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Influence of Heat Treatment of Clays on Their Adsorption of Methylene Blue Dye

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Влияние термической обработки глин на их адсорбцию по красителю метиленовый голубой

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The adsorption activity of soils largely depends on their composition and properties and, first of all, on the specific surface area and energy potential of clay particles.
For the formation of "specified" properties, including adsorption, various methods of clay activation have been developed: thermal, ultraviolet, ultrasonic, mechanical, acidic, alkaline. However, despite the published data, the issues of the influence of heat treatment on the formation of the clays properties, including adsorption ones, have not been sufficiently studied. In this regard, an assessment was made of the clays thermal activation effect on their adsorption activity for the methylene blue dye.
Experimental and theoretical studies have shown that the change in the adsorption activity of clays is associated with the degree of their heat treatment. When clays are treated with temperatures up to 200°C, energy centers on the surface of structural elements are activated, which leads to an increase in the clays adsorption in terms of methylene blue by 12–24%; with an increase in the clays processing temperature to 450–960°C, the processes of their (clays') structural transformation change, which reduces the adsorption activity of clays by 11–16 times.
In addition, the influence of the clays saturation degree with water vapor on their adsorption activity has been established. During the heat treatment of clays and their partial saturation with water vapor, water molecules occupy part of the energy centers on the surface of the particles; therefore, the particles have a sufficient energy potential, which is realized in the form of high values of their adsorption in terms of methylene blue.
During the clays thermal treatment and their complete saturation with water vapor, the charges on the surface of the particles are mostly compensated by water molecules. Water molecules, entering the inter-package space, compensate charges on the surface of the packages and minerals, which are realized in the form of clay swelling processes. The swelling processes lead to an increase in the size of structural elements, which manifests itself in the form of a decrease in the specific surface of clays. Therefore, clays completely saturated with water vapor are less active in terms of adsorption than clays partially saturated with water vapor.

Ключевые слова:
глина, каолин, монтмориллонит, бентонит, структура, свойства, адсорбция, термическая обработка, метиленовый голубой, активация, коллоид, энергетический потенциал, вода, минеральный состав, кристаллическая решетка.

Адсорбционная активность грунтов во многом зависит от их состава и свойств и, прежде всего, от площади удельной поверхности и энергетического потенциала глинистых частиц.
Для формирования «заданных» свойств, в том числе и адсорбционных, разработаны различные способы активации глин: термический, ультрафиолетовый, ультразвуковой, механический, кислотный, щелочной. Однако, несмотря на опубликованные данные, вопросы влияния термической обработки на формирование свойств глин, в том числе и адсорбционные, изучены недостаточно полно. В связи с этим осуществлена оценка влияния термической активации глин на их адсорбционную активность по красителю метиленовый голубой.
Экспериментальные и теоретические исследования показали, что изменение адсорбционной активности глин связано со степенью их термообработки. При обработке глин температурой до 200 °С активизируются энергетические центры на поверхности структурных элементов, что приводит к повышению адсорбции глин по метиленовому голубому на 12–24 %; при повышении температуры обработки глин до 450–960 °С процессы их (глин) структурного преобразования изменяются, что снижает адсорбционную активность глин в 11–16 раз.
Кроме того, установлено влияние степени насыщения глин парами воды на их адсорбционную активность. При термообработке глин и частичном их насыщении водяными парами молекулы воды занимают часть энергетических центров на поверхности частиц, поэтому частицы обладают достаточным энергетическим потенциалом, который реализуется в виде высоких значений их адсорбции по метиленовому голубому.
При термической обработке глин и полном насыщении их парами воды заряды на поверхности частиц в большей части компенсируются молекулами воды. Молекулы воды, поступая в межпакетное пространство, компенсируют заряды на поверхности пакетов и минералов, которые реализуются в виде процессов набухания глин. Процессы набухания в свою очередь приводят к увеличению размеров структурных элементов, что проявляется в виде уменьшения удельной поверхности глин. Поэтому глины, полностью насыщенные парами воды, адсорбционно менее активны, чем глины, частично насыщенные парами воды.

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Rationale

The adsorption activity of clays largely depends on the composition and properties of sorbents and, first of all, on the specific surface area and energy potential on the surface of clay particles [1–17].

In order to form the desired properties, including adsorption, various methods of clay activation have been developed: heat [1, 5], ultraviolet [4], ultrasonic, mechanical [2, 8, 18], acid [3, 10], alkaline [15] and others [7, 9, 16].

Thus, during ultraviolet activation [4] of clays metal ions leave the octahedral positions due to weakening of bonds in the crystal lattice of minerals. This helps to increase the sorption activity of clays by 1.3 times. The treatment of clays with ultrasound leads to the destruction of aggregates and completion of the crystal structure, which increases the sorption activity of clays [18–25]. Acid [3, 10] and alkaline [15] activation of clays changes their structure and, as a consequence, their physicochemical properties. Activation of clays by pressure [32–41], in addition to changing their structure, affects the pore fluid composition and specific surface area of particles which has conflicting effects on the adsorption properties of soils. Many scientists have been involved in heat treatment of clays [26–31]. The results of their studies have shown that the temperature of clay treatment has conflicting effects on their structure and properties [42–44]. Therefore, despite the published data, the issues of the heat treatment effect on formation of clays properties, including adsorption properties, have not been sufficiently studied.

The idea of this article lies in the fact that during technogenic treatment (heat and chemical treatment) the clay changes its composition and structure which form the physicochemical properties of the soil.

The subject of the research is Lobanovsk montmorillonite clay (LM), Chelyabinsk kaolin clay (ChK), and Kurgan bentonite clay (KB). According to the results of X-ray structural analysis, montmorillonite clay consists of montmorillonite (75 %), kaolinite (3.6 %), quartz (11.4 %), albite (6.7 %), and calcite (3.3 %). Kaolin clay contains kaolinite (76.7 %), montmorillonite (15.6 %), quartz (7.7 %). Bentonite clay contains montmorillonite (81.1 %), kaolinite (0.8 %), hydromica (0.8 %), quartz (14.1 %), plagioclase (1.9 %), potassium feldspars (0.4 %), calcite (0.9 %).

The Method of Clay Sample Preparation

In terms of methodology, the sample preparation was carried out using two schemes.

Scheme 1. Samples of soil were annealed at temperatures of t_1 = 200 °C, t_2 = 400 °C, t_3 = 600 °C and t_4 = 800 °C in a SNOL 12/1300 high-temperature furnace for 2 hours. Then the samples were placed in weighing bottles and kept in a desiccator with silica gel with a relative air humidity inside the room of φ = 30 % for 7 days. In total, 12 series of samples were prepared.

Scheme 2. Some of the annealed clay samples prepared using scheme 1 were saturated with water vapor. For this purpose the samples were placed in weighing bottles which were placed in a desiccator and kept there for 7 days. The bottom of the desiccator was filled with water, and the relative air humidity inside it was φ = 82 %.

Research Results and Their Consideration

1. Influence of Heat Treatment of Clays on Their Adsorption by Methylene Blue Dye (Scheme 1)

Dependence graphs of the heat treated clay adsorption activity index by methylene blue dye (MB) were plotted based on the results of experimental studies (Fig. 1).

The data in Fig. 1 show that clays treated at a temperature of 200 °C have the highest adsorption activity. In kaolin, adsorption increases by 12 %, in montmorillonite – by 16 %, and in bentonite - by 24 %. The adsorption activity of clays decreases when annealing temperature increases up to 600 °C: for example, in kaolin, adsorption of MB decreases by a factor of 11, montmorillonite – by a factor of 13, and bentonite – by a factor of 16.

The revealed change in the clays adsorption depending on the degree of their heat treatment is due to two factors. The first factor is associated with the formation of active centers on the surface of colloids (particles). Strongly and loosely bound water is removed from the surface of colloids at a clay processing temperature of up to 200 °C, thereby energy centers on the particle surface release and increase the clays adsorption by methylene blue. The structure of clays does not change.

The second factor is associated with a change of clays structure. Heat treatment of clays at a temperature above t > 400 °C changes their structure which reduces the energy activity of the colloid surface. Therefore, the adsorption activity of clays decreases significantly.

The data obtained are consistent with the research results [1, 6]. So, according to L. A. Binatova et al. [1], Dash-Salakhlin natural bentonite exhibits the maximum sorption capacity (A_{mg} = 66.9 mg/g) by methylene blue at a treatment temperature of 105 °C, and its monosubstituted forms of Al and Fe – at a treatment temperature of 200 °C (A_{mg} = 89 mg/g). When clays are activated at a temperature of 400 °C, a rigid crystalline structure is formed and as a result bentonite loses its ability to swell, which hinders the penetration of MB molecules into the interplanar space of sorbents and leads to decreased adsorption capacity of bentonite. The data of A.I. Yabugov also showed that the dynamic capacity of heat-treated bentonite (at 400 °C) of MB is 25 % lower than its statistical capacity without heat treatment [6].

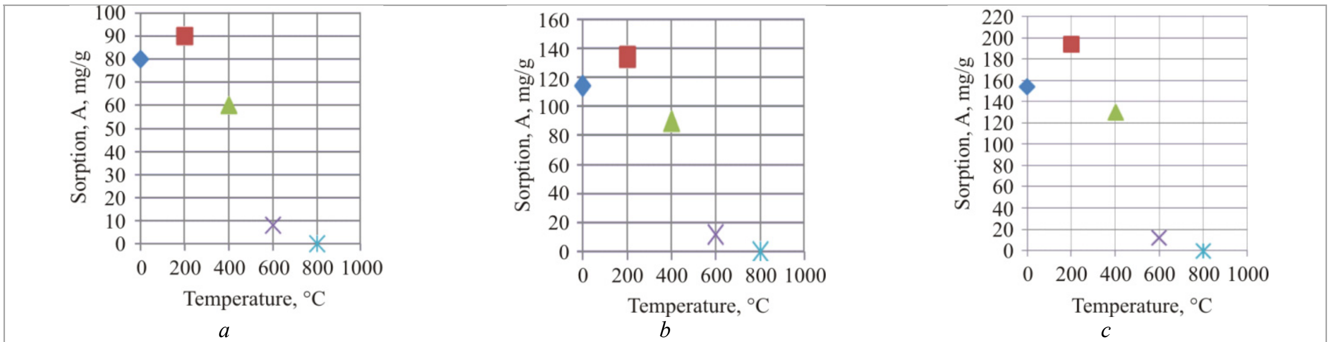

Fig. 1. Influence of the treatment temperature of kaolin (*a*), montmorillonite (*b*) and bentonite (*c*) clays on the adsorption by methylene blue (MB)

2. Influence of Heat Treatment on the Clays Structure Change

Research results are provided in Fig. 2.

Thermograms were obtained by the TG/DSC method, where the green solid line shows the TG curve, and the green dashed line shows the first derivative of TG (DTG). The blue solid line shows the DSC curve, and the blue dashed line shows the first derivative of *d*DSC.

Thermogram processing showed that the following endothermic effects are observed for montmorillonite clay:

1) the first effect (in the temperature range of 97–113 °C) is associated with the loss of loosely bound water in the amount from 4 to 11 %;

2) the second one – at 170 °C, is caused by the loss of strongly bound water (2 %);

3) the third one – 500–730 °C, is accompanied by a decrease in mass of up to 2 % due to the structure change;

4) the fourth – 890 °C, is an exothermic effect, where crystallization and destruction of the dehydrated montmorillonite crystal lattice occurs. The total weight loss (water, hydroxyl, CO_2) varies from 11 to 28.5 %.

The kaolinite clay has the following endothermic effects:

1) the first effect – 75–106 °C, is caused by the loss of loosely bound water, the weight loss here is 2–7 %;

2) the second one – 150–200 °C, is caused by the loss of strongly bound water;

3) the third – 487–527 °C, is associated with the release of hydroxyl groups in the amount of 4–6.5 % and kaolinite structure change;

4) the fourth effect – 960–970 °C, refers to exothermic effects; here, crystallization processes occur with the appearance of mullite or corundum, as well as (higher-temperature) crisstabalite. The total weight loss of the kaolinite clay fraction is from 10 to 18 %.

Thus, when processing montmorillonite clay at a temperature above 200 °C, active centers release on the particles surface due to the removal of strongly and loosely bound water molecules from it. When clay is heated to a temperature of 730–890 °C, the processes of montmorillonite dehydration occur in it:

$$Al_2O_3 \cdot 4SiO_2 \cdot nH_2O \rightarrow Al_2O_3 \cdot 4SiO_2 + nH_2O.$$

The processes of strongly and loosely bound water release are observed when kaolin clay is heated up to 200 °C. They result in increased energy on the particles surface.

When kaolin is treated at a temperature of 487–960 °C, the structure of kaolinite is modified due to the loss of the hydroxyl group and its transformation into metakaolinite.

The data obtained are consistent with the results of studies [19], where it was noted that kaolin dehydroxylation begins at 450 °C. Infrared (IR) spectra under thermal exposure of kaolin are characterized by a gradual intensity loss (Fig. 3).

T.V. Vakalova et al. came to similar conclusions set out in the article [16]. They found that when kaolinite is calcined (calcination temperature 370–660 °C), the process of dehydroxylation takes place therein, accompanied by removal of octahedral sheet hydroxyl groups. In this case, the aluminohydroxylated octahedral sheet is almost completely rebuilt into an alumina-oxygen tetrahedral layer of the generated metakaolinite.

Thus, changes in the montmorillonite and kaolin clays structure are observed during their annealing at a temperature range of 450–960 °C, which entails an 11–16-fold decrease in the adsorption activity of clays.

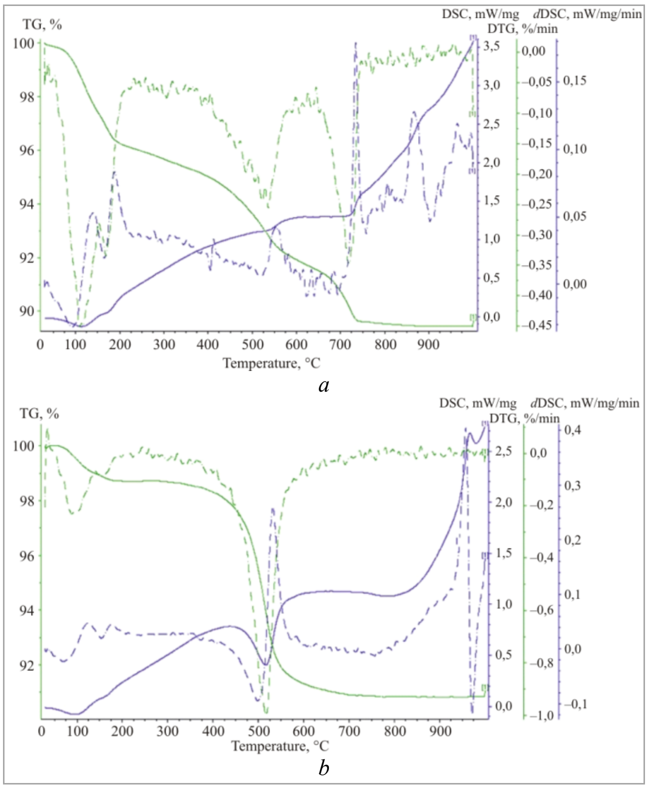

Fig. 2. Thermogram of montmorillonite (*a*) and kaolin (*b*) clays

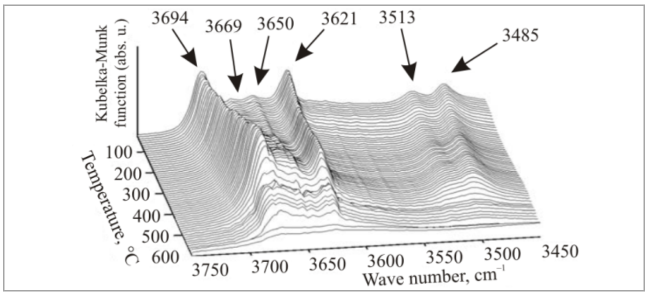

Fig. 3. Change of transmission intensity during heat treatment of kaolin (according to [19])

3. Influence of Clays Heat Treatment Followed by Their Complete Saturation with Water Vapor on the Adsorption of Clays by Methylene Blue (Scheme 2)

The results of experimental studies are shown in Fig. 4.

The data in Fig. 4 show that the adsorption properties of clays subjected to heat treatment and completely saturated with water vapor are lower than those of clays subjected to heat treatment and partially saturated with water vapor (in air-dried condition). So, at annealing temperature of 0 °C, the adsorption activity in kaolin clay decreases by 38 %, in montmorillonite - by 41 % and in bentonite - by 64 %, and at t = 200 °C it decreases by 45, 42 and 68 %, respectively (Table 1).

Table 2 shows the data on the moisture effect (the degree of clays saturation with water vapor) on adsorptionclays by methylene blue. The table shows that the lower the soil moisture, the higher the ratio of adsorption at t_1 = 200 °C (A_{200}) to the adsorption at t_0 = 0 °C (A_0). That means, the annealing temperature has greater influence on the adsorption activity of clays.

The influence of the degree of clays saturation with water vapor on their adsorption can be explained as follows. During

Table 1

Clay adsorption by methylene blue according to test schemes 1 and 2

Clay treatment type	Clay treatment temperature, °C	Clay adsorption by methylene blue, mg/g		
		kaolin	montmorillonitic	bentonite
Heat (scheme 1)	0	80	114	156
	200	90	132	194
Heat followed by saturation with water vapor (scheme 2)	0	58	80	98
	200	62	90	116

Table 2

Influence of moisture on the adsorption of clays by methylene blue

Clay treatment type	Parameter	Clay		
		kaolin	montmorillonitic	bentonite
Scheme 1	Moisture, %	2.4	4.8	7.5
	K_1, %	12.5	15.8	24.4
Scheme 2	Moisture, %	6.3	–	15.9
	K_2, %	6.8	12.5	18.4

Note: the effect of temperature on the adsorption of clays is calculated as the ratio of adsorption at t_1 = 200 °C (A_{200}) to adsorption at t_0 = 0 °C (A_0), that is $K_1 = A_{200} / A_0$.

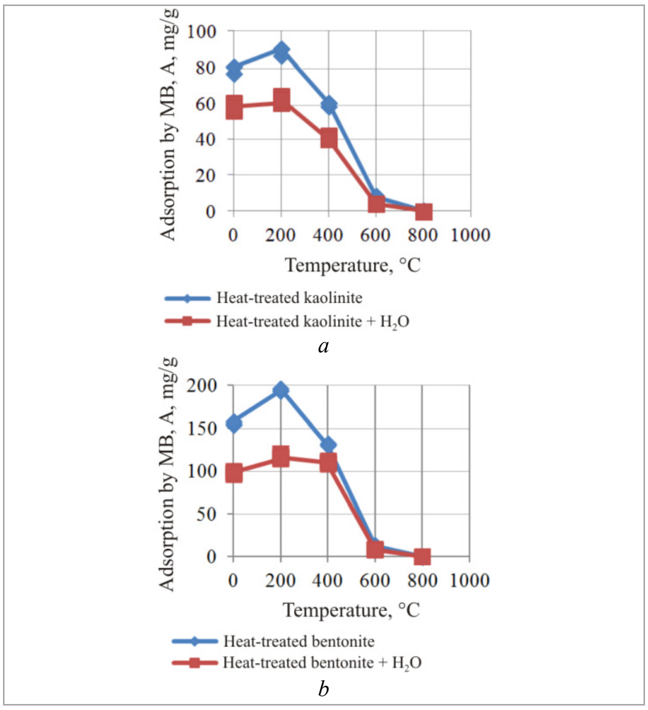

Fig. 4. Influence of heat treatment of clays (*a* – kaolin; *b* – bentonite) followed by saturation with water vapor on the adsorption of clays by methylene blue

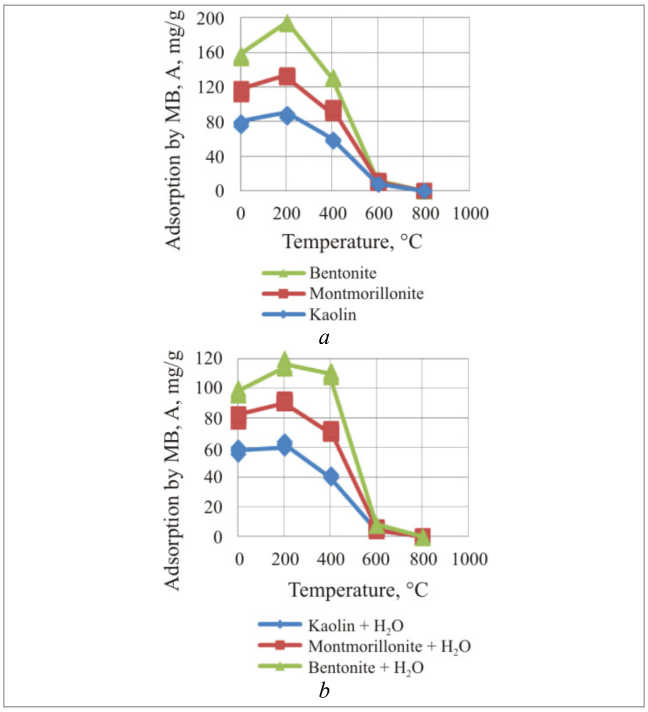

Fig. 5. Influence of the mineral composition on the adsorption of heat-treated clays saturated with water vapor: *a* – partially; *b* – completely

heat treatment of clays and their partial saturation with water vapor (Scheme 1), water molecules occupy part of the energy centers on the particle surface; therefore, the particles have a sufficiently high energy potential which is realized in the form of high values of their adsorption by methylene blue.

During thermal treatment of clays and their complete saturation with water vapor (Scheme 2), negative (positive) charges on the particle surface are compensated by water molecules which are located in the form of films of strongly and loosely bound water. In addition, water molecules, entering the inter-package space, compensate for the charges on the surface of packages and minerals, which are realized in the form of clay swelling processes. The swelling processes lead to an increase of the structural elements size which exhibits itself in the form of decreased specific surface area of clays. Therefore, clays completely saturated with water vapor are less active in adsorption than clays partially saturated with water vapor. This conclusion is consistent with the results of other researchers [33].

4. Influence of Mineral Composition on the Change of Heat-Treated Clays Adsorption

Fig. 5 shows graphs of the mineral composition influence on adsorption of heat-treated clays partially and completely saturated with water vapor.

Based on the data obtained, it can be traced that bentonite clay has the highest adsorption activity at the annealing temperature of up to 600 °C, montmorillonite clay is less active, and kaolin clay has the lowest adsorption activity. The research results are consistent with the data [14, 24].

Thus, the adsorption activity of clays is most influenced by the temperature of their treatment, less –

by the mineral composition, and least – by the degree of their saturation with water vapor.

Conclusion

Common factors of changes in the adsorption activity of heat-treated clays were revealed. They lie in the fact that during heat treatment of clays at temperatures of up to 200 °C, energy centers on the surface of their structural elements are activated, which leads to an increase in the adsorption of clays by methylene blue by 12–24 %. At a clay treatment temperature of 450–960 °C, the processes of their structural transformation take place, which reduce the adsorption activity of clays 11–16–fold.

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