THERMODYNAMICS OF THE DESORPTION PROCESS AND FEATURES OF REGENERATION OF ADSORBENTS BASED ON BENTONITE CLAY

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Abstract. *The article is devoted to the results of research on the study of regeneration processes of adsorbents after their use in wastewater treatment from metal ions. During the experiments, it was established that the process of moisture desorption from bentonite begins at temperatures above 97 °C and consists of two stages. The barogram equation, temperature ranges and thermodynamic characteristics of individual stages of the desorption process in bentonite clay have been compiled. The experimental data were processed using the least squares method at a 95% confidence level using the t-value of the Student coefficient. The effectiveness of bentonite clay in softening artesian water in Tashkent, used in "Bektemir metall constructions" OOO, has been established, when softening it with a total hardness index of 5.8 mEq/l, the Na-form of the tested sorbent allows reducing the total hardness to 1.4 mg-eq/l, which indicates the high efficiency of the water softening process.*

Keywords: *sorption, sorbents, adsorbent, wastewater sorption capacity, water treatment, aluminosilicates bentonite, regeneration, solution pH*

Introduction. Industrial wastewater treatment is relevant for all countries of the world, regardless of their level of water resource availability. It is believed that from a colloid-chemical point of view, wastewater is a heterogeneous mixture of dissolved, colloidal and suspended organic and inorganic impurities in water. One of the main pollutants of natural waters are heavy metal ions coming from wastewater from electroplating shops, mining enterprises, ferrous and non-ferrous metallurgy, and machine-building plants. There are quite a lot of purification methods, but adsorption methods are simple and effective methods of water purification. The advantages of these methods are high efficiency, the possibility of treating wastewater containing several substances, as well as the recovery of these substances. 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 accessibility, the chemical structure of the substance and the chemical form of its presence in the environment. As follows from the analysis of literature sources, adsorption purification in most cases ensures the production of water of the required quality with a wide variety of compositions of water supplied for treatment [1].

It should be noted that the issues of processes and mechanisms of adsorption reactions with clay adsorbents have been studied quite a lot. The results of the conducted research allow us to form general scientifically based ideas about the essence of the sorption process and the factors influencing the course of sorption processes during the treatment of industrial wastewater with various adsorbents in a wide range of technological features of each type of production that are possible in the industry. In the adsorption process, different types of adsorbents are used, including those based on natural clay components. For example, in the production of clay adsorbents, bentonite clays are widely used, consisting mainly of a layered aluminosilicate mineral - montmorillonite, which has pronounced sorption and ion-exchange properties. Montmorillonite contains metal cations that act as exchange cations. The most common exchangeable cation in bentonites is Ca^{2+}. Bentonites carrying Na+, K+ as exchangeable cations, which have significantly greater activity. Previous studies have shown high efficiency of water purification using materials based on mineral basalt fibers and bentonite clays. A number of works have been published devoted to the study of the chemical and mineralogical composition and sorption properties of bentonite clays and adsorbents obtained on their basis [2-3].

Experimental results. The chemical and mineralogical composition and properties of natural clays often lead to limitations in their practical use in various industries. In this regard, research on modifying the properties of clays deserves great attention, which is part of a large area of work related to modifying the properties of solids. The adsorption properties of clays can be significantly changed as a result of chemical modification. As a result of modification of bentonite, its surface, structure, porosity and exchange capacity change [4-5].

Currently, researchers have identified the role of individual factors that ultimately determine the amount of sorption, for example, the pH of the medium within narrow limits. However, many of them have not been studied enough.

Data on the influence of the composition and concentration of the “background” electrolyte are very contradictory; the behavior of microcomponents when their concentration changes over a wide range and the state of sorbents under sorption conditions have been little studied.

At the same time, the relationship between the state of the sorbent, such as, for example, natural clay adsorbents such as bentonite and the amount of sorption of 3d elements and dyes under the same conditions, has been least studied. Currently, the scientific foundations of technologies for treating water with aluminosilicate materials of natural origin, which have unique adsorption properties, are being actively developed. Such adsorbents include bentonite clays, consisting mainly of montmorillonite [6-10].

These regeneration methods are carried out directly in the adsorbers; thermal regeneration is carried out outside the adsorbers. The products of desorption and destruction of contaminants are condensed and recycled.

These methods are used to restore the sorption properties of active carbons containing non-volatile components that are difficult to desorb (temperature 650-920°C, heat treatment time 2-20 minutes). Electrothermal regeneration is carried out by external or internal heating by electric current in special continuous furnaces. Thermal regeneration is carried out by heating with flue gases, fuel combustion products in vertical shaft furnaces, in drum rotary kilns and fluidized bed furnaces [11-12].

To obtain controlled adjustable moisture-absorbing (AMA), a mixture of granules with a size of no more than 7.5 mm, preferably less than 1.0 mm and (or) 2.5-7.5 mm, of natural sodium bentonite clay containing at least 80% montmorillonite was used and calcium chloride according to GOST 450-77 with a granule size of up to 2.5 mm in percentage (by weight), respectively, 85-95% to 5-15%, with the ratio 90/10 being the most preferable.

The required mixture can be obtained by simple dry mixing of these components by any known method. The specified composition provides moisture capacity (in% of its own weight) of 18-19, 34-36, 55-60 and 120-130 at a relative humidity of 20, 40, 60 and 100%, respectively, the ability to sorb from the environment, bind and retain particles, ions and molecules of any electrolytes, resistance to repeated frosts without loss of AMA properties [13].

In order to study the process of desorption of bentonite clays, we conducted a study of the desorption process from bentonite clays. As a result of the research, it was shown that in the temperature range of 27-77 °C, the process of desorption of moisture from bentonite begins at temperatures above 97 °C (Table 1) and consists of two stages (Fig. 1). The barogram equation, temperature ranges and thermodynamic characteristics of individual stages of the process are given in table. 2.

Table 1

Vapor pressure values of natural moisture from bentonite clays

I-stage						
T.C	Ptotal	T.K	1/T(x)	lg(y)	x2	xy
101	108	374	2,673797	2,033424	7,149189	5,436962
110	158	383	2,610966	2,198657	6,817144	5,740619
135	246	408	2,45098	2,390935	6,007305	5,860135
160	340	433	2,309469	2,531479	5,333646	5,846372
175	414	448	2,232143	2,617	4,982462	5,841519
194	87	467	2,141328	1,939519	4,585284	4,153146
224	135	497	2,012072	2,130334	4,048435	4,286386
247	176	520	1,923077	2,245513	3,698225	4,318294
277	251	550	1,818182	2,399674	3,305785	4,363043

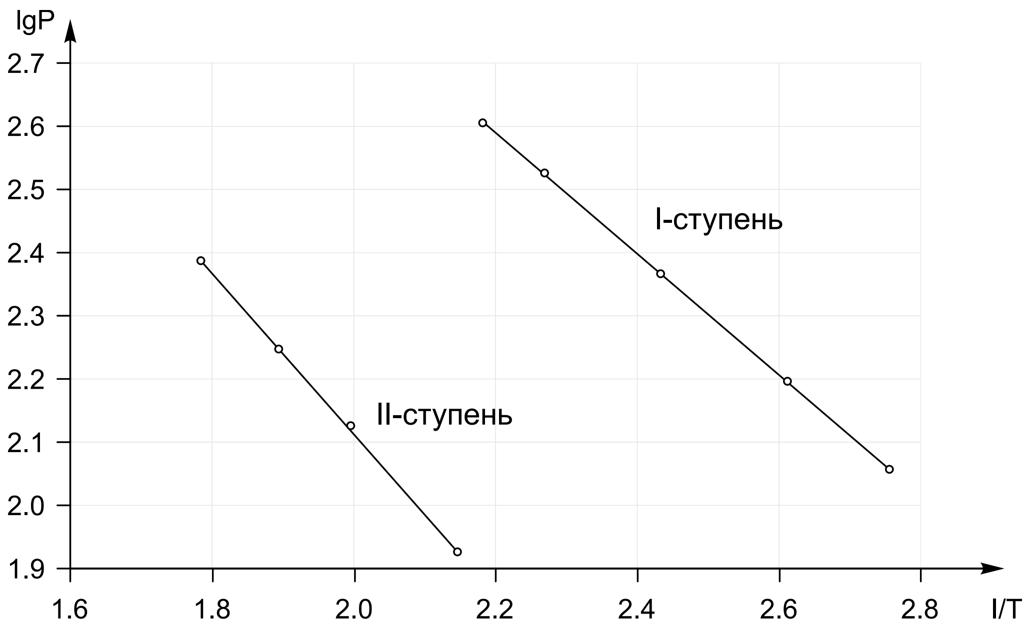

Fig. 1. Dependence of lgP on reverse temperature for both stages of the process of moisture desorption from bentonite

The process of desorption of mint essential oil from bentonite clays begins at temperatures above 77 °C and proceeds in one stage (Table 2).

Table № 2

Vapor pressure of peppermint essential oil depending on temperature

Bentonite sorbed with mint oil						
T, C	P_{total}.	T, K	1/T, X	lgP, У	X2	XУ
86	13	359	2,785515	1,113943	7,759096	3,102906
125	56	398	2,512563	1,748188	6,312972	4,392432
167	105	440	2,272727	2,021189	5,165289	4,593612
200	135	473	2,114165	2,130334	4,469693	4,503877
147	77	420	2,380952	1,886491	5,668934	4,491645
175	102	448	2,232143	2,0086	4,982462	4,483483

As is known, a significant part of the water used in everyday life and in production has a fairly high hardness, which reaches 12 mEq/l, instead of 27 mEq/l in accordance with the standard requirements.

In order to establish the effectiveness of bentonite clay in softening water, we selected artesian water from the city of Tashkent, used in “Bektemir metal constructions” OOO, as a test object.

As is known, the determination of the total hardness of water is hindered by: copper, zinc, manganese and a high content of carbon dioxide and bicarbonate salts. The influence of interfering substances is eliminated during the analysis.

The accuracy of determination when titrating 100 ml of sample was 0.05 mEq/L. 50-70 ml of filtered test water diluted to 100 ml with distilled water was added to a conical flask.

Then 5 ml of a buffer solution, 5-7 drops of an indicator or approximately 0.1 g of a dry mixture of chromogenic black indicator with dry sodium chloride were added and immediately titrated with vigorous shaking with a 0.05 N solution of Trilon B until the color changed at the equivalent point (in this case the color should be blue with a greenish tint).

During testing, these sorbents were used in Na-forms. For comparison, an industrial cation exchanger KU-2x8 was used.

The table shows data on the use of the resulting sorbent in water softening processes under static conditions in accordance with the requirements of GOST 4151-72.

Table 3
Results of research on water softening under static conditions

Sorbents	Total water hardness, mEq/l:	
	before	after
	contact with sorbents	
The resulting sorbent Na-form	5,8	1,4
КУ-2х8 H-form Na-form		1,6 1,0

The total hardness of water (X) in mEq/l is calculated using the formula:

$$X = \frac{v \cdot 0{,}05 \cdot K \cdot 1000}{V},$$

where, v – the amount of Trilon B solution consumed for titration, ml;

K – correction factor to the normality of the Trilon B solution;

V – volume of water taken for determination, ml.

During titration, more than 10 ml of a 0.05 N solution of Trilon B was consumed, this indicates that in the measured volume 0.5 mEq. In such cases, the determination should be repeated, taking a smaller volume of water and diluting it to 100 ml with distilled water.

A slight change in color and equivalent point indicates the presence of copper and zinc. To eliminate the influence of interfering substances, 1-2 ml of sodium sulfide solution is added to the water sample measured for titration, after which the test is carried out as indicated above.

If, after adding a buffer solution and an indicator to a measured volume of water, the titrated solution gradually becomes discolored, acquiring a gray color, which indicates the presence of manganese, then in this case, five drops of 1% should be added to the water sample taken for titration before adding the reagents. hydroxylamine hydrochloric acid solution and then determine the hardness as indicated above.

If the titration becomes extremely protracted with an unstable and unclear color at the equivalent point, which is observed with high alkalinity of water, its influence is eliminated by adding to the sample of water taken for titration, before adding the reagents, a 0.1 N solution of hydrochloric acid in the amount necessary for neutralization alkalinity of water, followed by boiling or blowing the solution with air for 5 minutes. After this, a buffer solution and an indicator are added and then the hardness is determined as indicated above.

From the data in Table No. 1 it can be seen that when softening water with a total hardness of 5.8 mEq/l, the Na-form of the tested sorbent can reduce the total hardness to 1.4 mEq/l, which indicates the high efficiency of the water softening process .

The equilibrium state in the studied systems was achieved by holding each figurative point on the curve of vapor pressure versus temperature (barogram) isometrically for 6–10 hours (for the evaporation process) and 20–24 hours (for the desorption process) until a constant pressure value is achieved. Equilibrium was also checked by the coincidence of the barogram curve during heating and cooling of the system. The pressure in the system was measured with an accuracy of +50 Pa, and the temperature was +0.2 degrees.

Experimental data, presented in the form of LgP from the inverse temperature, were processed using the least squares method at a 95% confidence level using t - the value of the Student coefficient [14].

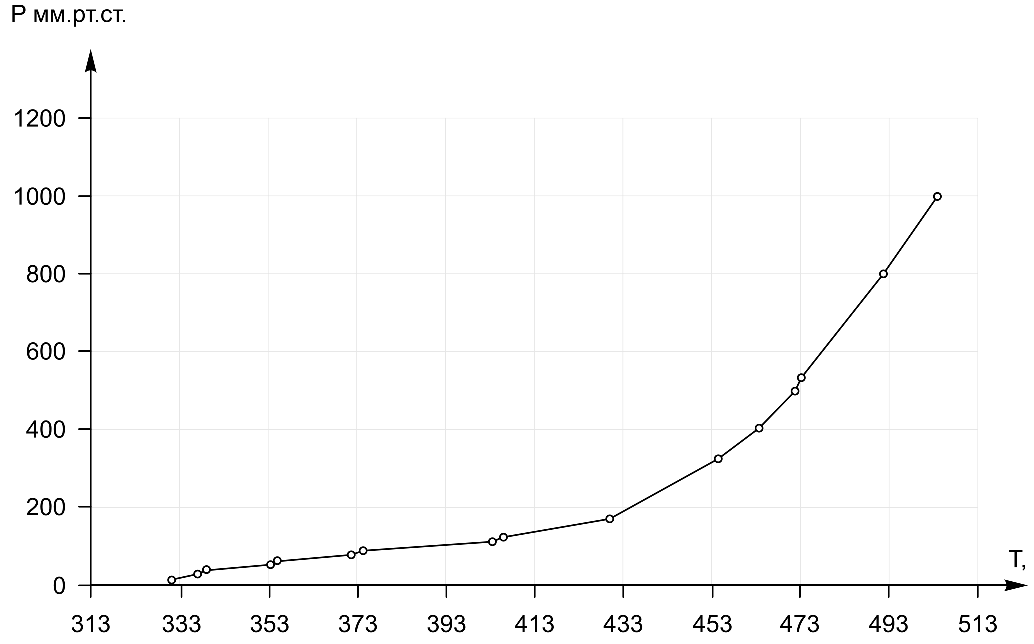

Fig.2. Dependence of vapor pressure of essential oil mint from temperature

Summary: Systematic studies of the processes of evaporation of methanol and mint essential oil and their desorption from bentonite clays of the Shafirkan deposit were carried out.

From an economic point of view, the use of local sorbents in the process of water treatment for industrial needs eliminates the forced import of expensive sorbents at the expense of foreign currency.

Thus, based on pilot industrial tests of the developed sorbent based on bentonite clay, it was established that this sorbent, which has a sufficiently high sorption capacity for calcium and magnesium ions, can be successfully used in the process of softening domestic and industrial waters.

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