

COMPOSITION, STRUCTURE AND TEXTURAL CHARACTERISTICS OF DOMESTIC ACID ACTIVATED BENTONITE

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Abstract: Bentonites are aluminosilicate minerals which, due to their porosity, layered structure and composition have a wide application. Structural and textural characteristics of bentonite may be improved by different modification procedures. The aim of this study was to investigate compositional, structural and textural characteristics of domestic bentonite in place Gerzovo, before and after the activation with sulfuric acid. These characteristics were investigated by analytical methods, X-ray diffraction (XRD) and the method of low-temperature nitrogen adsorption (BET). Characteristics of acid-activated bentonite were compared with the characteristics of commercial active clay. The obtained results showed that the activation of bentonite with sulfuric acid leads to a significant improvement in structural and textural characteristics. Using these results it can be assumed that this bentonite will have good adsorption characteristics and can serve as an alternative in comparison with imported commercial aluminosilicate-based adsorbents.

Keywords: bentonite, acid activation, composition, structural and textural characteristics.

1. INTRODUCTION

A variety of imported commercial active clays based on aluminosilicate are used as adsorbents during the treatment process of mineral based oils, regeneration of used lubricating oils, bleaching of edible oils, protection of the environment and other. Natural materials used for this purpose are: bentonites, zeolites, bauxites, kaolinite, sepiolite, etc. [1–5]. Their adsorption characteristics depend on chemical and mineralogical composition as well as on textural, structural and morphological characteristics. Bentonite clays are ores with montmorillonite as basic mineral, and depending on its content, bentonite clays are categorized and valued in geological and applicative sense. Besides montmorillonite, bentonite contains other minerals, such as: quartz, calcite, feldspar, muscovite and biotite. Montmorillonite $\text{Al}_2[(\text{OH})_2\text{Si}_4\text{O}_{10}] \cdot n\text{H}_2\text{O}$ belongs to a group of layered silicates, whose basic structure is composed of tetrahedral layers, formed by interbinding of tetrahedral sheets with Si^{4+} ion in the centre

and four O^{2-} ions on the tops, and octahedral layers, formed by binding of octahedral sheets with Al^{3+} ion or Mg^{2+} ion in the centre and six OH^- ions on the corners [6]. In nature, calcium bentonite is prevalent, while the content of sodium bentonite (Wyoming) is much smaller. A very important characteristic of bentonite is capability of ion exchange Si^{4+} and Al^{3+} with a lower valency cations Na^+ , H^+ , Ca^{2+} , Mg^{2+} . In addition, bentonite has high adsorption capability, ability of swelling and possibility of processing, which allow its wide range of use. Adsorption capability of natural bentonites can be improved by various methods of activation, modification with various metals, pillaring, etc. [7–16]. The effect after acid activation (HCl or H_2SO_4) depends on activation parameters (type and acid concentration, contact time, temperature), as well as on the characteristics of natural bentonite and montmorillonite content. In the Republic of Srpska there are multiple deposits of bentonite, and the most important one is located in Sipovo municipality [17].

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2. EXPERIMENTAL

2.1. Materials

- The natural bentonite from Gerzovo, municipality of Mrkonjic Grad (GP).
- Commercial active clay Tonsil Standard 316 FF (KG).
- 20 % m/m solution of H_2SO_4 .
- 2 % m/m solution of $Ca(OH)_2$.

2.2. Methods of work

Experimental part of this paper represents a small part of performed researches of modification and application of different materials (bauxite, bentonite, white fillers, colloidal SiO_2) as adsorbents during refining of mineral alkaline oils [4]. In this paper, activation of domestic bentonite by sulfuric acid, characterization of natural and activated bentonite, and comparison with analyzed and available data of commercial active clay were done. Tests were performed at the Faculty of Technology Zvornik, Company „Alumina“ Zvornik and the laboratories of the Novi Sad Faculty of Technology.

2.2.1. Activation of natural bentonite

Activation of natural bentonite was performed under laboratory conditions and with the following selected parameters:

1. The concentration of sulfuric acid: 20% m/m.
2. The ratio between bentonite and acid is 1:5.
3. Temperature: 95 °C.
4. Activation time under intensive stirring: 3 hours.

The sample of natural bentonite before acid activation was thermally prepared (annealed for 3 h at 450°C). The mass of 400g thermally prepared natural bentonite was poured into a glass with 2000 g of previously prepared 20% sulfuric acid solution and then intensively stirred for 3 hours at the set temperature 95 ± 1 °C. After the activation, a Buchner funnel was used for filtration and then activated bentonite was flushed with 2% solution of $Ca(OH)_2$ (to remove excess sulfuric ions and neutralize pH value from 1–2 to 4–5). After filtration and flushing, activated bentonite was dried for 2 h at 110 °C, then ground in a mill and sifted through a sieve with aperture size of 160 μm and 100 μm .

2.2.2. Characterization of natural and activated bentonite

Characterization of natural and activated bentonite was performed using a number of test methods:

– The particle size distribution was determined by laser method MA.TS.03a with a Mikrosizer 201 S (VA INSTRUMENTS, Sankt Petersburg, Russia) at Company „Alumina“ Zvornik. Scanning was performed under the following conditions: measurement range of 0–300 μm , without US, and then with US power of 50 W, 100 W, 150 W and 200 W, treatment time 0–15 min at intervals of 30 s or 1 min.

– Determination of chemical composition of natural and activated bentonite was performed using various experimental techniques such as: gravimetric method (SiO_2), volumetric method (Fe_2O_3), potentiometric method (Al_2O_3), spectrophotometric method (TiO_2), atomic absorption spectrophotometric, and method ISO 6606 (determination of loss of mass at 1075°C).

– Phase identification of natural and activated bentonite and commercial active clay was performed by powder XRD method with automatic powder diffractometer PHILIPS PW-1710 (Netherlands) at Company „Alumina“ Zvornik. Scanning was performed under the following conditions: $CuK\alpha$ anticathode, voltage 40 kV, current 50 mA, width 5–60°, scanning rate of the counter 0.02°.

– Thermal Analysis of natural and activated bentonite (DTA, DTG, TG) was performed by „DERIVATOGRAPH“ (MOM Budapest Q1500 D, Hungary) at Company „Alumina“ Zvornik. Phase transformation temperature and loss of mass that occur during thermal activation were determined by these methods. Scanning was performed under the following conditions: inert material – Al_2O_3 , air, ceramic crucible, TG sensitivity 200 mg, heating rate of 15 °C/min, maximum time 130.0 min, maximum temperature 1000 °C, sample weight 500 mg.

– Texture characteristics of natural and activated bentonite were determined by the method of low temperature nitrogen adsorption with Micromeritics ASAP 2010 at the laboratory for physical chemistry and catalysis of the Novi Sad Faculty of Technology.

3. RESULTS AND DISCUSSION

Activation of natural bentonite with dilute sulfuric acid resulted in changes of particle sizes, chemical and phase content, and structural and textural

characteristics. The formation of unsaturated valence bond occurs during the process of activation, while a large part of OH⁻ ions are removed from lattice and the specific surface area increases during the transition of Al₂O₃ and other oxides in solution. Removing impurities, exchanging Ca²⁺ ions, that are bound on the surface of montmorillonite with H⁺ ions, and removing Al³⁺ ions from tetrahedral layers, and Fe³⁺, Fe²⁺, Mg²⁺ and Al³⁺ from octahedral layer, also occurs. The particle size distribution of natural and activated bentonite was determined by laser method (Figure 1). Based on the analysis of the given diagram as well as the particle diameter size d₁₀, d₅₀ and d₉₀, it can be concluded that consolidation or agglomeration of smaller particles occurs by activation of bentonite with sulfuric acid. The size d₅₀ of natural bentonite is 3,69 μm, and of activated bentonite 18,8 μm [4]. According to available data, we can conclude that the particles of commercial active clay KG have a slightly bigger diameter than the particles of activated bentonite.

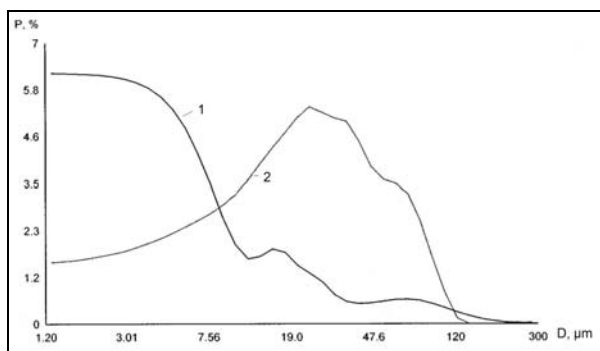


Figure 1. The partial size distribution: 1- natural bentonite (GP); 2- activated bentonite (AB)

Chemical compositions of natural and activated bentonite and commercial active clay Tonsil Standard 316 FF are given in Table 1, while Figure 2. shows a diagram which describes a share of oxides (SiO₂, Al₂O₃, Fe₂O₃).

Based on the results given in Table 1 and the diagram in Figure 2, we can conclude that the activation of bentonite with sulfuric acid has led to a decrease of share of Al₂O₃, Fe₂O₃, CaO and Na₂O, an increase in share of SiO₂, TiO₂ and a loss of mass by annealing (GŽ). A higher share of SiO₂ is registered in active clay (KG) and lower share of Al₂O₃ and Fe₂O₃ than in activated bentonite (GA). Also, the loss of mass by annealing in active clay is substantially lower than in the activated bentonite.

Figures 3-5 show diffractograms of natural (GP) and activated bentonite (GA), and commercial active clay (KG). Phase identification in test samples was performed using computer software that contains database with ASTM cards [18].

Table 1. Chemical composition of natural (GP) and activated bentonite (GA), and active clay (KG)

Component	GP	GA	KG
Al ₂ O ₃	23.72	18.14	15.20
Fe ₂ O ₃	6.80	4.40	4.10
SiO ₂	52.88	54.88	66.00
TiO ₂	0.83	0.86	–
CaO	1.83	0.12	1.70
Na ₂ O	0.02	0.00	0.60
K ₂ O	–	–	1.80
MgO	–	–	2.70
GŽ	12.62	18.97	7.20

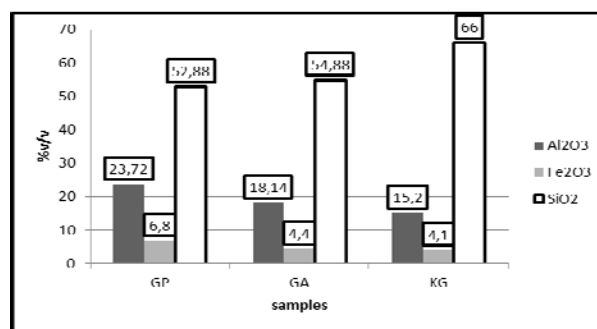


Figure 2. The share of some oxides in natural (GP) and activated bentonite (GA), and active clay (KG)

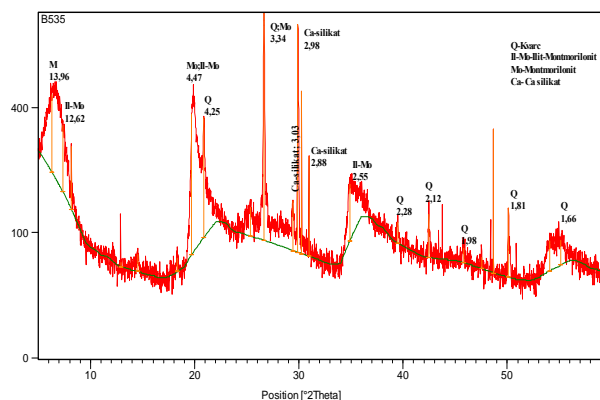


Figure 3. Diffractogram of natural bentonite (GP)

In the sample of natural bentonite (GP) the following phases were identified: quartz, mixture of illite-montmorillonite, montmorillonite, and calcium silicate by Rontgen diffraction analysis, using the following ASTM cards: 5-490, 12-219, 29-1495, 25-1456. By activation of bentonite the amount of calcium silicate decreased so that the residual amount could not be identified, and montmorillonite decreased, due to the exchange of metal ions with H⁺ ions in the structure of natural bentonite. More phases were identified on diffractogram of active clay (KG) compared to diffractogram of activated bentonite (BA), and by using ASTM cards: 5-490, 19-931, 20-572, 25-1349, 2-462, 24-72, the following phases were registered: quartz, muscovite, orthoclase, albite, clinoptilolite, illite and hematite.

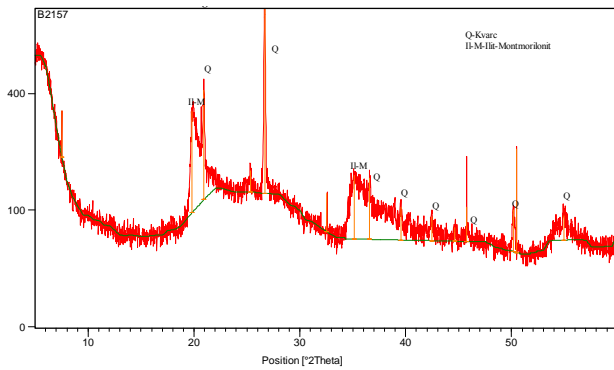


Figure 4. Diffractogram of activated bentonite (GA)

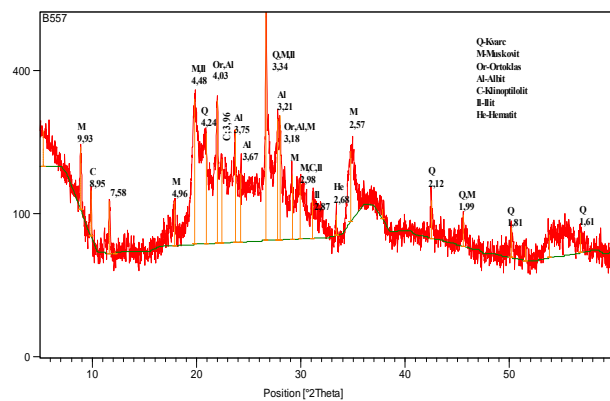


Figure 5. Diffractogram of active clay (KG)

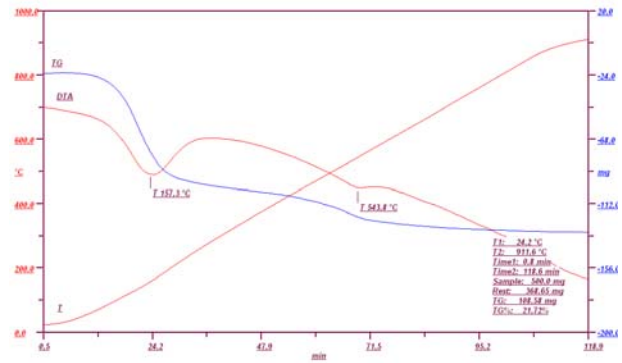


Figure 7. Thermogram of activated bentonite (GA)

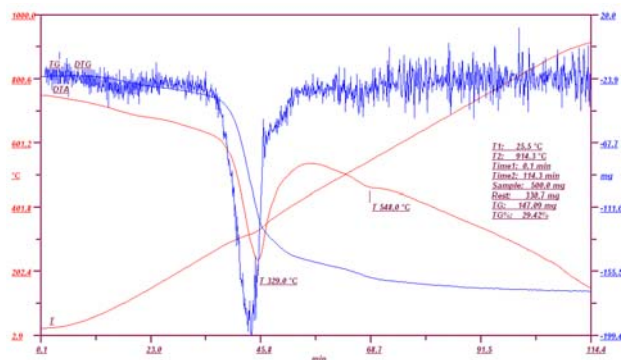


Figure 8. Thermogram of active clay (KG)

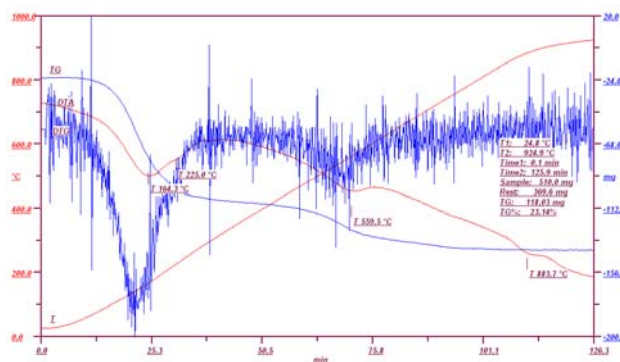


Figure 6. Thermogram of natural bentonite (GP)

Figures 6–8 show thermograms of natural (GP) and activated bentonite (GA), and commercial active clay (KG). Temperatures of phase transformation as well as the loss of mass of test samples were determined from presented thermograms [19].

The present phase in test samples was indentified by XRD method and confirmed by thermal analysis. The value of mass loss by annealing activated bentonite (GA), that was determined by this method is approximate to the value obtained by classical method. However, the loss of mass by annealing natural bentonite (GP) and active clay (KG), which is determined by thermal method is significantly higher compared to the value obtained by classical method.

Adsorption isotherms of natural (GP) and activated bentonite (GA) are presented in Figure 9. Adsorption isotherms are used to determine the type of adsorption, adsorption capacity, specific surface area and pore shape. Nitrogen on natural bentonite (GP) gives the adsorption isotherm type II according to IUPAC classification [20,21].

This isotherm is characteristic for non-porous and macro-porous solids and for substances with mixed micro and meso pores, and it is also characteristic of monolayer-multilayer adsorption. Adsorption isotherm on activated bentonite is of II b type, subtype of adsorption isotherm [22], which is given by porous solids with significantly large external surface area. Both adsorption isotherms of nitrogen (on both natural and activated bentonite) show hysteresis loop of type H3, according to IUPAC classification [20,21].

The appearance of the hysteresis loop is a consequence of mesoporous filling and emptying (diametar 2–50 nm) and macroporous (diametar > 50 nm) by capillary condensation and evaporation respectively. Hysteresis loop of type H3 is given by aggregates of plate particles or by porous solids, including cracks.

Some more important textural characteristics of natural (GP) and activated bentonite (GA) are given in Table 2.

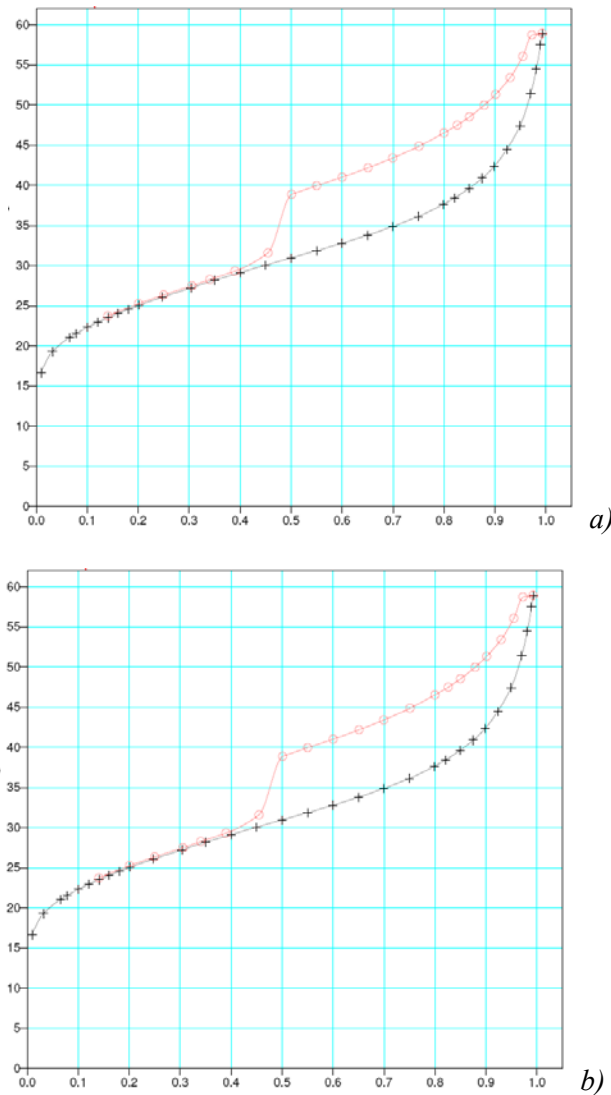


Figure 9. Adsorption isotherm of nitrogen at 77 K on natural (a) and activated bentonite (b)

Table 2. Textural characteristics of natural (GP) and activated bentonite (GA)

Characteristic	Samples of bentonite	
	GP	GA
Specific surface area, SP_{BET} , m^2/g	87.872	264.196
Constant, C_{BET}	1103.69	114.111
Microporous volume, $V_{\mu p}$, cm^3/g	0.012603	0.007489
External specific surface area, SP_{ext} , m^2/g	28.274	21.999
Microporous surface area, $S_{\mu p}$, m^2/g	59.597	242.196
Average porous diametar, d_p , nm	3.6210	5.8265

By analyzing the results it can be concluded that the activation of natural bentonite (GP) gave activated bentonite (GA) with significantly larger specific surface area, microporous surface area and the average porous diameter, with smaller external

specific surface area and microporous volume. Also, an increase in specific surface area influenced the increase in adsorption capacity by approximately 4.3 times.

The quantity of adsorbed nitrogen on activated bentonite (GA) is approximately $260 \text{ cm}^3/g$, and on natural bentonite (GP) is approximately $60 \text{ cm}^3/g$. The constant C_{BET} for adsorption of nitrogen on activated bentonite (GA) at 77 K usually has values ($C_{BET} \approx 80-150$), and on natural bentonite (GP) has a very high value (the strong interactions adsorbent-adsorbat, well defined monolayer and clearly expressed point B).

The microporous volume $V_{\mu p}$ and the microporous surface area $S_{\mu p}$ were determined by t-method, and for natural bentonite (GP) are $0.0126 \text{ cm}^3/g$ and $28.27 \text{ m}^2/g$ respectively, and for activated bentonite (GA) $0.0075 \text{ cm}^3/g$ and $21.99 \text{ m}^2/g$, respectively. Acid activation led to a decrease of volume and microporous surface area (by 1.68 times and 22.2 %), and an increase in porous size (the average porous diametar of natural bentonite is 3.6210 nm, and of activated bentonite 5.8265 nm) which means that mesoporous character of bentonite increased.

External specific surface area SP_{ext} was determined by t-method, for natural bentonite it is $59.60 \text{ m}^2/g$ ($\approx 68\%$ of total surface area), and for activated bentonite $242.20 \text{ m}^2/g$ ($\approx 92\%$ of total surface area). Both samples of activated bentonite are predominantly mesoporous, whereas the obtained experimental results of nitrogen adsorption at 77 K indicate that they contain a part of larger, as well as smaller micropores, too.

4. CONCLUSION

Based on the performed experimental tests it can be concluded:

- The parameters for acid activation of tested bentonite were selected on the basis of previously performed researches.

- Activation of bentonite with dilute H_2SO_4 leads to certain changes in chemical composition, structural and textural characteristics, and adsorption capacity.

- There is a decrease in a share of Al_2O_3 and increase in share of other components (Fe_2O_3 , SiO_2 , TiO_2 and CaO), as well as an increase in particle diametar, i.e. formation of particles with larger diametar.

- The phase composition of natural (GP) and activated bentonite (GA): montmorillonite, illite, quartz, calcium silicate and commercial active clay:

quartz, muscovite, orthoclase, albite, clinoptilolite, hematite and illite was determined by XRD, DTA, DTG and TG method.

– Natural bentonite (GP) gives type II adsorption isotherms (non-porous and macro-porous substances), while activated bentonite (GA) gives type IIb adsorption isotherms (porous solids with a large external surface area). Both adsorption isotherms show a hysteresis loop type H3, for porous solids including cracks.

– Activated bentonite (GA) has significantly larger specific surface area (3 times), smaller micro-pore volume and surface area, and slightly larger pores compared to the natural bentonite pores (GP).

– The activation process has led to a slight decline of mesoporous character, and an increase in microporous character.

– Adsorption capacity of nitrogen on activated bentonite (GA) is 4.3 times higher compared to adsorption capacity of natural bentonite (GP).

– A specific surface area of activated bentonite (GA) is significantly larger than the specific surface area of active clay (KG), which is used at the local refinery mineral oils and in the production of edible oils.

– Activated bentonite with very good textural characteristics was derived by using selected parameters for activation of natural bentonite from Gerzovo.

– Obtained structural and textural characteristics of activated bentonite (GA) are an assumption of good adsorption characteristics in the processing of mineral alkali oils and decolorization of edible oils, as an alternative to imported commercial active clay (KG).

– The obtained results indicate a need for continuous research of natural bentonite (GA), as an adsorption agent in various adsorption processes, as well as in the process of activation with other parameters.

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САСТАВ, СТРУКТУРА И КАРАКТЕРИСТИКЕ ТЕКСТУРЕ КИСЕЛИНОМ АКТИВИРАНОГ ДОМАЋЕГ БЕНТОНИТА

Сажетак: Бентонити су алумосиликатни минерали који због своје порозности, слојевите структуре и састава имају широку примјену. У производњи минералних и јестивих уља, бентонит се као адсорбент, примјењује у процесима рафинације и бијељења. Карактеристике структуре и текстуре бентонита могу се побољшати различитим поступцима модификације. Циљ овог рада је био испитивање састава, структуре и карактеристика текстуре домаћег бентонита са лежишта Герзово, прије и после активације сумпорном киселином. Наведене карактеристике испитиване су аналитичким методама, методом рендгенске дифракције (XRD) и методом нискотемпературне адсорпције азотом (ВЕТ). Карактеристике киселином активираниог бентонита упоређиване су са карактеристикама комерцијалне активне глинне. Резултати истраживања су показали да активација бентонита сумпорном киселином доводи до знатног побољшања карактеристика структуре и текстуре, на основу којих се може претпоставити да ће исти имати добре адсорпционе карактеристике, те да може послужити као алтернатива за увозне комерцијалне адсорбенте на бази алумосиликата.

Кључне ријечи: бентонит, активација киселином, састав, карактеристике структуре и текстуре.

