UDC 628.316.12:[666.321](045)
DOI: 10.15587/2706-5448.2022.254584
Article type «Original research»

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# WATER PURIFICATION FROM CATIONIC ORGANIC DYES USING KAOLIN-BASED CERAMIC MATERIALS

*The development of effective sorbents based on cheap natural raw materials for water purification from synthetic organic dyes is an important environmental problem. It is known that layered silicates are distinguished by mechanical strength, thermal and chemical resistance, high dispersion, ion exchange, availability and low cost. However, the main disadvantage of natural clays is their insufficiently high sorption capacity with respect to organic toxicants. Therefore, to increase it, the surface of clay minerals is modified by various physical and chemical methods. The object of study is kaolin from the Glukhovets deposit (Ukraine), the main rock-forming mineral of which is kaolinite. After its thermal modification followed by acid activation with chloride acid, sorbents with sufficiently high structural-sorption properties and increased sorption capacity with respect to the synthetic organic dye, methylene blue, are obtained. The influence of the conditions for the synthesis of ceramic materials on the physicochemical features of the dye removal from the aqueous medium is studied. The dependence of the values of methylene blue sorption by silicate sorbents on the temperature of kaolin treatment and the concentration of chloride acid, which was used for its acid activation, is studied. It has been established that the specific surface of the obtained samples is significantly affected by both the kaolin treatment temperature and the concentration of perchloric acid. Thus, under certain experimental conditions, sorption materials were obtained with a specific surface area of 140 m$^2$/g, which significantly exceeds that for the original kaolin, which is 9 m$^2$/g. A significant increase in the sorption capacity of acid-activated samples compared to the original clay and heat-treated forms was established. The value of the maximum sorption of methylene blue for acid-activated samples exceeds that for natural kaolin by almost 2 times and reaches 16 mg/g.*

**Keywords:** *effective sorbents, ceramic materials, thermal modification, acid activation, water purification, organic dyes.*

*Received date: 23.02.2022*
*Accepted date: 01.04.2022*
*Published date: 15.04.2022*

***How to cite***

*Bondarieva, A., Yaichenia, I., Zahorodniuk, N., Tobilko, V., Pavlenko, V. (2022). Water purification from cationic organic dyes using kaolin-based ceramic materials. Technology Audit and Production Reserves, 2 (3 (64)), 10–16. doi: http://doi.org/10.15587/2706-5448.2022.254584*

## 1. Introduction

One of the most important problems in environmental protection is the development of efficient and cost-effective technologies for water purification from organic pollutants, such as synthetic dyes. As a result of the activity of enterprises of the light, chemical, food industries, wastewater is formed, which contains many different organic compounds. For example, the cationic dye methylene blue (MB) is widely used in dyeing fabrics, paper, cotton, silk, and leather.

To remove organic dyes from wastewater, sedimentation, filtration, chemical treatment, oxidation, electrochemical, biological, adsorption and ion exchange methods are used. But one of the most effective among them is adsorption methods. To date, a large number of sorption materials have been developed from both natural and artificial raw materials [1, 2]. Synthetic sorbents are characterized by high sorption capacity and selectivity, but their disadvantage is their relatively high cost. That is why, when choosing materials for the purification of large volumes of water from organic dyes, sorbents based on cheap natural raw materials are promising [3]. These include materials based on clay minerals, along with availability and low cost, they exhibit adsorption capacity for cations of inorganic and organic nature. However, the most natural clays, such as kaolin, are not very effective in removing synthetic dyes. Therefore, to increase its sorption capacity, various modification methods are used, one of which is heat treatment followed by acid activation. As a result, it is possible to obtain sorbents with sufficiently high structural sorption properties and increased sorption capacity with respect to pollutants of various nature.

Thus, the relevance of research is due to the need to develop effective sorbent materials based on cheap natural raw materials for water purification from synthetic organic dyes.

## 2. The object of research and its technological audit

*The object of research* is kaolin from the Glukhovets deposit (Ukraine), the main rock-forming mineral of which is kaolinite. Halloysite, hydromica, quartz, feldspar, and iron compounds may be present as impurities. Kaolinite refers to layered silicates with a rigid structural cell having a two-layer package. It consists of a tetrahedral layer formed by silicon oxygen tetrahedra and an octahedral layer formed by aluminum hydroxyl octahedra (denoted 1:1). Clay minerals of this group are characterized by the presence of only the outer sorption surface. Their porosity is due to the gaps between the contacting lobules. The specific surface is determined mainly by the dispersity of the lobules.

Technological audit shows that sorption materials with unique physicochemical and structural sorption properties are obtained on the basis of layered silicates, which can be used in various technological processes. This is due to the availability of natural raw materials, their cheapness and the existence of a large number of methods for regulating their structure and surface chemistry. Heat treatment of kaolin and its subsequent acid activation makes it possible to obtain effective sorption materials with a high specific surface without the use of expensive reagents and does not require unique equipment. Therefore, the use of such silicate sorbents for post-treatment of water from pollution by cationic organic dyes is quite promising.

## 3. The aim and objectives of research

*The aim of research* is to obtain ceramic materials based on kaolin for water purification from cationic dyes.

Research objectives:

1. Study the influence of the main parameters of the synthesis of sorption materials based on kaolin on their structural-sorption and physic-chemical properties.
2. Investigate the phase composition and parameters of the porous structure of the obtained silicate sorbents.
3. Study the physical and chemical features of the extraction of methylene blue from water using activated ceramic materials.

## 4. Research of existing solutions to the problem

To solve the problem of protecting the water basin from pollution by the methylene blue dye, many different sorbent substances have been obtained. Some of them are developed on the basis of organic materials, such as activated carbon [4], while others are based on inorganic iron-containing compounds [5]. At the same time, the economic feasibility of using them in the treatment of large volumes of polluted waters is important. In this regard, the attention of researchers is focused on the use of cheap raw materials, for example, waste from various industries [6, 7]. As a result, so-called «low-cost» sorbents are obtained, including those based on food industry waste [8]. Such sorbent materials also include natural clays [9, 10]. In addition to layered and layered-tape silicates, zeolites exhibit the sorption capacity for methylene blue [11]. To increase the sorption capacity of inorganic silicates with respect to cationic dyes, they are additionally modified [12]. For example, heat treatment of kaolin leads to the production of a more reactive cellular material, metakaolin [13, 14]. When it is treated with acids, sorbents with a high specific surface area and better physicochemical properties, including sorption ones, are obtained [15, 16].

## 5. Methods of research

To purify natural kaolin from impurities, a traditional method was used [17]. To obtain thermally modified forms of kaolin, samples were fired in a muffle furnace at different temperatures, namely 500 °C, 600 °C, 700 °C and 800 °C. The holding time at the maximum temperature was 2 hours. After cooling, the samples were sifted through a sieve to obtain a fraction ≤0.315 mm. Acid activation of samples of kaolin, which was burned at temperatures of 600 °C and 800 °C, was carried out according to a modified procedure [18]. The ratio of the hard phase to the liquid was 1:10. For acid activation, solutions of perchloric acid were used: 0.25 M, 0.5 M, 1.5 M, and 2.5 M. Ceramic sorption materials were prepared at two temperatures (60 °C and 80 °C) with constant stirring for 4 hours. After the suspension was cooled to room temperature, the samples were repeatedly washed with distilled water and the solid phase was separated by filtration through several layers of filter paper on a Buchner watering can under vacuum. The resulting precipitate was dried in an oven at 80 °C X-ray phase analysis of the original kaolin and thermally modified samples was carried out using a DRON-4-07 diffractometer (USSR) equipped with two Soller slits, using filtered CuKα radiation, in the range from 2–60° (2θ). The interpretation of the phase composition and the interpretation of the results obtained are based on the literature data [19].

The structural and sorption properties of natural kaolin and its acid-modified samples were determined using the low-temperature nitrogen adsorption/desorption method. All calculations were made using the Quantachrome Nova 2200e Surface Area and Pore Size Analyzer instrument software, USA. The specific surface area and total pore volume of the samples were calculated using the BET method (Brunauer, Emmett and Teller). The pore size distribution was determined by the Barrett-Joyner-Halendi (BJH) method, and the meso- and micropore size distributions were determined by the Density Functional Theory (DFT) method. Before recording the sorption isotherm, the studied samples were evacuated at room temperature for 30 minutes and kept for 5 minutes after equilibrium was established at each point.

The study of the sorption properties of ceramic materials based on kaolin with respect to methylene blue was carried out at room temperature under static conditions and continuous shaking on a shaker for 1 hour. For the sorption experiment, a sample of 0.1 g of the studied material was used. The solution volume was 50 cm$^3$, and the range of initial dye concentrations was 5–30 mg/dm$^3$. After adsorption equilibrium was established, the liquid phase was separated from the solid by centrifugation, and the equilibrium dye concentration in the aqueous phase was determined spectrophotometrically. The optical density of solutions was determined using a UNICO-UV 2100 spectrophotometer (USA) at $\lambda = 665$ nm and an absorbing layer thickness of 1 cm.

The sorption value of methylene blue $a$ (mg/g) was calculated by the formula:

$$a = (C_i - C_{eq}) \cdot V/m,$$

where $C_i$, $C_{eq}$ – initial and equilibrium dye concentration, mg/dm$^3$; $V$ – volume of the solution, dm$^3$; $m$ – weight of the sorbent sample, g.

The sorption isotherms of methylene blue by ceramic materials were processed using the Langmuir mathematical model:

$$C_{eq}/a_{eq}=1/(K_L\cdot a_m)+(1/a_m)\cdot C_e,$$

where $a_{eq}$ – equilibrium sorption, mg/g; $K_L$ – Langmuir constant characterizing the sorption energy, dm$^3$/mg; $C_{eq}$ – equilibrium concentration, mg/dm$^3$; $a_m$ – sorption capacity of the monolayer, mg/g.

As well as the Freundlich models:

$$\lg a_{eq}=\lg K_F+(1/n)\cdot\lg C_{eq},$$

where $K_F$ – Freundlich constant characterizing the sorption capacity, dm$^3$/g; $1/n$ – Freundlich constant characterizing the intensity of sorption.

To assess the authenticity of the obtained experimental data, statistical methods for processing the results obtained were used. The number of definitions averaged three. The relative measurement error did not exceed 2 %. When plotting the kinetic curves and sorption isotherms, the B-spline approximation ($R^2>0.9$) was used.

## 6. Research results

It is known that the thermal modification of kaolin leads to the transformation of the natural clay mineral kaolinite into a more chemically active metakaolin [13, 14]. Fig. 1 shows the data of X-ray phase analysis of the original kaolin and its thermally modified form at 600 °C. The data obtained indicate the practical monomineral nature of the original kaolin (K) with small impurities of quartz. Its heat treatment leads to a gradual weakening of the intensity of the characteristic reflexes in the diffraction patterns, which indicates a partial destruction of the crystalline structure of kaolin at a given temperature (K-600). Increasing the temperature of kaolin treatment, for example, up to 800 °C, leads to the transition of kaolinite to an almost X-ray amorphous state [19].

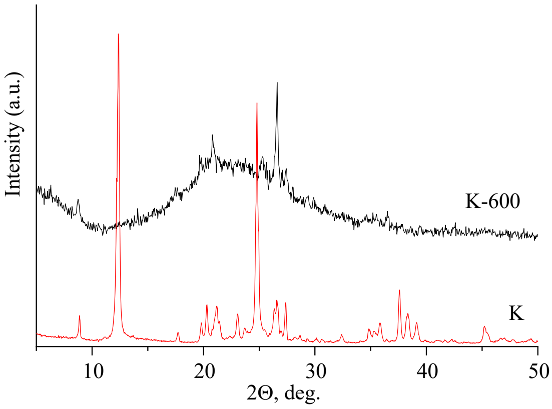

**Fig. 1.** Diffractograms of original (K) and heat-treated (K-600) kaolin

When studying the optimal conditions for the removal of pollutants from waters by sorption materials, the time of establishment of sorption equilibrium is important. Fig. 2 shows the dependences of the MB sorption values on the contact time of the solution with a natural and thermally modified kaolin sample.

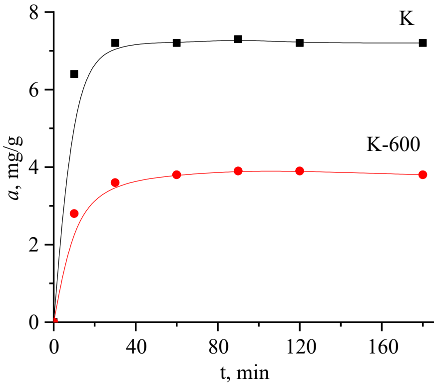

**Fig. 2.** Sorption kinetics of methylene blue on the original (K) and thermally modified at 600 °C (K-600) kaolin

The data obtained indicate that the process of sorption of methylene blue by both natural and thermally modified kaolin proceeds quite quickly and more than 90 % of the dye cations under the given experimental conditions ($C_{MB}$=15 mg/dm$^3$, $V/m$=500) by materials in during the first 20 minutes. After 1 hour of contact between the MB solution and the surface of the samples, the sorption value practically does not change. However, it should be noted that the heat treatment of kaolin (600 °C for 2 hours) reduces the sorption of the dye, which is due to a decrease not only in the number of sorption centers in the structure of the mineral during dehydroxylation under given conditions, but also in the specific surface due to the irreversible aggregation of particles.

Thus, the obtained results indicate that the process of sorption equilibrium in the studied system methylene blue – thermally treated kaolin is established within 1 hour. In all subsequent experiments, it was precisely at this time that the sorption extraction of pollutants from waters was carried out.

Sorption characteristics of kaolin thermally modified at different temperatures (500–800 °C) by MB were studied in the concentration range of 5–30 mg/dm$^3$. Sorption isotherms are shown in Fig. 3.

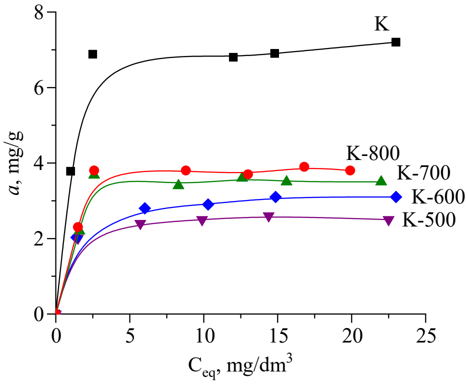

**Fig. 3.** Sorption isotherms of methylene blue by thermally modified kaolin samples

The data obtained indicate that the heat treatment of kaolin reduces the sorption capacity with respect to methylene blue compared to the original mineral. However, it should be noted that the maximum dye sorption value increases with an increase in the kaolin firing temperature. Moreover, the difference in the sorption capacity of kaolin, thermally modified at 500 °C and 600 °C, and 700 °C, and 800 °C, is not significant. Thus, the maximum MB sorption value is 2.8 mg/g, 3.3 mg/g for samples treated at 500 °C, 600 °C and 3.9 mg/g and 4.1 mg/g for samples treated at 700 °C and 800 °C, respectively. This is due to the fact that with an increase in the processing temperature, the number of active sorption centers on the silicate surface increases due to the removal of physically and chemically bound water and the gradual transformation of the kaolinite structure from crystalline to amorphous.

Thus, the obtained results indicate that sorption materials based on thermally modified kaolin samples exhibit sorption capacity with respect to cationic dyes and are promising materials for their removal from waters in the range of low concentrations.

It is known that acid activation of natural clay minerals leads to a significant improvement in their structural-sorption and physic-chemical properties. Thus, the treatment of layered silicates with solutions of inorganic acids, mainly HCl or $H_2SO_4$, significantly increases the specific surface area of the samples and their porosity. This is due to changes in the structure of aluminosilicates in the course of acid activation, namely, partial or complete dissolution of the marginal layers of clay minerals and leaching of aluminum from the structure, depending on the conditions of the process [20].

Fig. 4 shows isotherms of sorption/desorption of nitrogen, and in Table 1 parameters of the steam structure of kaolin samples acid-activated with 2.5 M HCl solution (K-600/2.5 M/60 and K-600/2.5 M/80). In the name of the samples, K is kaolin, 600 is the temperature of processing kaolin, 2.5 is the concentration of perchloric acid, 60 and 80 are the temperatures for acid activation of the samples. For comparison, the results of the study of the original kaolin (K) are presented.

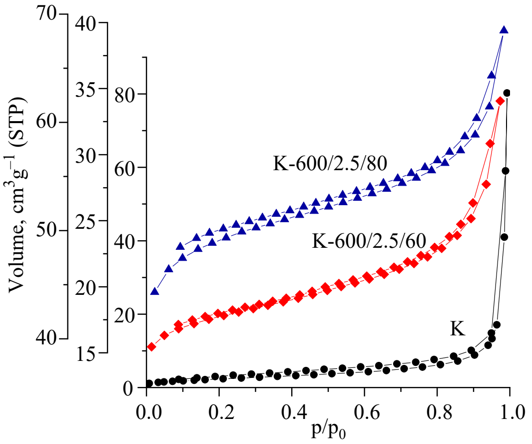

**Fig. 4.** Sorption/desorption isotherms of nitrogen on acid-activated samples of thermally treated kaolin

Shape of nitrogen sorption isotherm in initial kaolin (K), Fig. 4 indicates that this sample is dominated by macropores with a small amount of micropores. A narrow hysteresis loop indicates narrow macropores. In addition, the presence of macropores is confirmed by the low specific surface area of kaolin (Table 1). After acid activation of thermally modified mineral samples, a significant increase in the specific surface area of ceramic materials and the appearance of macropores are observed. Moreover, the higher the acid activation temperature, the higher the specific surface area and pore volume. Thus, for sample K-600/2.5 M/60, acid activation at 60 °C led to an increase in the specific surface area from 8.98 m$^2$/g (K) to 60.77 m$^2$/g. An increase in temperature to 80 °C led to an even greater increase in the specific surface area – 140.06 m$^2$/g (K-600/2.5 M/80).

Thus, the obtained results indicate that the acid activation of heat-treated kaolin under the given experimental conditions leads to a significant improvement in the structural-sorption properties of the obtained materials.

Therefore, it was interesting to study the main physicochemical features of the removal of blue methylene from the solution by acid-activated kaolin samples. To study the optimal conditions for the extraction of MB from solution, kinetic experiments were carried out. Fig. 5 shows the dependences of the dye sorption on the contact time of the rigid and liquid phases.

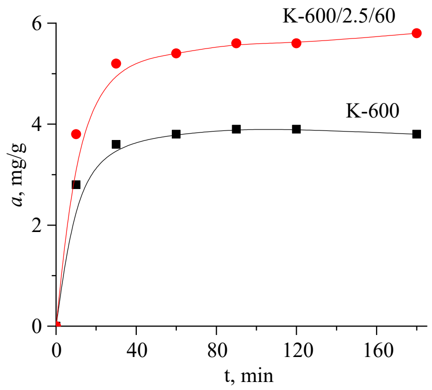

**Fig. 5.** Kinetics of methylene blue sorption by ceramic materials

The data obtained indicate that the removal of MB from the solution by ceramic materials occurs quite quickly, and the state of sorption equilibrium is reached in 1 hour. Shown in Fig. 5, the results indicate that the sorption capacity of the acid-activated sample (K-600/2.5 M/60) is higher than that of the heat-treated sample (K-600). Under given conditions of the experiment (initial $C_{MB}$= =15 mg/dm$^3$), the sorption values are 5.8 mg/g and 3.5 mg/g, respectively.

**Table 1**

Steam structure parameters of acid-activated samples of thermally treated kaolin

| Sample | *S*, m$^2$/g | $V_\Sigma$, cm$^3$/g | $V_\mu$, cm$^3$/g | $V_{\mu\%}$, % | Pore size distribution, nm | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | *BJH dV (log r)* | | *DFT dV (log r)* | |
| | | | | | $r_1$ | $r_2$ | $r_1$ | $r_2$ |
| Kaolin | 9 | 0.124 | 0.003 | 2.18 | – | – | 1.25 | 31 |
| K-600/2.5/60 | 61 | 0.057 | 0.004 | 6.70 | 3.26 | 17.6 | 0.92 | – |
| K-600/2.5/80 | 140 | 0.104 | 0.008 | 8.03 | 3.26 | 16.5 | 0.92 | – |

**Note:** *S* – specific surface area, m$^2$/h; $V_\Sigma$ – total pore volume, cm$^3$/h; $V_\mu$ – volume of micropores, cm$^3$/g; $r_1$, $r_2$ – pore size distribution, nm

The influence of the concentration of perchloric acid, which was used to activate samples of heat-treated kaolin, the efficiency of removing MB from the solution by ceramic samples is shown in Fig. 6.

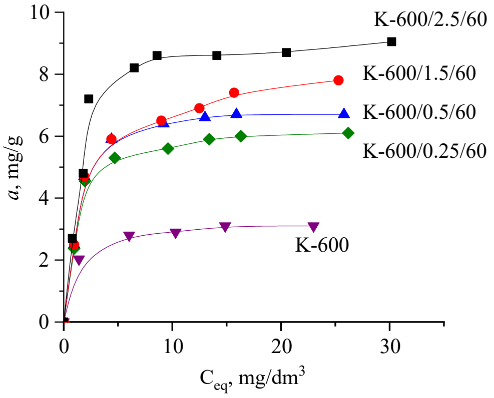

**Fig. 6.** Sorption isotherms of methylene blue on acid-activated samples

The data obtained indicate that the acid activation of heat-treated kaolin significantly increases the sorption capacity with respect to methylene blue. Moreover, the higher the concentration of perchloric acid, the higher this ability. Thus, the maximum sorption value is observed for the K-600/2.5/60 sample obtained by treating thermally modified kaolin with a 2.5 M acid solution. After the sorption experiments, the following data were obtained: the maximum sorption value for the K-600/2.5/60 sample is 9.2 mg/g; for the K-600/1.5/60 sample, 8.2 mg/g; for K-600/0.5/60 – 7.5 mg/h, and for K-600/0.25/60 – 6.9 mg/h. The obtained values indicate that the acid concentration affects changes in the structure of the heat-treated kaolin, which lead to an improvement in the sorption characteristics of the samples. This is due to the partial destruction of the crystal lattice of metakaolin during treatment with acid solutions and the appearance of a larger number of active sorption centers on the surface. As can be seen from the given isotherms, heat-treated kaolin (K-600) exhibits the lowest sorption capacity with respect to methylene blue (3.3 mg/g).

The influence of the temperature of acid activation of kaolin samples on the efficiency of MB removal from the solution was studied. For this, ceramic samples thermally modified at 600 °C (K-600) and 800 °C (K-800) were used. Acid activation with 2.5 M HCl was carried out at two different temperatures, 60 °C and 80 °C. Fig. 7 and Fig. 8 show the sorption isotherms of methylene blue ceramic samples, and in Table 2, the coefficients of the Freundlich and Langmuir equations are calculated.

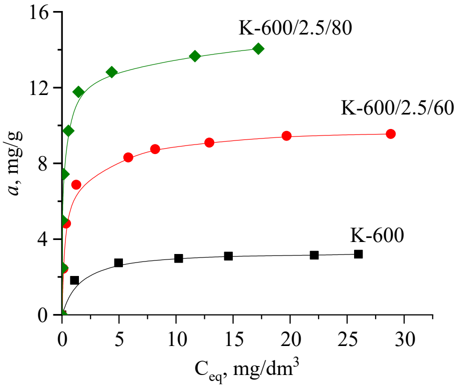

**Fig. 7.** Sorption isotherms of methylene blue on acid-activated samples heat-treated at 600 °C

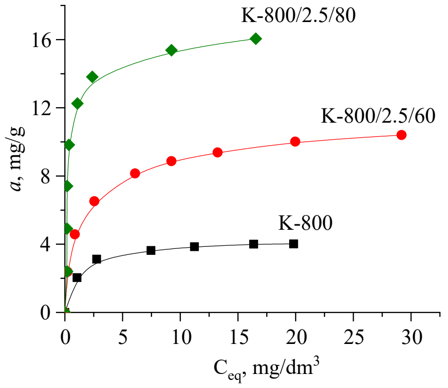

**Fig. 8.** Sorption isotherms of methylene blue on acid-activated samples heat-treated at 800 °C

The obtained experimental data indicate that the processing temperature of the initial kaolin affects the sorption capacity of materials for MB after their acid activation. So, the data shown in Fig. 7 and Fig. 8 indicate that a higher MB sorption value (16.05 mg/g) is observed for the K-800/2.5/80 sample (Fig. 8), obtained by thermal treatment with a 2.5 M solution of perchloric acid at 80 °C of thermal modified kaolin at 800 °C. The lowest sorption capacity is exhibited by sample K-600/2.5/80, which is based on kaolin treated at 600 °C. It is 14.2 mg/g (Fig. 7). Carrying out acid activation of metakaolins at a lower temperature (60 °C) leads to a decrease in sorption capacity, but it still exceeds that of heat-treated kaolin. During the experiments, the following data were obtained: the maximum sorption values for K-600/2.5/80 are 14.1 mg/g, K-600/2.5/60 – 9.0 mg/g, K-600 – 3.1 mg/g (Fig. 7) and for K-800/2.5/80 – 16.05 mg/g, K-800/2.5/60 – 10.4 mg/g, K-800 – 4.05 mg/g (Fig. 8).

**Table 2**

Coefficients of the Freundlich and Langmuir equations for acid-activated samples

| Sample | Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|---|
| | $a_{max}$, mg/g | $K_L$ | $R^2$ | $1/n$ | $K_F$ | $R^2$ |
| K-600 | 3.29 | 1.64 | 0.989 | 0.176 | 1.898 | 0.928 |
| K-600/2.5/60 | 9.17 | 2.15 | 0.930 | 0.112 | 6.728 | 0.993 |
| K-600/2.5/80 | 14.32 | 2.28 | 0.999 | 0.0707 | 11.497 | 0.998 |
| K-800 | 4.54 | 0.575 | 0.985 | 0.219 | 2.225 | 0.911 |
| K-800/2.5/60 | 10.604 | 0.654 | 0.997 | 0.209 | 5.463 | 0.985 |
| K-800/2.5/80 | 16.36 | 2.037 | 0.999 | 0.106 | 12.330 | 0.976 |

**Note:** $a_{max}$ – sorption capacity of the monolayer, mg/g; $K_L$ – Langmuir constant characterizing the sorption energy, dm$^3$/mg; $1/n$ – Freundlich constant characterizing the intensity of sorption; $K_F$ – Freundlich constant characterizing the sorption capacity, dm$^3$/g; $R^2$ – correlation coefficient

The data are presented in Table 2 indicate that the experimental results of sorption values are better described by the Langmuir model. For samples showing the maximum sorption capacity with respect to methylene blue (K-600/2.5/80 and K-800/2.5/80), the correlation coefficients are 0.999.

## 7. SWOT analysis of research results

*Strengths.* The main strengths of the use of kaolin-based silicate sorbents for water purification from pollution by cationic dyes are the availability of raw materials, their ease of production, and manufacturability. The prospect of using such materials in the post-treatment of large volumes of polluted water is due to the economic feasibility of the proposed sorption technologies.

*Weaknesses.* When concentrated acid solutions are used to activate thermally modified clays and prolonged phase contact, the structure of clay minerals can be destroyed. In addition, acidic wastewater is formed after washing the sorbents, which must be neutralized.

*Opportunities.* The resulting ceramic materials with a sufficiently high specific surface area can be used as a substrate for the synthesis of selective sorbents. The application of compounds with reactive functional groups to the surface of acid-activated kaolin samples will make it possible to obtain effective sorption materials for water purification from inorganic and organic pollutants.

*Threats.* Despite the availability and low cost of natural clays, artificial sorbents based on organic substances are distinguished by the purity of the chemical composition, uniformity, and greater selectivity. The widespread use of low-cost sorption materials requires deeper research and investment.

## 8. Conclusions

1. The influence of the main parameters of the synthesis of sorption materials based on kaolin (heat treatment of the initial clay, concentration of chloride acid, acid activation temperature) on their structural-sorption (specific surface area, volume and pore size) and physicochemical (sorption) properties was determined. It is shown that with an increase in the kaolin treatment temperature from 500 °C to 800 °C, the adsorption capacity of the samples in relation to methylene blue increases from 2.2 to 3.8 mg/g, respectively. It has been established that with an increase in the temperature of acid activation of thermally treated kaolin and the concentration of chloride acid, the specific surface area of sorbents and their adsorption capacity for methylene blue increase. Thus, samples of thermally treated kaolin (800 °C), which are activated with a 2.5 M solution of perchloric acid at 80 °C, have the maximum sorption value (16 mg/g). At the same time, sorbents obtained under other conditions (treatment temperature 600 °C, activation with a 0.25 M solution of chloride acid at a temperature of 60 °C) show a significantly lower efficiency of dye removal – 6 mg/g. Structurally, the sorption properties of sorbents depend on the temperature of acid activation of the samples. Thus, an increase in temperature from 60 °C to 80 °C leads to an increase in the specific surface and total pore volume of the samples by a factor of 2.

2. The phase composition and parameters of the porous structure of the modified samples were studied using X-ray phase analysis and the method of low-temperature nitrogen sorption-desorption. It has been established that the acid activation of metakaolinite leads to a significant increase in the specific surface area and pore volume of the obtained ceramic materials. In this case, there is a direct relationship between the temperature of the acid activation of metakaolinite and the structural-sorption properties of the samples. The higher the temperature, the higher the specific surface of the sorbents – 140 $m^2$/g at 80 °C and 61 $m^2$/g at 60 °C, which significantly exceeds that for the original clay mineral – 9 $m^2$/g.

3. The main physical and chemical features of the removal of organic dyes are determined using ceramic materials as an example of methylene blue from water. It is shown that the modification of the target surface of kaolinite with perchloric acid leads to a significant increase in the sorption capacity. The value of the maximum sorption of methylene blue for acid-activated samples is 16 mg/g, and for natural kaolin – 7 mg/g.

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