Adsorption of aromatic nitro and amino compounds with modified bentonite

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Abstract. Wastewater of many types of industries contribute to the entry into open water bodies of toxic organic compounds, the concentrations of which in some cases exceed the Maximum Permissible Concentration for Water in Commercial Fishery Reservoirs. Typical representatives of toxic organic pollutants in the aquatic environment are aromatic nitro and amino compounds. Currently, a significant number of wastewater treatment methods have been developed. One of the most promising methods of water treatment are adsorption methods. Of considerable interest is the use of natural clay minerals as sorption materials for wastewater treatment. The object of the study is model solutions of nitro and amino compounds, the adsorption of which was studied on different versions of modified bentonites. In this work, the adsorption capacity of modified bentonite with five different acid activation variants upon extraction of p-dinitrobenzene and o-phenylenediamine from solutions was studied. The adsorption parameters of the studied variants of bentonite, such as the adsorption value G, mg/g; interfacial distribution coefficient Kd, mg/dm$^3$; degree of adsorption recovery S, %. The constructed adsorption isotherms made it possible to identify the most effective variants of modified bentonite with additional activation by acid to extract aromatic nitro and amino compounds from solutions. The best adsorption ability upon extraction of p-dinitrobenzene from a solution was shown by glycerin-modified bentonite, subjected to heat treatment at 550 °C, the average fraction of granules, after activation with 9 % HCl solution and 30 % CaCl$_2$ solution. The best adsorption ability upon extraction of o-phenylenediamine from a solution was shown by glycerin-modified bentonite, subjected to heat treatment at 550 °C, the average fraction of granules, after activation with 18 % HCl solution and 38 % CaCl$_2$ solution.

1. Introduction
In conditions of constant pollution of the aquatic environment with various chemicals, high-quality wastewater treatment before it is discharged into natural water bodies or urban sewers is of particular importance.

Wastewater from chemical, light, pharmaceutical, paint and varnish and other industries usually contain a range of organic pollutants, including aromatic nitro and amino compounds.

Monitoring of natural water bodies of the Saratov region in places of waste water discharge from enterprises showed excess of maximum permissible concentration. aromatic substances in water by 5–28 %.

Aromatic nitro and amino compounds are among the common and highly toxic pollutants of the aquatic environment. Their widespread use is associated with active industrial use [1]. Nitro and amine compounds are most characteristic of the wastewater of enterprises producing dyes, pharmaceuticals, varnishes and paints, textile, synthetic polymers, plastics, rubbers, pesticides, cosmetic and rubber
products [2, 3]. In addition, aromatic amino compounds can be formed during the destruction of soil organic matter, as well as some antiseptics and pesticides [1].

The main representatives of aromatic amino compounds include aniline, toluidines, phenylenediamines, xylidines, toluene diamines, etc. and their various derivatives. Aromatic nitro compounds are, first of all, nitrobenzenes, nitrotoluenes, dinitro- and trinitrobenzenes. Aromatic nitro and amino compounds are toxic. So, the ingress of amino derivatives of benzene into sources used for the preparation of drinking water can lead to negative consequences for the population and the environment. Their reactivity with respect to chlorine is very high, and at the stage of water disinfection with chlorine, the formation of various chlorine-substituted amines can occur – for example, aniline at a minimum dose of chlorine forms significant amounts of \( \text{p} \)- and \( \text{o} \)-chloroalanines and dichloroanilines [1]. In this case, the toxicity of amines, as a rule, increases with the appearance of chlorine atoms in the molecule [1, 4].

The most characteristic manifestation of the toxic effect of aromatic amino compounds is selective damage to red blood cells; it is also possible to damage the central nervous system, liver and kidneys, although in general they do not possess selective hepato- and nephrotropy [3].

Aromatic nitro compounds are also characteristic of wastewater from the production of explosives and various nitro products [2, 4]. For fish, they are all very toxic; symptoms of poisoning are most often manifested in the form of apathy, stunning and anesthesia. A number of dinitro compounds affect the metabolism, exerting a uncoupling effect on the processes of conjugated oxidative phosphorylation. Aromatic nitro compounds, as well as amino compounds can cause dermatitis, eczema, allergies [4].

Among others, the adsorption method is included in the list of physico-chemical methods for wastewater treatment and water treatment.

The advantage of the adsorption method over others is that it has high efficiency at a low concentration of impurities in water, i.e. when the use of other methods becomes economically impractical or even impossible. The essence of the method is the concentration of impurities contained in water on the surface of a solid sorbent. This method can be used as an independent one for deep water purification in circulating and drainless water supply systems. The effectiveness of the use of sorption materials depends on their nature, specific surface area, the ratio of micro- and macropores and other factors that determine their different adsorption capacity [5–9].

The efficiency of adsorption purification reaches 80–95 % and depends on the chemical nature of the adsorbent, the size of the adsorption surface and its availability, on the chemical structure of the substance and its state in an aqueous solution [6].

Recently, bentonite adsorbents have gained particular popularity among sorption materials [9, 10]. Sorption materials based on natural clay minerals have significant advantages over synthetic aluminosilicates. These advantages include significant resistance to high temperatures, intense radioactive radiation, and the effects of oxidizing environments [11, 12]. Natural clay materials are widely distributed in the Russian Federation and abroad. Therefore, the prospect of their use as adsorbents for the purification of water from aromatic nitro and amino compounds is promising, which is the focus of this article.

2. Methods and materials

Sorption materials, which are bentonite modified with glycerin with various activation options, were accepted for research. The initial bentonite was brought from the Sarigyukh deposit. The modification of bentonite was carried out on the basis of the LISCON Research and Production Enterprise (Saratov).

For experimental studies, bentonite granules of the middle fraction (size 0.5–1.0 mm) were selected. The preference of the middle fraction of bentonite granules is justified by the results of earlier experiments [9].

The composition of the studied sorption materials included:

- No. 1 – bentonite, modified with glycerin, subjected to heat treatment at 550 °C, the average
fraction of granules, without activation,
- No. 2 – glycerin modified bentonite, subjected to heat treatment at 550 °C, the average fraction of granules, activation with 9 % HCl solution,
- No. 3 – glycerin-modified bentonite, subjected to heat treatment at 550 °C, the average granule fraction, activation with an 18 % HCl solution,
- No. 4 – glycerin-modified bentonite, subjected to heat treatment at 550 °C, the average granule fraction, activation with 9 % HCl solution and 30 % CaCl₂ solution,
- No. 5 – glycerin-modified bentonite, subjected to heat treatment at 550 °C, the average granule fraction, activation with 18 % HCl solution and 38 % CaCl₂ solution.

The laboratory experiment was carried out with 3 and 4-fold repetition in accordance with standard methods. To assess the static sorption, solutions of \( \pi \)-dinitrobenzene of the following concentrations were prepared: 5, 10, 20, 30, 40, 50, 55 and 60 mg/dm³. Solutions of o-phenylenediamine of the following concentrations were also prepared: 100, 300, 500, 700, 900, 1500, 2000, 2500 and 3000 mg/dm³.

The activation method of the sorption material was as follows. Before the start of the experiment, a weighed portion of 60 g of the initial bentonite granules was placed in a 400 ml previously washed and thoroughly dried measuring cup, after which the bentonite granules were soaked in water for 24 hours. Then, the sorption material was transferred to a Petri dish and dried at room temperature to obtain an air-dry sample, from which a sample weighing 10 g was taken for studies (Fig. 1).

Figure 1. Air-dry sample of sorption material

For acid activation after the operations, either 10 ml of a 9 % HCl solution (hereinafter activation option No. 1) or 10 ml of an 18 % HCl solution (hereinafter activation option No. 2) was poured onto a sample, which depended on the method chosen. After that, bentonite granules in an acid solution were intensively mixed for an hour and left for 6 hours in a glass with an acid solution. After keeping in acid, the solution was removed, and the granules were washed until the acidity of the water obtained after washing was completely neutralized and left in air to obtain an air-dry sample.

The granules were also activated by preliminary acid activation and final salt using a CaCl₂ solution. Such a change in the activation procedure was chosen on the basis of the assumption that the best sorption of organic substances occurs when ions with a large core radius are in the interlayer space of aluminosilicate. The stage of acid activation is similar to that described above, but after acid removal, without receiving an air-dry sample, the obtained bentonite was kept for one hour with periodic stirring in 40 ml of either 30 % CaCl₂ solution (hereinafter activation option No. 3) or 38 % CaCl₂ solution (hereinafter, activation option No. 4). The activation procedure with a CaCl₂ solution was repeated three times for the largest possible replacement of cations in the interlayer space. After washing the granules from the remainder of the CaCl₂ solution, the presence of Ca₂ + ions in the
washed water was checked by titration of the washed water with Trilon B solution according to the procedure in accordance with [13], since the presence of calcium ions would not allow determination of the substance due to the reaction with NaOH.

To study the adsorption capacity of modified bentonites, \( p \)-dinitrobenzene and \( o \)-phenylenediamine were chosen as typical representatives of aromatic nitro and amino compounds. Thus, studies of the adsorption capacity of bentonite were carried out on model solutions of these representatives of benzene derivatives.

The methods for determining the concentration of \( p \)-dinitrobenzene and \( o \)-phenylenediamine are adopted in accordance with the recommendations of I.M. Korenman [14].

3. Results

The sorption ability of modified bentonites with respect to \( p \)-dinitrobenzene and \( o \)-phenylenediamine was evaluated under static conditions [15, 16]. According to the results of a laboratory experiment, the following were established: adsorption value \( G \), mg/g; interfacial distribution coefficient \( K_d \), mg/dm\(^3\); degree of adsorption recovery \( S \), % on the studied variants of modified bentonite.

The calculated sorption parameters of \( p \)-dinitrobenzene on the studied sorption materials are presented in Table 1.

The general adsorption isotherms of \( p \)-dinitrobenzene on modified bentonite are shown in Fig. 2 and fig. 3. Here, the residual concentration of \( p \)-dinitrobenzene in the solution is denoted by \( C_i \), and the equilibrium concentration is denoted by \( C_p \), mg/dm\(^3\).

| Substance          | No. of sorption material | \( \Gamma \), mg/g | \( K_d \), mg/dm\(^3\) | \( S \), % |
|--------------------|--------------------------|-------------------|------------------------|----------|
| \( p \)-dinitrobenzene | 1                        | 0.60±0.05         | 0.01±0.00              | 25.12±1.80 |
|                    | 2                        | 0.72±0.06         | 0.02±0.00              | 30.00±2.28 |
|                    | 3                        | 0.91±0.07         | 0.02±0.00              | 38.4±3.10  |
|                    | 4                        | 1.50±0.12         | 0.07±0.00              | 62.50±6.00 |
|                    | 5                        | 1.00±0.09         | 0.03±0.00              | 41.67±3.63 |

**Figure 2.** Sorption isotherms \( \Gamma = f(C_i) \) \( p \)-dinitrobenzene on bentonite of various activation options.
Figure 3. Sorption isotherms \( G = f (C_{pi}) \) of p-dinitrobenzene on bentonite of various activation options

The results of the study and the obtained sorption characteristics of the studied variants of bentonite with respect to \( \text{o-phenylenediamine} \) are presented in table 2.

Table 2. Parameters of sorption of \( \text{o-phenylenediamine} \) on the studied bentonite variants

| Substance                  | No. of sorption material | \( \Gamma, \text{ mg/g} \) | \( K_a, \text{ mg/dm}^3 \) | \( S, \% \) |
|----------------------------|--------------------------|-----------------------------|-----------------------------|------------|
| \( \text{o-phenylenediamine} \) | 1                        | 38.43±2.84                  | 0.01±0.00                   | 32.03±2.63 |
|                            | 2                        | 46.12±3.36                  | 0.01±0.00                   | 38.43±3.07 |
|                            | 3                        | 48.79±3.61                  | 0.02±0.00                   | 40.66±3.17 |
|                            | 4                        | 50.84±3.86                  | 0.02±0.00                   | 42.36±3.47 |
|                            | 5                        | 52.52±4.04                  | 0.02±0.00                   | 43.76±3.60 |

The general adsorption isotherms of \( \text{o-phenylenediamine} \) on modified bentonite are shown in Fig. 4 and 5.

Figure 4. Sorption isotherms \( G = f (C_i) \) \( \text{o-phenylenediamine} \) on bentonite of various activation options
An analysis of the obtained adsorption parameters of p-dinitrobenzene and o-phenylenediamine on different versions of modified bentonite under static conditions, as well as the constructed adsorption isotherms made it possible to perform a comparative assessment of the sorption ability of the studied adsorbents.

4. Conclusion
A laboratory experiment and the constructed adsorption isotherms \( \Gamma = f (C_i) \) showed (see Fig. 2) that the best adsorption ability with respect to p-dinitrobenzene from all the adsorbents studied is shown by glycerin-modified bentonite, which is subjected to heat treatment at 550 °C, middle fraction of granules, activation with 9 % HCl and 30 % CaCl\(_2\). It exceeds the closest value of the sorption limit value to modified bentonite with an activation option of 18 % HCl solution and 38 % CaCl\(_2\) solution by 1.5 times, which in absolute terms is 0.5 mg/g.

Modified bentonite, which has not undergone activation, exhibits the worst adsorption capacity upon extraction of p-dinitrobenzene from a solution under static conditions. In terms of the limiting value of sorption, it is inferior to the nearest bentonite with the activation option of 9 % HCl by 17 %, and to the variant with the best adsorption efficiency, it is 60 %.

Additional activation of modified bentonite with CaCl\(_2\) causes a significant increase in the limiting value of sorption for the variant with activation of 9 % HCl and insignificant for the variant with activation of 18 % HCl. So for the first of these options, the increase of the limiting value of sorption is 52 %, which is 0.78 mg/dm\(^3\) in absolute terms, for the second option, these indicators are 9 % and 0.09 mg/dm\(^3\), respectively.

The values of the limiting value of sorption of p-dinitrobenzene for all variants of modified bentonite under static conditions are reached only at sufficiently large values of the concentration of the model solution in the concentration range from 40 to 55 mg/dm\(^3\).

Activation of modified bentonite with an 18 % acid solution shows the best result of the adsorption ability of bentonite with respect to p-dinitrobenzene compared with activation of bentonite with a 9 % solution. However, upon subsequent activation of the sorption material with a CaCl\(_2\) solution, this cannot be said, because a significant superiority of the bentonite variant with activation of 9 % HCl solution and 30 % CaCl\(_2\) solution is observed in comparison with other variants. This fact can be explained on the basis of published data [17] by the fact that upon activation in bentonite many macro- and micropores are formed, macropores appear due to leaching of metal clay from the crystal lattice,
which leads to the formation of a certain amount of silica gel, which causes an increase sorption of non-polar substances. When using high acid concentrations, a disorder of the aluminosilicate layers can be observed, therefore, subsequent activation with a CaCl$_2$ solution has a greater effect after activation with a 9 % HCl solution than after activation with an 18 % HCl solution, since in the second case, due to large disturbances in the structure of the material, to obtain a smaller volume of Ca-bentonite than in the case of activation with a weaker acid solution [9, 17].

The best adsorption effect of $o$-phenylenediamine was shown by the variant of activation of modified bentonite with 18 % HCl solution and subsequent activation of 38 % CaCl$_2$ solution. Its advantage over the second most effective version of the activation of bentonite modified with glycerin and subjected to heat treatment at 550 °C, followed by activation with 9 % HCl solution and 30 % CaCl$_2$ solution, is 3.2 % or 1.64 mg/dm$^3$ in absolute values.

The worst results are achieved when using modified bentonite without activation (adsorbent No. 1), however, it is still quite effective and the value of the maximum sorption value for it is 38.43 mg/dm$^3$, which is 27.83 % or 14.09 mg/dm$^3$ lower better rate.

Analysis of graphical dependencies in Fig. 4 shows that at the point with an abscissa C = 100 mg/dm$^3$, the value of the maximum sorption of $o$-phenylenediamine for activation options No. 3 and No. 4 is higher than for the closest in effectiveness version of activation No. 2 by 1.5 and 1,9 mg/g, respectively, as in Fig. 5 is expressed as a significant difference between the equilibrium concentrations of $o$-phenylenediamine for different variants of modified bentonite. So for options No. 3 and No. 4, the value of the equilibrium concentration after sorption of a solution of a concentration of 100 mg/dm$^3$ is 28.1 mg/dm$^3$ and 18.23 mg/dm$^3$, respectively, and for activation option No. 2 it is 67 mg/dm$^3$, therefore, the efficiency sorption at this stage is much higher than when full saturation is achieved.

In absolute values, the sorption of the secondary aromatic amine ($o$-phenylenediamine) turned out to be many times higher than the sorption of the secondary nitro compound ($p$-dinitrobenzene): $G = 52.52$ mg/dm$^3$ against $G = 1.5$ mg/dm$^3$ for better results after activation. It can be assumed that for amines there are fewer obstacles to penetration of bentonite into the interlayer space than for nitro compounds, and this is expressed in a lesser effect of steric and energy effects of adsorption centers.

The values of the interfacial distribution coefficient and the degree of adsorption extraction in the case of complete saturation of the sorption material for both substances are approximately the same and make up slightly more than 40 % for better results, while the activation option by 9 % HCl solution and 30 % CaCl$_2$ solution with the degree of adsorption extraction of $p$-dinitroaniline 62.5 %.

Both studied substances saturated the adsorbent completely only at very high concentrations of the substance solution (for $n$-dinitrobenzene – 55–60 mg/dm$^3$; for $o$-phenylenediamine – 2500–3000 mg/dm$^3$).

All the considered options for the activation of modified bentonite had a lesser effect on the ability of the adsorbent to adsorb $o$-phenylenediamine than on the ability to adsorb n-dinitrobenzene. Such a difference can be explained by differences in the necessary conditions for establishing a strong bond of the substance with the sorbent. So, unlike nitro compounds, the interaction of amines with modified aluminosilicates is realized by the ion exchange mechanism, which results in the release of counterions to the aqueous phase of the solution and the binding of amines in the structure of aluminosilicate, as well as due to the molecular sieve mechanism, which assumes the key role of the steric factor in establishing the interaction “adsorbent – adsorbate” [9].

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