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CHANGE OF CATION EXCHANGE CAPACITY DURING THE THERMAL TREATMENT OF BENTONITE AND THEIR TEXTURAL CHARACTERISTICS

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Abstract: This article presents a comprehensive study aimed at analyzing the changes in cation exchange capacity (CEC) of bentonite clays during their beneficiation and subsequent thermal treatment. Using X-ray diffraction analysis, key alterations in the mineralogical composition of the bentonite samples were identified, enabling the assessment of the beneficiation efficiency in terms of montmorillonite content and the reduction in proportions of quartz, kaolinite, and illite. Special attention is devoted to the influence of these processes on the cation exchange properties of bentonite, highlighting a significant increase in CEC after beneficiation and the modification of this characteristic depending on the conditions of thermal treatment. Possible mechanisms underlying the observed changes are analyzed, along with their potential application in creating bentonites with specified properties for various fields of use, particularly in the context of adsorption and wastewater treatment.

Keywords: cation exchange capacity, beneficiation, bentonite, thermal treatment, X-ray diffraction analysis, montmorillonite.

Introduction. The relevance of studying the cation exchange properties of bentonite clays is justified by their significant potential for developing new and improved materials with specialized functional characteristics. Considering the ever-increasing demands for environmental safety and the efficiency of industrial processes, particularly in the areas of wastewater treatment, pollutant removal from the environment, and the development of new filtration materials, the search for and modification of materials with high sorption activity is a priority direction for scientific research [1-3].

The findings of this research not only enable a deeper understanding of the mechanisms of cation exchange reactions in bentonites but also facilitate the development of methodologies for their targeted modification to obtain materials with specified properties. As a result, it is possible to significantly broaden the applications of bentonites, including the creation of new composite materials for effective water purification, combating oil spills, extracting heavy metals and radionuclides from wastewater, as well as for use as carriers for slow-release agrochemicals in the agricultural industry [4-6].

Studying the influence of surfactants on the cation exchange properties of bentonite opens up new possibilities for controlling and fine-tuning its sorption characteristics, thereby facilitating the creation of more efficient and economically viable materials. This undoubtedly contributes to sustainable development in various fields, including environmental engineering, industrial purification, and agriculture, thus opening up new horizons for scientific research and technological innovations [7-10].

The aim of the study is to establish the influence of thermal treatment on Li-substituted bentonites on the alteration of the cation exchange capacity of bentonite.

Experimental Section. The object of investigation was the mineralogical composition of bentonite (BC), and its modified versions underwent comprehensive analysis using X-ray diffraction methods (XRD - Shimadzu 6100 X-ray diffractometer using CuKα radiation), thermogravimetric analysis (Paulik-Paulik-Erdey derivatograph), and scanning electron microscopy (EVO MA10 SEM Carl Zeiss), allowing the examination of substance properties changes during its modification process. Additionally, this chapter presents the results of infrared spectroscopic, microscopic, and thermal analyses. Based on this analysis, the mineralogical composition of this bentonite was determined.

In the study on the beneficiation of bentonite for the creation of adsorbents, the following methods were employed: mechanical separation and leaching; treatment with a solution of calcined soda. This method enables the production of montmorillonite-enriched bentonite with minimal content of sand impurities [11].

The enriched bentonite clay (BC) was subjected to lithium ion (Li^+) saturation using lithium chloride (LiCl). Thermal treatment was applied to modify the cation exchange capacity (CEC) of the bentonite by subjecting the sample of bentonite 104-BC to heat for a duration ranging from one to 24 hours [12].

In this study, the low-temperature nitrogen adsorption method at 77 K was employed using the Quantachrome Nova 1000e static adsorption setup to determine the porous structure characteristics of the bentonite samples. Prior to measurements, the samples underwent vacuum pre-treatment at 100°C for 12 hours. Nitrogen partial pressure values ranged from 0.005 to 0.995 P/P0 for nitrogen adsorption and desorption isotherms. The BET, Langmuir, Dollimore-Heal (DH), Dubinin-Radushkevich (DR), t-plot, and αs-plot methods were utilized for processing the adsorption curves to determine micropore volume and average pore diameter, while the Barrett-Joyner-Halenda (BJH) method was employed to evaluate mesopore volume. The pore volume and area distributions were determined using the Density Functional Theory (DFT) and Barrett-Joyner-Halenda (BJH) methods. The average pore diameter was calculated using the BET formula: $D_{avg} = 4V/S$, where V represents the volume of adsorbed nitrogen.

Results and Discussion. Table 1 presents data on establishing the mineralogical composition of bentonite samples based on X-ray diffraction analysis.

Table 1. Mineralogical composition of samples, %

Sample	MM	quartz	kaolinite	illite	chlorides	impurities
Initial	44.5	10.1	9.8	23.5	2.3	9.8
Enriched.	91.8	0.2	0.9	6.1	0.1	0.9

The study of the mineral composition of the clay reveals significant differences after its enrichment. The percentage of montmorillonite in the sample after enrichment increases from 44.5 % to 91.8 %, demonstrating the high efficiency of this process in increasing the concentration of this primary element. The enrichment process also significantly reduces the level of quartz, from 10.1 % to just 0.2 %, highlighting the effective elimination of this mineral, which negatively affects the clay's adsorption properties.

The amount of kaolinite decreases, albeit not as significantly, from 9.8 % to 0.9 %. There is also a reduction in the presence of illite from 23.5 % to 6.1 %, which may improve the adsorption properties of bentonite. As a result of enrichment, the quality of bentonite significantly increases due to the increased proportion of montmorillonite and the reduction in the proportion of undesirable impurities and other minerals. Enriched samples exhibit a noticeable increase in dispersity, which is an important factor for their utilization.

A profound understanding of the cation exchange properties of clays opens up opportunities for creating new modified forms of bentonite with optimized or specific functional characteristics suitable for particular areas of industrial application, including adsorption processes.

Table 2. The composition of the cation exchange complex (mg*eq/100 g) of the enriched bentonite.

Na^+	K^+	Ca^{2+}	Mg^{2+}	Σ_{cation}
88,6	11,8	3,1	0,5	104,0

As can be seen from the data in Table 2, sodium cations constitute the largest share of the CEC (88.6 mg*eq/100 g), indicating a high saturation of bentonite with sodium ions. Calcium and magnesium are present in small amounts (3.1 and 0.5 mg*eq/100 g, respectively), indicating the effectiveness of the enrichment process in reducing their concentrations.

The CEC of bentonite directly influences the material's ability to modify its composition and characteristics. Studying and modifying the CEC will optimize the sorption properties of the formed complexes, which is critically important for achieving the desired characteristics [13, 14].

According to the Hofmann-Klemen effect, when bentonite is heated to a certain temperature, small lithium ions can migrate into its structure, remaining inaccessible for replacement by other cations. As a result of this process, the cation exchange capacity (CEC) of lithium-treated bentonite decreases. The volume of displaced lithium ions, as well as the corresponding reduction in CEC, is proportional to the processing temperature. This method allows for the control of the CEC of bentonite.

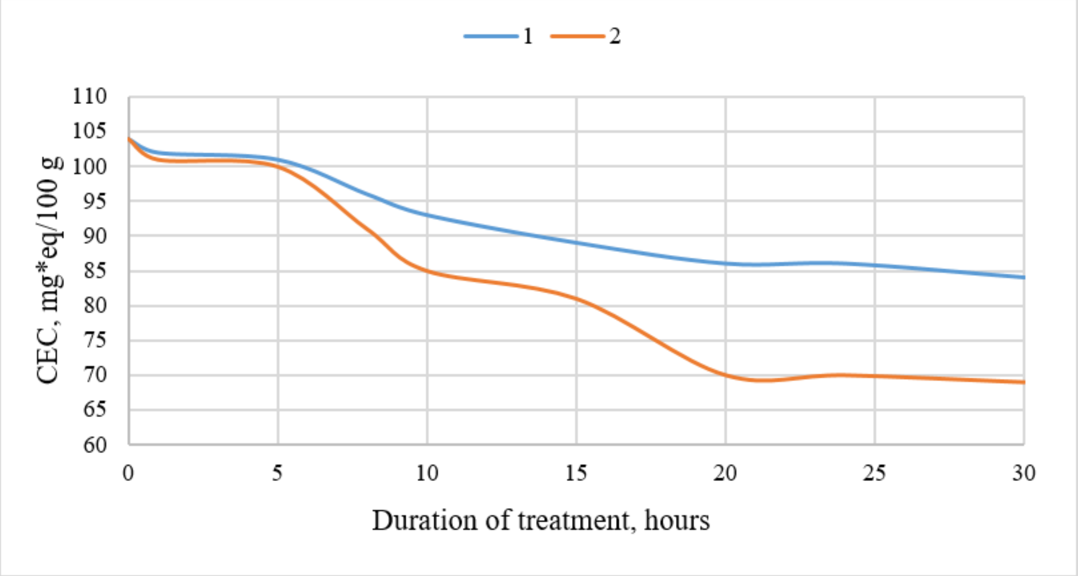

Figure 1. The effect of the duration of thermal treatment at different temperatures on the CEC of the BC sample: 1) 120°C; 2) 135°C

Figure 1 illustrates the effect of thermal treatment time on the cation exchange capacity (CEC) of bentonite. Line 1 corresponds to treatment at 120°C, while line 2 corresponds to treatment at 135°C. Both plots demonstrate a decrease in CEC with increasing duration of thermal treatment. The reduction in CEC is more significant for the sample treated at a higher temperature (135°C), indicating a more intense influence of temperature on the cation exchange properties of bentonite. These results can be utilized for controlling the properties of bentonite in industrial and other practical applications.

High processing temperatures lead to a more significant reduction in CEC, highlighting the importance of temperature conditions in the modification process of montmorillonite. The obtained bentonite samples with cation exchange capacities of 86 (BC86) and 70 mg*eq/100 g (BC70) will be further used for modification with organic surfactants.

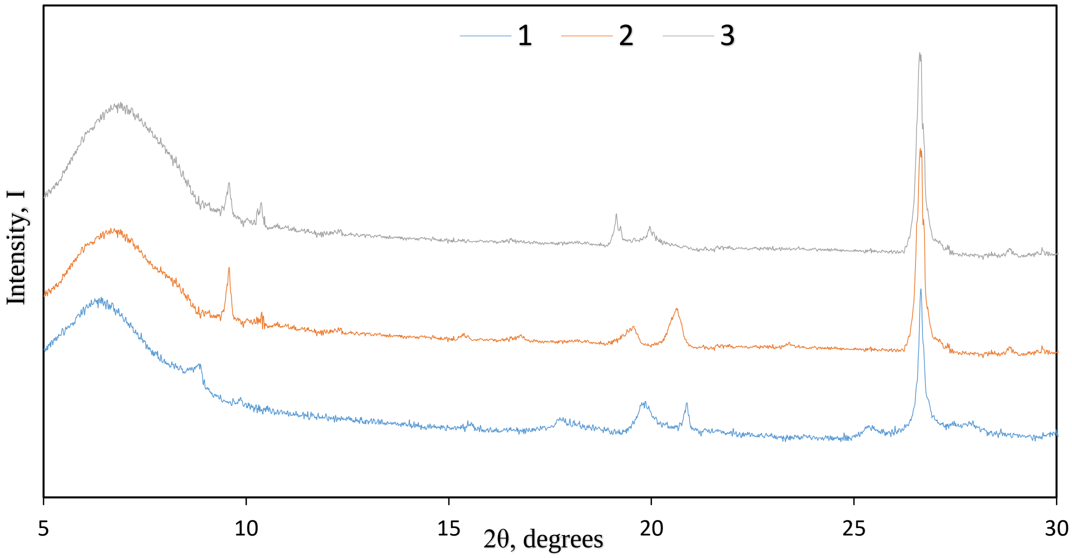

Figure 2. X-ray diffraction patterns of samples: 1) BC; 2) BC86; 3) BC70.

The analysis indicates that differences in the cation exchange capacity of the samples lead to changes in the interlayer distance [15]. The main peak d_{001} for samples BC and BC86 is located at approximately 1.261 nm and 1.253 nm, respectively. In the case of sample BC70, a shift of the peak towards a higher 2θ angle is observed, corresponding to a smaller interlayer distance of approximately 1.199 nm. It is presumed that the reduction in the concentration of hydrophilic cations leads to a decrease in the volume of interlayer water, resulting in a reduction in the interlayer distance. This may indicate the loss of some bound water by montmorillonite and changes in the pore space, which, in turn, affects the surface acidity.

Based on the obtained adsorption isotherms, the surface properties of the bentonite samples were calculated.

Table 3. Textural characteristics of the samples based on nitrogen adsorption and desorption.

Sample	S^1, m^2/g	*t-Plot*, m^2/g	V_a, sm^3/g	V_b, sm^3/g	*R*, Å	*D*, Å
BC	53,13	0,941	0,039	0,087	44,6	14,23
BC86	57,07	1,031	0,040	0,093	44,1	14,33
BC70	48,01	0,894	0,033	0,079	44,7	14,37

[1] *- Specific surface area according to the BET method; R - mean pore size.*

The analysis of Table 3 of the texture characteristics of the samples based on nitrogen adsorption and desorption indicates differences in porosity and structure among the three bentonite samples with different CEC values. Sample BC86 exhibits the highest specific surface area according to the BET method and mesopore volume, which may suggest a more developed porous structure compared to BC and BC70. The observed decrease in cation exchange capacity (CEC) in sample BC86 compared to enriched BC does not hinder it from demonstrating higher values of texture properties based on nitrogen adsorption data.

BC70 exhibits the lowest specific and external surface area, which may indicate lower porosity. The average pore size and micropore size are similar among all samples, indicating similarities in their microstructural features. The decrease in texture characteristics based on nitrogen adsorption for sample BC70 compared to BC and BC86 may suggest lower porosity and consequently a lower specific surface area available for adsorption.

The investigation of structural features of bentonites with different levels of cation exchange capacity has led to conclusions that variations in the cation exchange capacity directly influence their structural and textural characteristics, including specific surface area and porosity. Changes in cation exchange capacity can result in modifications of pore sizes and distributions, which are crucial for adsorption purposes.

Conclusions. The study of the mineralogical composition and cation exchange properties of bentonite has revealed significant changes after the enrichment process. The increase in montmorillonite content from 44.5% to 91.8% in the enriched samples emphasizes the high efficiency of enrichment in the concentration of this key component. Substantial reductions in quartz, kaolinite, and illite levels not only enhance the material's adsorption properties but also underscore its purification from undesirable impurities. X-ray diffraction analysis and changes in cation exchange capacity, particularly after thermal treatment, indicate the possibility of controlling these properties to achieve optimal characteristics of bentonite.

The identified data demonstrate that the enrichment of bentonite not only enhances its quality by increasing the content of montmorillonite but also increases its dispersity, which is important for industrial applications. Understanding the mechanisms of interaction between cations and montmorillonite opens up new avenues for creating modified bentonites with targeted properties, which can find application in various fields, including adsorption and wastewater treatment.

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