



The Influence of Acid Activation on Surface Characteristics of Natural Bentonite

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Bentonite clay is a valuable material in various process industries, thanks to its specific properties. Easy availability, low cost and their effectiveness are the main factors that have made bentonite adsorbent in the edible oil industry. The textural characteristics of bentonite clay play an important role in its performance. In its natural form, as an aluminosilicate material, bentonite does not show satisfactory sorption and catalytic properties, and it needs to be activated. The main goal of this research is to increase the adsorption capacity of bentonite clay by modifying its properties by treatment with organic acid. Activation of bentonite clay in the experimental part was performed with different concentrations of sulfuric acid. The chemical composition of the natural bentonite sample

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was determined using XRF alongside the influence of acid activation of bentonite with H₂SO₄ on the surface characteristics (such as specific surface area, pore volume and average pore diameter, adsorption capacity and isotherm type) of bentonite clay. The XRF analysis of the natural bentonite, which contains 56.35% SiO₂ and 19.82% Al₂O₃ as its primary components, confirms that it is an aluminosilicate material. Except for SiO₂, which recorded a consistent increase in quantity from 56.35% to 74.15% with increasing acid concentration, the composition of other components, after activation slightly decreased or remained the same.

The acid concentration that yielded the highest increase in specific surface area, as measured by the Brunauer–Emmett–Teller (BET) method, was selected as the optimal concentration for activating bentonite. The specific surface area almost tripled (from 95.519 m²/g to 346.467 m²/g) by activation with 15% sulfuric acid, with an activation time of 3 hours and a bentonite: acid ratio of 1:5. The research results show the effectiveness of acid modification in terms of improving the characteristics of the porous structure of bentonite samples.

Keywords: Acid activation; adsorption capacity; bentonite clay; specific surface area.

1. INTRODUCTION

Bentonite is an aluminosilicate clay composed of colloidal and plastic clays, mainly from the mineral montmorillonite. In addition to montmorillonite, bentonite also contains feldspar, biotite, kaolinite, illite, pyroxene, zircon and crystalline quartz. The industrial term and industrial material are important. It consists of several minerals, and therefore does not have a chemical formula. The dominant mineral of bentonite is montmorillonite and makes up at least 70% of its composition. Montmorillonite belongs to the smectite group. The chemical formula is: (Mg, Al)₂ [(OH)₂Si₄O₁₀](Na,Ca)_x·nH₂O.

Chemical nature of the surface and textural properties of bentonite (specific surface area, total pore volume, pore volume distribution by pore diameters and porosity) determine its sorption properties and they have crucial influence on selectivity and the speed of adsorption. Also the studies show that the raw material influences the process parameters, and it is dependent of factors such as temperature, reaction time and adsorbent dosage [1].

In terms of industrial use, there are two main classes: sodium bentonite and calcium bentonite. They were named after the dominant chemical element. The specific properties of bentonite clay have made them a valuable material in various process industries. Easy availability, low price and their effectiveness are the main factors that made this clay an adsorbent in the edible oil industry. The textural characteristics of bentonite clay play an important role in its performance. In its natural form, as an aluminosilicates, bentonite does not show satisfactory sorption and catalytic properties, so it needs to be activated.

By activating bentonite, a porous material is obtained which, compared to the starting raw clay, has two to four times better sorption properties and greater catalytic activity. Activation usually takes place using mineral acids. The textural properties of activated bentonites (specific surface area, total pore volume, pore volume distribution by their diameters) determine their sorption properties and have a decisive influence on the selectivity and speed of adsorption [2-5]. The specific surface area is a control parameter in the adsorption process, but the maximum specific surface area is not always followed by the maximum degree of removal of impurities [6]. Bentonite clay has found application as a bleaching agent and additive in the food industry, as a component in cements, ceramics, paper, paints and pigments, and as an ion exchange agent, adsorbent and catalyst [7]. Therefore, the aim of this paper was:

- determine the chemical composition of a sample of natural bentonite using XRF
- determine the influence of acid activation of bentonite with H₂SO₄ on the surface characteristics (specific surface area, pore volume and average pore diameter, adsorption capacity and isotherm type) of bentonite clay.

2. MATERIALS AND METHODS

Samples of ground natural clay from the "Šipovo" site were used for experimental research, the preparation of which was realized in industrial conditions in the production facility of the company Bentoproduct doo, Šipovo. Activation of natural bentonite with diluted sulfuric acid, in order to determine the optimal acid

Table 1. Methods used for physical-chemical characterization of bentonite

| Parameters | Methods |
|--|--|
| Adjusting and measuring the pH value | Potentiometric method using a pH-meter with a combined electrode brand Mettler Toledo 220. |
| Chemical composition (%) | X-ray fluorescence analysis (XRF), (BAS EN 15309:2010) Bruker S8 Tiger. |
| Moisture content | Drying method (105°C, time 3 hours) |
| Surface area (m ² g ⁻¹) | Brunauer–Emmett–Teller (BET) method. Calculation of the specific surface area of the sample by the integrated software was carried out using the standard Brunauer-Emmett-Teller (BET) equation. |

concentration, it was performed with the following parameters:

- Concentration of sulfuric acid: 15%, 20% and 25% m/m
- Bentonite:acid ratio = 1:5,
- Activation temperature: room temperature,
- contact time with intense mixing: 3 hours.

Table 1 shows methods of bentonite characterization.

After the activation of bentonite, the optimal concentration of sulfuric acid was chosen based on the highest value of the BET surface area.

Before acid activation, a sample of natural bentonite was annealed for three hours at a temperature of 450°C. 100 g of thermally prepared natural bentonite was weighed on an analytical balance, and added to a beaker with 500 g of a sulfuric acid solution of a given concentration and intensively mixed for three hours at a temperature of $98 \pm 1^\circ\text{C}$. The ratio of bentonite to acid in these activation samples was 1:5. After the activation was completed, filtration was performed on a Büchner funnel, and the activated bentonite was washed with distilled water and a 2% solution of $\text{Ca}(\text{OH})_2$ (in order to remove excess sulfate ions) and neutralized to a pH value of 4-5.

After filtration and washing, the activated bentonite was dried for 3 h at a temperature of 105°C. After that, the dried activated bentonite was ground in a mill and sieved through sieves with openings of 160 µm and 100 µm.

3. RESULTS AND DISCUSSION

Physical characteristics of the bentonite used:

- raw bentonite moisture (105 °C) = 10%
- montmorillonite content = 90%

- residue on sieve (0.063mm) = 27.7%

pH, density and viscosity have a significant influence on suspensions. The pH of the suspension can modify the surface charge of the particles, which in turn affects the viscosity of the suspension and the resulting properties of the granules. pH cannot determine the way of bonding between bentonite particles, but it can affect the rheological behavior that determines particle interactions. Assessment of bentonite pH value is important to define the nature of raw untreated bentonite. The typical pH of Ca-bentonite suspension varies from 7 to 8, in contrast to Na-bentonite suspension whose pH varies from 9 to 10 [7]. To determine the pH value of the suspension, 5 g of bentonite was suspended in 50 ml of distilled water and occasionally stirred in a closed PVC container for 72 hours, after which the pH value of the prepared suspension of unactivated bentonite was measured.

In the laboratory of the Faculty of Technology in Tuzla, the pH value of 10% bentonite suspension, unactivated bentonite, was determined, which was 9.26, which indicates that it is Na-bentonite.

Table 2 shows the results of chemical analysis of bentonite samples before and after acid activation. The results (SiO_2 -56.35% and Al_2O_3 (19.82%)) show that it is an aluminosilicate material. Smaller amounts of oxides such as Fe_2O_3 , Na_2O , CaO , MgO , K_2O are also present (Table 2).

Except for SiO_2 , which recorded a consistent increase in quantity from 56.35 % to 74.15% with increasing acid concentration, the composition of the other components, after activation, slightly decreased or remained the same. Residual Ca^{2+} , Na^+ and K^+ are caused by the presence of impurities such as mica and feldspar, which are

insoluble in an acidic environment. The increase in the content of SiO₂ and the decrease in others is in accordance with the results published by Usman et al., (2012) and Arfaoui et al., (2008) which indicated the partial destruction of the octahedral form by the dissolution of exchangeable cations.

Determination of moisture content was done using the method of drying in a dryer. A 1.0 g sample of activated bentonite (m₁) was weighed on an analytical balance and dried for 2 hours in an oven at a temperature of 105–110 °C. After cooling in a desiccator, a measurement was made and the mass of the dried sample (m₂) was calculated. The moisture content is determined based on equation 1 and is expressed in percentages:

$$W = \frac{m_1 - m_2}{m_1} \cdot 100\% \quad (1)$$

where: m₁ - sample mass before drying (g), m₂ - sample mass after drying (g), W- moisture content in the sample (%).

Results shown in Table 3. have shown that initially with increasing acid concentration, the moisture content also increased, i.e. the capacity of bentonite to retain water. After that, the moisture content decreased as the acid concentration further increased. This can be attributed to the increase in vacancies that have been created, as the exchangeable metal ions have been displaced by hydrogen ions that have a smaller volume than the metal ions. Bentonite and other clay minerals strongly adsorb polar water molecules.

The BET method was used too determination of adsorption capacity, specific surface area, isotherm type, pore volume and average pore diameter by low-temperature nitrogen adsorption, on the device Micromeritics ASAP 2010.

Table 2. Results of XRF analysis expressed as oxides (%)

| Compounds | A sample of bentonite | | | |
|--------------------------------|-----------------------|--------|--------|--------|
| | NB | AB 15% | AB 20% | AB 25% |
| SiO ₂ | 56.35 | 67.45 | 71.25 | 74.15 |
| Al ₂ O ₃ | 19.82 | 14.36 | 9.47 | 7.36 |
| Fe ₂ O ₃ | 5.01 | 2.89 | 1.83 | 1.57 |
| TiO ₂ | 0.99 | 0.55 | 0.49 | 0.65 |
| CaO | 3.18 | 2.77 | 0.89 | 0.55 |
| MgO | 3.34 | 1.12 | 0.60 | 0.74 |
| At ₂ O | 0.52 | 0.45 | 0.42 | 0.51 |
| K ₂ O | 0.12 | 0.19 | 0.36 | 0.37 |

Where: NB - unactivated bentonite, AB15% - bentonite activated with H₂SO₄ at 15 ratio, AB120% - bentonite activated with H₂SO₄ at 20 ratio, AB25% - bentonite activated with H₂SO₄ at 25 ratio

Table 3. Values of moisture content in samples of activated and non-activated bentonite

| Drying time 2h Drying temperature 105° -110° C | |
|---|----------------------|
| A sample of bentonite | Moisture content (%) |
| NB | 0.1059 |
| AB 15 % H ₂ SO ₄ | 0.1904 |
| AB 20 % H ₂ SO ₄ | 0.5127 |
| AB 25 % H ₂ SO ₄ | 0.1495 |

Table 4. Textural characteristics of unactivated and activated bentonite samples

| Textural characteristics | A sample of bentonite | | | |
|---|-----------------------|---------|---------|--------|
| | NB | AB15% | AB20% | AB 25% |
| Specific surface SP _{BET} , m ² /g | 95.519 | 346.467 | 309.889 | 315.16 |
| Constant, C _{BET} | 1397.315 | 109.560 | 106.228 | 114.37 |
| Volume of micropores V _{μp} , cm ³ /g | 0.0149 | 0.0068 | 0.00526 | 0.0082 |
| Micropore surface S _{μp} , m ² /g | 33.482 | 22.124 | 18.136 | 24.43 |
| External specific surface SP _{ext} , m ² /g | 62.036 | 324.343 | 291.752 | 290.7 |
| Average pore diameter d _p , nm | 3.434 | 4.219 | 4.9312 | 5.9771 |

The Brunauer-Emet-Teller (BET) equation is the most commonly used model for determining the specific surface area of porous materials [8]. Table 4 shows the values of the textural characteristics of all activated bentonite samples (AB 15%, AB 20% and AB 25%) as well as the non-activated bentonite sample.

Figs. 1, 2, 3 and 4 show the adsorption isotherms of the non-activated bentonite sample NB and the activated bentonite samples AB 15%, AB 20% and AB 25%.

All samples show type IV isotherms, which indicates single-layer - multilayer adsorption. Before the loop, the sample behaves as a type II isotherm. Therefore, it has an inflection point that represents a clear transition from monolayer to multilayer adsorption. Similar results were obtained in other similar studies [9]. This characterizes mesoporous materials with an H3-type hysteresis loop, which is associated with the appearance of pore condensation and limited adsorption in a certain range of high pressures and indicates the formation of aggregates of

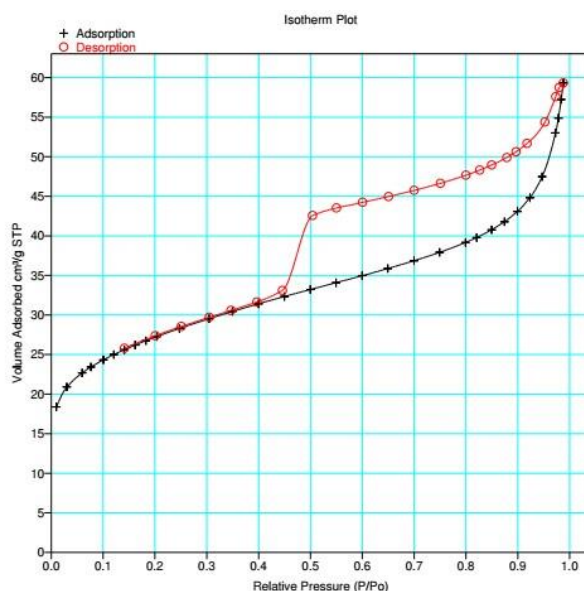


Fig. 1. Adsorption isotherm of unactivated bentonite NB

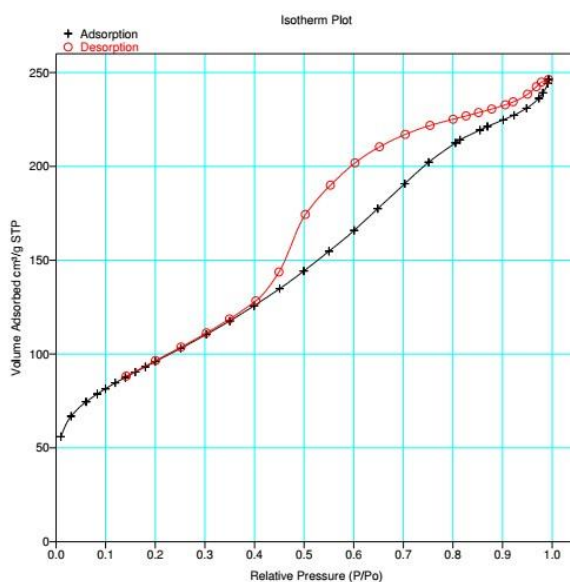


Fig. 2. Adsorption isotherm of activated bentonite AB 15%

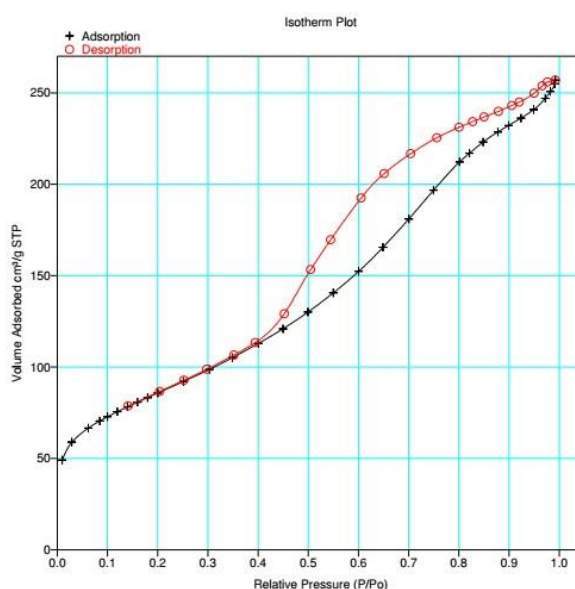


Fig. 3. Adsorption isotherm of activated bentonite AB 20%

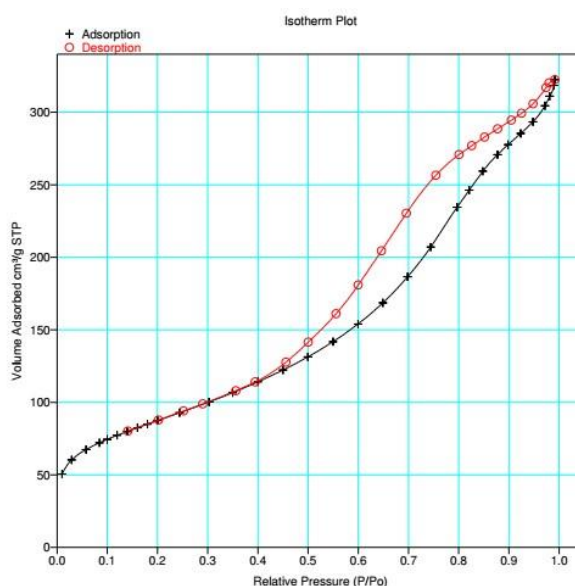


Fig. 4. Adsorption isotherm of activated bentonite AB 25%

plate particles or porous solids, including cracks [10]. The results of the analysis shown in Table 1 show that the highest value of the specific surface area ($SP_{BET} = 346.4676 \text{ m}^2/\text{g}$) was obtained for the sample that was activated with 15% sulfuric acid. Acid treatment of bentonite causes replacement of exchangeable cations with H^+ ions, resulting in increased surface acidity and leaching of Al and other cations from octahedral and tetrahedral sheets to a certain extent resulting in significant destruction of SiO_4 groups.

The most important physical change in activated clays in general, and also in the examined bentonite, by removing the desired part of octahedral cations, is the development of new pores and an increase in porosity, which leads to a significant increase in surface area with increased surface acidity. As expected, metal leaching by formation of charged surfaces almost tripled the specific surface area value, with the largest increase recorded by activation with 15% sulfuric acid. The removal of soluble constituents increased the specific surface area of the clay by creating pores. In contrast to the specific surface

area value, which increased with increasing acid concentration, the pore size decreased. According to the above mentioned, bentonite activated with 15% acid had the smallest pore size value, 4.219 nm. During the activation of clay with acid, the clay is reduced to a fine powder state, and the reduction in particle size also increases the reactivity of the bentonite powder.

The acid concentration for which the largest increase in the specific surface was determined was chosen as the optimal value for bentonite activation.

4. CONCLUSION

By acid activation of untreated bentonite from Šipovo (BiH) the specific surface is almost tripled (from 95.519 m²/year at 346.467m²/g) by activation with 15% sulfuric acid.

The dimensional characteristics of the pores of the untreated bentonite (NB) sample changed slightly after activation and their average size increased. This indicates additional pore formation in the interfibrillar regions during acid activation.

The research results show the effectiveness of acid modification in terms of improving the characteristics of the porous structure of the samples.

Acid activation of bentonite is a simple and economically acceptable method, which aims to lead to partial dissolution of the material and thereby increase crystallinity, surface acidity, specific surface area, porosity and pore volume.

An increase in the specific surface area improves the adsorption capacity of metal impurities, phosphatides and coloring substances.

Using the BET method, based on changes in the textural characteristics of the analyzed samples of activated bentonite, it was determined that the optimal concentration of sulfuric acid for bentonite activation is 15%, with a duration of 3 hours and a bentonite:acid ratio of 1:5.

The obtained results are in accordance with the results of other researchers who were involved in testing the effectiveness of bentonite as an adsorbent for oil bleaching. The mineralogical and physicochemical characteristics of bentonites and other clays vary significantly

depending on the acid as well as alkali treatments [11-14].

Optimizing the clarification of vegetable oil with bentonite as a natural resource is of great interest to the oil production industry.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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