

Activation of bentonite and palygorskite adsorbents by acid under microwave radiation

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Abstract. The problem of wastewater treatment, since the second half of the 20th century, is relevant for all countries of the world. There are quite a few purification methods, however, 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. Active carbons, synthetic sorbents and some production wastes (ash, slag, flask, sawdust), mineral sorbents - clays, silica gels, alumogels and metal hydroxides are used as sorbents. The research illustrates the possibility of acid activation of bentonite and palygorskite clays using microwave radiation. It has been established that the microwave activation of bentonite leads to the destruction of the structure, the expansion of the surface and the change in the pore structure, which affects the textural characteristics. The concentration values of hydroxyl groups indicate the presence of surface active sites that can participate in adsorption. The results were presented as tables and as a graph.

1 Introduction

Adsorption phenomena occur, as a rule, in a liquid medium, which contains substances of different classes; the medium is not inert in composition and property and is directly involved in these processes. Here, the main component is the adsorbent, which is selected based on the nature of the liquid to be purified, the polarity of the substances to be removed, their concentration, etc. Moreover, such processes carry out in heterogeneous systems regulated by the used adsorbent properties and the technological parameters of their functioning [1].

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Adsorption methods for cleaning liquids, in particular vegetable oils, are widely used in many countries, where they mainly use their own local activated clays. Today, the purchase and transportation of imported activated clays to oil and fat enterprises are expensive for hard currency, which in turn increases the cost of manufactured goods. Despite the presence in the Republic of more than 100 large deposits of natural clays (kaolin, bentonite, palygorskite, etc.), there is no production of activated adsorbents on an industrial scale. [2].

In this regard, it is necessary to study the compositions and properties of natural clays suitable for obtaining adsorbents, especially the methods and technologies for their enrichment and activation, including non-traditional ones.

2 Experimental

Bentonites and palygorskite differ from kaolinites in their mineralogical and chemical compositions. Therefore, their activation also has its characteristics, primarily the leaching conditions and the types of reagents used. In practice, bentonites and palygorskite are treated with solutions of inorganic acids (sulfuric, hydrochloric, phosphoric, etc.)

We, to obtain activated adsorbents for bleaching (purification) of vegetable oils, have chosen Navbakhor alkaline, alkaline earth bentonites and carbonate palygorskite (Navoi region) [3], Tamdy-Tau bentonite (Navoi region) [4], Logon bentonite (Fergana region), Kattakurgan bentonite (Samarkand region), Beshtubinskaya (Republic of Karakalpakstan) and bentonite "Jakhon" (Samarkand region). In this case, the well-known arcanite-bentonite (Georgia) [5] was used as a control sample.

The clay's chemical and mineralogical compositions were determined using special instruments of the Central Laboratory of the Ministry of Geology of the Republic of Uzbekistan. In this case, the content of silicon was determined by gravimetric and colorimetric methods [6], aluminium, iron, calcium and magnesium - by volume complexometric [7] and atomic absorption spectroscopy [8], sodium and potassium gravimetric [7, 8] and flame photometry [9]. Table 1 shows the chemical composition of selected local bentonites and palygorskite.

Table 1. The content of chemical elements in clays selected for obtaining adsorbents

Clay name	Content of chemical elements, % per abs. dry clay												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	TiO ₂	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Loss on ignition	Sum %
Kattakurgan bentonite (KB)	57,62	16,63	5,63	-	1,4	0,78	2,32	1,06	4,05	-	0,36	9,76	99,61
Navbakhor alkaline bentonite (NAB)	57,91	13,69	5,1	-	0,48	0,35	1,84	1,53	1,75	0,43	0,75	16,17	99,98
Logon bentonite (LB)	55,05	16,67	5,60	-	2,52	0,71	1,71	1,74	4,28	-	0,31	10,86	99,45
Beshtubin bentonite (BB)	64,96	15,59	4,59	-	1,12	0,78	1,63	2,03	2,72	-	0,081	6,26	99,76
Shafirkan bentonite (SB)	57,65	13,69	5,77	-	3,08	0,87	1,81	1,12	1,72	-	2,59	11,21	99,51
bentonite from the Zhakhon deposit (BZD)	58,24	13,81	8,33	0,15	3,74	0,55	2,94	1,47	1,53	-	0,43	8,55	100,0

Navbakhor carbonate palygorskite (NCP)	46,79	8,63	-	3,41	10,08	-	2,74	-	1,6	1,99	-	24,33	99,75
Bentonite Wyoming (USA)* (control)	55,44	20,14	3,67	-	0,49	-	2,49	2,76	0,60	-	-	13,5	99,09
Georgian ascanite-bentonite (GAB) (control)	54,14	18,74	4,98	0,22	2,41	0,38	4,64	2,82	0,64	-	0,07	10,94	99,98

Note: The abbreviation of the names of clays is made to simplify the further description of the work.

Table 2. Indicators of granulometric composition and differential thermal analysis of selected bentonites and palygorskite to obtain adsorbents from them

Clay name	Granulometric content, %		Temperature "effects" of DTA, °C		
	sieve residue with mesh 02K	sieve residue with mesh 0063	first	second	third
Kattakurgan bentonite (KB)	4,9	95,1	200-230	500-650	750-850
Navbakhor alkaline bentonite (NAB)	3,5	96,5	200-235	550-700	800-900
Logon bentonite (LB)	3,7	96,3	200-250	600-750	850-950
Beshtubin bentonite (BB)	5,3	94,7	250-300	650-750	900-950
Shafirkan bentonite (SB)	4,8	95,2	225-250	550-670	800-850
bentonite from the Zhakhon deposit (BZD)	5,2	94,8	250-260	525-650	825-875
Navbakhor carbonate palygorskite (NCP)	5,3	94,7	250-300	650-750	900-950
Bentonite Wyoming (USA)* (control)	4,2	95,8	240-275	550-625	850-950
Georgian ascanite-bentonite (GAB) (control)	4,1	95,9	200-250	500-700	850-900

From the data in Table 1, the selected bentonites and palygorskite differ significantly from each other in the content of certain chemical compounds, which should be taken into account when choosing the methods and conditions for their activation. So, for example, bentonites and palygorskite with high calcium oxide (CaO) should be treated with weak hydrochloric acid, which forms the smallest amount of gypsum, and with a low content (CaO) should be activated with a solution of hydrochloric acid with higher concentration.

The above-selected bentonites and palygorskites were analyzed by the Sabanin-Robinson sedimentation method [10,11]. Differential thermal analysis (DTA) of initial clays and adsorbents was carried out on a Kurnakov FPK-55 pyrometer at a rate of 30°C min [12].

The results of sedimentation and DTA analyses of local bentonites and palygorskite selected for obtaining adsorbents are presented in table 2.

From Table 2, the selected clays are close to each other in terms of particle size distribution, and DTA shows significant differences in the temperature "effects" between them, which should be taken into account when selecting the optimum temperature for their activation.

Acid activation of silicon-containing minerals is the most common method for obtaining adsorbents for vegetable oil purification and bleaching. However, the adsorbents obtained by this method, when bleaching dark-coloured cottonseed oils containing pigments of gossypol, chlorophyll and their derivatives, do not always provide the colour of the oil, which is acceptable by the standard [13]. This prompted us to find a more effective method for bentonite and palygorskite clays acid activation.

Of particular interest in this aspect for us was the method of microwave radiation at a frequency of 2450 MHz, where in a short time, the clay is heated volumetrically up to 100°C and 5-10 times faster than with the traditional method of convective heat transfer [14]. The use of this method for acid activation of clay adsorbents is of both scientific and practical interest, especially considering that the traditional clay activation method today lasts 6 hours or more.

Bentonite and palygorskite adsorbent activation is carried out in a specially mounted unit in a microwave oven.

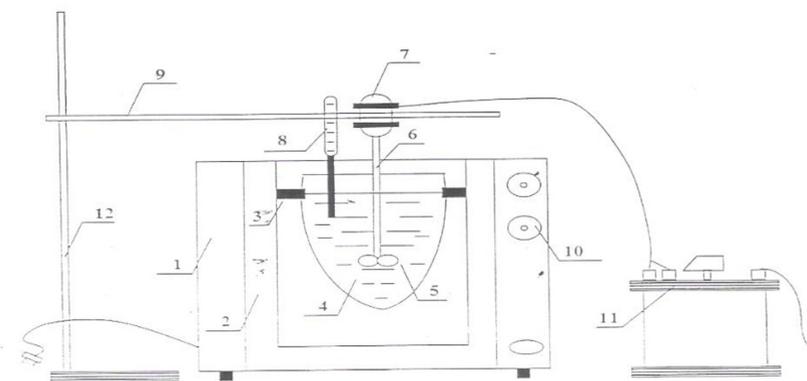


Fig.1. Laboratory setup for acid activation of adsorbents under microwave radiation

Figure 1 shows a diagram of this laboratory setup, which consists of 1 magnetron; 2 resonators; 3- fastening units; 4-glass flasks; 5-activated liquid with the adsorbent (clay); 6-glass stirrer and shaft; 7-engine; 8-thermometer; 9 engine mounts; 10-microwave control unit - installation; 11-LATR; 12-stand for fixing the engine, instrumentation and etc.

The method for implementing the acid activation process of clay minerals at this facility is as follows: a certain amount (for example, 200 ml) of a liquid solution (for example, a 15% aqueous solution of H_2SO_4) with an activated clay adsorbent is poured into flask 4. This flask 4 is installed using holder 3 inside resonator 2. In order to create the required speed and intensity of phase mixing, a glass stirrer 6 is additionally used, which is fixed to the motor rotor 7 with a glass shaft. The number of revolutions of engine 7 is regulated employing LATR 11. The temperature of the activating liquid with a clay adsorbent is controlled using a glass (alcohol) thermometer 8. Engine 7 is mounted with a clamp 9 on a tripod 12.

After closing the microwave oven door, microwave generator 1, controlled by unit 10, is turned on. In this unit, in addition to the positions, the microwave radiation time is also regulated, i.e. microwave processing of clay minerals.

The laboratory unit is designed for 600 W, and this power is sufficient for research on the acid activation of clay minerals under microwave radiation. On this installation, it is possible to carry out acid, alkali and salt activation of clay minerals with microwave

radiation. In addition, this installation can be used to study the effect of microwave radiation on the quality indicators of the obtained adsorbents and the regularities of the process under consideration. Therefore, this installation contributes to the expansion of experimental studies on the liquid activation of clay adsorbents and the regulation of their properties.

Acid activation is carried out as follows: in a 500 ml round-bottom flask equipped with an external reflux condenser, 50 g of dry, crushed and sifted through a 0.25 mm sieve of clay and 250 ml of 15% sulfuric acid, taken at the rate of 50% acids from the weight of dry clay. Clay activation was carried out by boiling with stirring. The resulting clay samples were filtered on a Buchner funnel and washed with heated (up to 40-45°C) distilled water until neutral with litmus. Samples were dried in a thermostat at a temperature of 105-110°C to a moisture content of 7.5-8.0%. The dried clay was ground in a porcelain mortar and sifted through a fine sieve with holes of 1200-1600 per 1 cm². Adsorbents store in separate desiccators. Their sorption activity evaluates by the heat of wetting [15].

3 Results and discussion

Next, the textural characteristics of the original bentonite and its activated forms were studied. Adsorption isotherms of benzene vapor show that it belongs to type II according to the IUPAC systematics. The BET equation was used to calculate the specific surface area (S_{sp}) of the samples, and the micropore volume (V_a) was obtained by the *t-Plot* method. The total volume (V_{total}) of meso- (V_b) and micropores was determined using the adsorption isotherm of adsorbates at the ratio $P/P_0=1$.

The textural characteristics of the sorbents were calculated using the BET equation from polymolecular adsorption isotherms using the formula:

$$A = \frac{A_{\infty} K P/P_s}{(1 + P/P_s)(1 + (K - 1)P/P_s)}, \quad (1)$$

Where: A - the amount of adsorption, mmol/g; A_{∞} - the capacity of the monolayer, mmol/g; K - BET constant; P - the equilibrium vapour pressure of the adsorbate above the surface of the adsorbent, P_s - the pressure of saturated vapour above the surface of a pure liquid adsorbate.

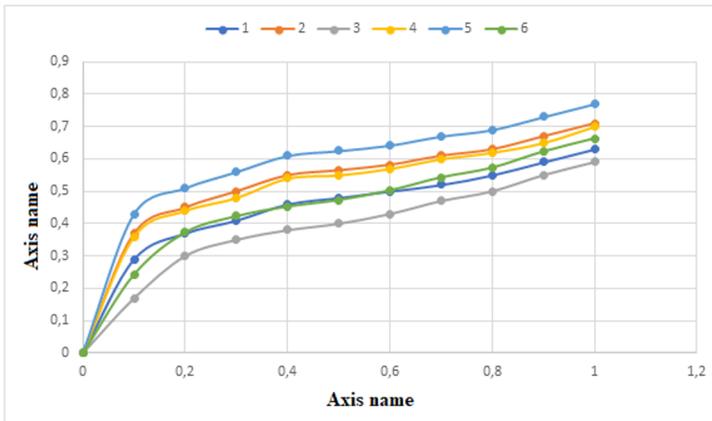


Fig.2. Adsorption isotherms of benzene vapour on samples: 1 - NCP; 2 - BZD; 3 - NAB; 4 - NCP+MR; 5 - BZD+MR; 6 - NAB+MR

All isotherms have almost the same shape and only differ in values at the corresponding relative pressure values (P/PS). As the isotherm shows, the adsorption parameters value increases as the pressure approaches the saturated vapours values. The calculated data are given in the table 3.

Table 3. Calculations of the textural characteristics of the original bentonite and its activated forms

Sample	S_{sp} , m ² /g	A_{∞} mol/kg	V_a , cm ³ /g	V_{total} , cm ³ /g	V_b , cm ³ /g	Pore radius,mm
NCP	55,39	0,23	0,044	0,054	0,01	1,90
BZD	81,22	0,33	0,055	0,065	0,01	1,56
NAB	67,43	0,28	0,048	0,056	0,01	1,66
NCP+MR*	80,6	0,33	0,056	0,061	0,005	1,71
BZD+MR*	101,3	0,42	0,071	0,076	0,005	1,48
NAB+MR*	93,3	0,39	0,061	0,069	0,008	1,58

**Activated by microwave radiation*

Upon microwave activation of bentonite, the following processes occur, which can explain the changes in textural characteristics:

microwave radiation heats the bentonite sample, causing rapid heating and reheating of the sample. This leads to thermal cracking and degradation of the bentonite structure. The destruction of the structure promotes the formation of a porous structure and an increase in pore volume, which can explain the mesopore volume (V_b) increase and total pore volume (V_{total}) increase for activated forms.

Microwave activation can also cause the surface of the bentonite to expand. The impact of microwave radiation on the surface of bentonite causes heating and thermal gradients, which leads to the expansion of the surface area. The surface expansion increases the surface area (S_{sp}) and creates additional active surfaces for adsorption.

Also, microwave activation can cause changes in pore sizes. Heating a bentonite sample under the action of microwaves leads to the diffusion of molecules inside the pores and changes in their sizes. This can lead to a decrease in the pore radius, which is reflected in the pore radius data for the activated forms.

In general, microwave activation of bentonite leads to structure destruction, the expansion of the surface and the change in the pore structure, which affects the textural characteristics. These changes can be explained by the influence of thermal destruction and microwave radiation effects on the structure and properties of bentonite.

From the presented data (Table 3), it can be seen that the activation of bentonites using microwave radiation (MI*) leads to an increase in the surface area compared to the original bentonites. The activated forms of bentonite BZD+ MR* and NAB+MR* have the highest surface area values, respectively, 101.3 and 93.3 m²/g. The values of the concentration of hydroxyl groups indicate the presence of surface active sites that can participate in adsorption.

The volume of mesopores remains approximately the same for the activated forms compared to the original bentonites. The total pore volume increases for the activated forms compared to the original bentonites, especially for the BZD+ MR* and NAB+MR* forms. The pore radius decreases for activated forms compared to the original bentonites. Based on these data, it can be concluded that the activation of bentonites using microwave radiation (MI*) leads to an increase in the surface area, pore volume, and concentration of hydroxyl groups. This indicates the creation of additional active surfaces for adsorption and the improvement of the adsorption properties of bentonite.

The distribution of hydroxyl groups on the surface, the state of the surface, and the internal structure of water in selected bentonites and palygorskite, after their acid activation were studied by the deuterium exchange method [16]. The results obtained are presented in the Table 4.

Table 4. The concentration of surface hydroxyl groups of selected local bentonites and palygorskite

Name adsorbent	Number of hydroxyls on the surface			Complete content structural water, α^3/g , mol/kg
	α_{OH} *) mol/kg	$\alpha_{OH} \cdot 10^{-6}$ mol/m ²	group OH/nm ²	
NCP	0.55	12.8	7.4	3.7
NAB	0,64	13,9	8,5	4,25
BZD	0,61	13,8	8,4	4,18
NCP+MR *	0.62	14.7	8.9	5.4
NAB+MR *	0.71	16.2	9.6	6.3
BZD+ MR *	0.75	17.4	10.4	6.9

Note: *) Converted to OH number and related to 1 kg of adsorbent

From Table 4, the values of α_{OH} for NAB and BZD are close to each other. In such montmorillonite clays, hydroxyl groups are located on the surface of the aluminosilicate layer and adsorbed cations in the form of bound water. For NAB, the average value of α_{OH} is 13.9×10^{-6} mol/m² and for the sample NAB+MR * 16.2×10^{-6} mol/m², which in mainly depends on the value of its silicate module. The greater the ratio of SiO₂ to Al₂O₃ in palygorskite, the lower the concentration of surface hydroxyls. In other words, the greater the content of Al₂O₃ in the adsorbent, the greater the value of α_{OH} .

4 Conclusions

It is established that for the activation of local bentonites and palygorskite, it is advisable to select solutions of inorganic acids based on their mineralogical and chemical compositions. At the same time, the use of volumetric heating of clays, i.e. microwave radiation, makes it possible to intensify the process of their activation, and increase the volume of micro-, macro- and transitional pores of the adsorbent, in comparison with traditional convective heating.

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