data treatment.

We selected nitro and amino compounds as model pollutants in our study. The presence of those was detected in sewage waters of paint and textile production enterprises of Saratov Region [5]. These included o-toluidine, o-phenylenediamine and p-dinitrobenzene. In the course of laboratory studies of multicomponent adsorption filters’ effectiveness, complex model solutions were used, comprising of various nitro and amino aromatic compounds, such as p-dinitrobenzene, m-aminophenol, p-nitrophenol, p-nitroaniline, o-toluidine, and others.

**Results and Discussion**

The results of our research revealed the features of the adsorption processes of the studied pollutants by various bentonite modifications.

**Studying the adsorption mechanism of nitro and amino compounds**

Justification of the adsorption capacity of modified bentonites presumed studying their adsorption characteristics in laboratory conditions. Estimation of sorption efficiency parameters was carried out by establishing equilibrium concentrations of organic substances. In each experiment, an equilibrium concentration of organic substances was determined from the steady-state values of each studied substance concentration over time.

The results of conducted studies of organic substances’ adsorption on bentonites of various modifications under static conditions made it possible to establish the characteristics of the adsorption process, such as static exchange capacity (SEC), $K_a$, $S$, which allowed the selection of the adsorbent under specific conditions of predominance of polluting organic matter in wastewater [6].

Analysis of the adsorption isotherms of o-toluidine and o-phenylenediamine on modified and unmodified bentonites under static conditions showed that this process was most accurately described by the Freundlich isotherm. Thus, we concluded that the adsorption of o-toluidine and o-phenylenediamine on the studied sorbents proceeded according to the ion-exchange mechanism. Addition of glycerol to bentonite modified by CNT somewhat reduced the effectiveness of the adsorbate interaction with aluminosilicate and nanotubes, which could be explained by the intrinsic adsorption of glycerol on the adsorbent and reduction of the adsorption centers’ numbers [7].

Analysis of the adsorption isotherms of p-dinitrobenzene on the studied bentonites under static conditions showed that this process was most accurately described by Langmuir isotherms. In this case, monomolecular layers of the adsorbate were formed on the adsorbent surface. The highest adsorption efficiency of p-dinitrobenzene was manifested by the bentonite modified by CNT [8].

The established efficiency parameters of the interaction of o-toluidine, o-phenylenediamine and p-dinitrobenzene ions with the studied modifications of bentonites under dynamic conditions were dynamic exchange capacity (DEC), $K_{ds}$, and $S$. It is worth noting that DEC of the studied bentonites
with respect to ions of organic substances was decreasing in the following series: p-dinitrobenzene > o-toluidine > o-phenylenediamine.

The adsorption effectiveness of organic substances’ ions under dynamic conditions was the highest for the bentonite modified with CNT. It was slightly less for the bentonite modified with glycerol, and even less for the bentonite modified with glycerol and CNT. The lowest values were found for unmodified granular bentonite.

The results of investigating the adsorption mechanism of composite adsorbents with respect to the studied organic substances confirmed the expediency of using the proposed adsorbents as the constituents of sorption filters for treating the wastewaters of chemical industry enterprises.

**Developing the composition of multicomponent adsorption filters**

Comparison of the efficiencies of water purification from various nitro and amino compounds made it possible to single out the following compositions of the filtering loads for multicomponent adsorption filters (the list of filter layers is presented in a top-down direction):

- Zeolite; bentonite modified with CNT and glycerol after thermal treatment at 550 °C with a gradual increase in temperature; organobentonite TU 952752-2000; bentonite modified with CNT and glycerol after heat treatment at a temperature of 550 °C; silica gel brand ASKG; Bentonite after heat treatment at a temperature of 800 °C. The efficiency of water treatment was 98.9%;
- Bentonite modified with CNT thermally treated at a temperature of 550 °C; AB-17-8 anion-exchange resin; ASKG silica gel. The efficiency of this composition was 98.8%;
- Peat; zeolite; organobentonite TU 952752-2000; bentonite after heat treatment at 650 °C; bentonite modified with glycerol after heat treatment at 650 °C. The efficiency of water treatment was 95.4%.

Therefore, we recommend these filtering load compositions for using in multicomponent adsorption filters designed for industrial sewage treatment from nitro and amino compounds.

**Developing innovative technological designs for wastewater treatment from aromatic compounds**

Multicomponent adsorption filters (MAF) with described filtering load compositions are advisable to use at local wastewater treatment plants. The proposed technological design of the local wastewater treatment station is shown in Fig. 1.

![Figure 1 - Technological design of the plant for treating industrial wastewater of a complex composition](image-url)

The technology of the proposed design presumes the following stages of water purification:

- Wastewater enters the receiving tank, neutralized by chemical interaction with substances (mixing acidic wastewater with alkaline waters, addition of the reagent in required concentrations). Volume of incoming sewage is measured by water meters. Further, settling of water in the water intake tank takes place;
- Wastewater neutralized and suspended from mechanical impurities is subjected to rough cleaning on filters;
- At the next stage, preliminarily treated wastewater is subjected to aeration using an oxygen compressor;
- Then, water is deferred, softened and purified from organic substances while passing through a multicomponent adsorption filter with a complex filtering load consisting of various modified bentonites;
- Further on, purified water passes the post-treatment stage in the nanofiltration block, dripping through the membrane filters;
- Treated water enters a storage tank for clean water, where its volume is measured, and then discharges into an open reservoir;
- Filtering load, including several types of sorbents, which are placed in a multicomponent adsorption filter, periodically undergoes regeneration;
- Sorbent, completely saturated with contaminants, is utilized with lowering its hazard class and its further use in construction.

A sorbent of a multilayer filtering load is placed in each of the MAF cassettes. The number of drawable cassettes can be from 3 to 7 pieces (Fig. 2).

**Figure 2** - Multicomponent adsorption filter with retractable cassettes: 1 - cassette; 2 - support; 3 - branch pipe; 4 - metal case; 5 - guides; 6 - side wall; 7 - perforated tube; 8 - upper cassette; 9 - bracket; 10 - grid; 11 - distributing device; 12 - short branch pipes; 13 - catchment tray; 14 - bolt; 15 ... 17 - sorbents [9]

The adsorption filter [9] includes cassettes located one above the other, filled with various kinds of sorbents, and a branch pipe for the drainage of purified water. Cassettes are made of high-strength plastic and placed in a metal case; they extend along the guides, fixed to the side walls of the housing. In the ceiling part of the metal case, there are perforated tubes, through the holes of which water to be purified is fed into the upper cassette. The lower part of each cassette is equipped with a grid and a distributing device, guiding the water to be purified from the upper cassette into the lower cassette through short branches. In the bottom of the metal case, there is a catchment tray for purified water, to which a branch pipe for draining purified water is attached.

The team of scientists at the Scientific and Educational Center "Industrial Ecology", SSTU, proposed and patented several innovative designs of adsorption filters for local wastewater treatment plants [10]. The results of industrial tests conducted at the scientific-industrial enterprise "LISSKON" confirmed the feasibility of the proposed technological solutions for industrial wastewater treatment.
Conclusions

We proposed and investigated the principle of combining various sorbents in a single multicomponent filter, based on their selection for various groups of organic contaminants and on the ability of these contaminating substances to ionize in an aqueous environment.

The parameters, characterizing the adsorption efficiency of organic compounds by unmodified bentonite and bentonite modifications under different static and dynamic conditions, were identified. Bentonite modified with CNT proved to be the most effective with respect to organic compounds. Its parameters with respect to o-toluidine were: SEC = 58.42 meq / g, Kd = 0.07 mg / l, S = 73.03%. Its parameters with respect to o-phenylenediamine amounted to: SEC= 51.31 meq / g, Kd = 0.05 mg / l, S = 64.14%. For p-dinitrobenzene, SEC = 1.56 meq / g, Kd = 0.14 mg / l, S = 83.57%.

Adsorption of o-toluidine and o-phenylenediamine on the studied bentonites proceeded according to the ion-exchange mechanism. The adsorption of p-dinitrobenzene under static conditions was described by the Langmuir isotherm.

We developed and tested innovative designs of multicomponent adsorption filters for water treatment from a complex of organic pollutants [9, 10], designed to provide comprehensive purification of wastewaters, contaminated with a complex of organic compounds. The expediency of using the proposed multicomponent adsorption filters was confirmed by the results of production tests at a scientific-industrial enterprise "LISSKON".

Acknowledgements and Conflict of Interests

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