

Sorption Material Based on Modified Bentonite for Water Filtering Systems

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Abstract – Adsorption methods are among the most promising water treatment approaches of today. Application of clay materials as sorption agents for surface and waste water treatment are of particular interest. The object of current study is bentonite mainly containing montmorillonite. The micro- and meso-porosity of bentonite can be increased by introduction of pillars into the interlayer structure of aluminosilicates. The work describes a technology for bentonite gel production by modification of bentonite by glycerol. The elemental composition of bentonite was investigated by electronic microscopy of the specimen surface. The analysis of electronic microphotographs of the side face and side surface of the granules of annealed modified bentonite specimen and results of electronic microscopy have shown that bentonite granules during annealing are modified by pyrolysis carbon produced after decomposition of glycerol in oxygen-free atmosphere. It was established that bentonite modified by glycerol has four times larger specific surface area as compared with non-modified bentonite.

Keywords – *montmorillonite; bentonite; adsorption; bentonite gel; interlayer space; platelet; silicate layer; granule specific surface.*

I. INTRODUCTION

Contemporary challenges of industrial ecology in the sphere of purification of polluted natural and waste water necessitate the elaboration of approaches to improve technologies for water purification from various high-priority pollutants.

Wastewater treatment is performed by mechanical, chemical, physicochemical and biological methods. When the enumerated methods are applied cumulatively, such method of water purification and disinfection is called combined method. Adsorption methods possess a number of advantages over existing ways of water treatment. The main strong points of these methods include simple technical implementation, possibility to extract many pollutants from water (heavy metals, surfactants, aromatics, etc.), even biologically resistant ones that cannot be removed by other methods. A significant advantage of adsorption methods in the absence of secondary pollution [1].

Adsorption at the interface of two media (solid body-liquid) is spontaneous concentration of a dissolved substance in the vicinity of adsorbent surface. More dense phase is referred to as adsorbent, while the substance which molecules are adsorbed is referred to as adsorptive. The substance that is formed after adsorption is called adsorbate.

The nature of adsorption forces promotes one of two adsorptions: physical or chemical one. The sorption purification is based on the capability of pollutants to interact with extended surface of the sorbent due to physical forces (physical adsorption) and due to chemical interaction (chemisorption) [2].

The adsorption purification of water involves a variety of natural and artificial materials. The most widely used and known among them is activated carbon. However, increasing interest in this sphere is drawn by non-carbon materials (clay rocks, zeolites and other), which is conditioned by their rather high efficacy, relatively low cost and high availability, especially as a locally excavated material [1]. A sorption material can be also represented by silicagel, peat, coke fines, ash, saw dust and other [3].

In recent time, the promising application of clay materials as sorption agents for surface and waste water treatment has been of particular interest. Clay rocks are polymineral formations consisting of various minerals, most frequently silicates [4]. A particular specificity of these rocks is the presence of clay minerals in their composition that have specific structure and properties [4]. As a rule, they have high ion exchange capacity. A particular group of minerals, such as montmorillonite, that have expandable crystal lattice should be particularly noted. During interaction of montmorillonite with water, the water molecule can penetrate layers of its crystal lattice and appreciably extend them. The denoted specifics of the clay minerals enable their high adsorption capacity [3].

Clay minerals considered as natural sorption materials have a number of advantages as compared with synthetic and ion-exchange materials. Such advantages include resistance to high temperature, intense radiation and oxidative environment [5–6].

Clay materials are fairly cheap and frequently occurring in nature. However, the application of natural clay materials as adsorbents for water purification, one should solve the problem of its granulation. This work is devoted to the solution of this problem.

II. METHODS AND MATERIALS

The object of study is bentonite mainly containing montmorillonite. Montmorillonite is finely dispersed natural mineral of white, pinkish or greenish color which belongs to the group of smectites. This natural sorption material has high exchange capacity reaching 1.5 mg-equiv./g [5]. Ideal smectites are dioctahedral ones with the following crystallochemical formula: $\text{Si}_8\text{Al}_4\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$, which corresponds to the following average chemical composition: 66.7% SiO_2 ; 28.3% Al_2O_3 ; 5% H_2O . Interestingly, natural montmorillonite composition most often differs from that theoretically established. The reason is that the tetrahedral grid of the natural mineral includes isomorphic substitution of silicon for aluminium; the octahedral layer also has substitutions of aluminium for iron, magnesium and lithium [7].

The identification of the adsorption properties, specific surface in particular, of bentonite clays with large content of montmorillonite required studying their specificity and structure. The elemental composition of bentonite was investigated by an energy dispersive spectrometer.

The morphology of sorption material surface was studied by a scanning electron microscope TESCAN MIRA II LMU. The principle of such microscopy method is in scanning of the specimen surface by a focused beam and analysis of particles reflected from the surface and X-ray radiation caused by electrons interacting with the substance. This allows obtaining images of the object's surface with high spacial resolution (up to several nanometers). During the study, the specimens were strongly charged, so to drain the charge, 10-nm gold sputtering was used.

Montmorillonites are clay materials. The shape of their minerals is imperfect. The structure of montmorillonite crystals is similar to that of pyrophyllite and talc. It differs in irregular arrangement of layers (Fig. 1). Between talc-like silicate layers, water molecules are distributed. Besides water, between the silicate layers in the structure of montmorillonite present positively charged exchange cations [4].

The layers in the montmorillonite structure are disorderly arranged above each other. The content of magnesium in montmorillonite varies from 1 to 2/3 of Mg atom per layer in elementary cell (containing four ions in hexad coordination). The octahedral positions in the scheme are orderly populated. Their true distribution can be less ordered.

The size of cations in octahedral positions of the silicate skeleton varies from 4.00 to 4.44 Å and from 5.76 to 6.00 Å. Thus, naturally occurring are two types of montmorillonite: dioctahedral corresponding to pyrophyllite and trioctahedral corresponding to talc [8].

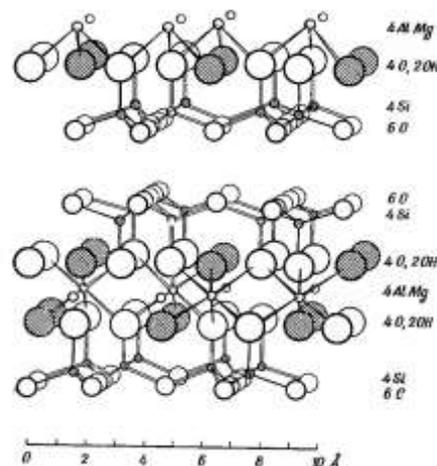


Fig. 1. Montmorillonite structure in the plane along axis a.

The silicate layer has some negative charge, if octahedral aluminium in its composition is partially substituted by magnesium or iron (II), while silicon, to some extent is substituted by aluminium. In this case, positive cations located between the mineral layers neutralize the negative charge.

Consecutive analysis of montmorillonite hydration stages confirms that between the silicate layers 0, 1, 2, 3 or 4 layers of water molecules can be arranged.

The structural layers of montmorillonite are connected with each other by molecular forces and cations that are arranged in the interlayer space. However, this bond is not enough for resistance to hydration in the interlayer space, which leads to intracrystalline swelling of montmorillonite structure. The intracrystalline swelling promotes the appreciable change to the interplane distance in the montmorillonite structure that depends on the composition and moisture of the interlayer complex. For instance, air-dry state of Ba^{2+} , Na^{+} and Li^{+} -forms of montmorillonite demonstrates interplane distances close to 12.4 Å, while those of Ca^{2+} and Mg^{2+} -forms are close to 15.5 Å. The structural layers of montmorillonite have overlaps without definite periodicity in the direction of plane axes, a and b. A monoclinic structure is formed with the parameters of elementary cell depending on the hydration degree and chemical composition of the interlayer space [9].

The electron microscopy of montmorillonite specimens most frequently demonstrates not separate particles of the mineral, but ultramicro-aggregates and micro-aggregates of its particles which morphology and size usually depend on the composition of exchange cations. For example, montmorillonites with sodium cation on the micro-photographs are imaged as solid gray background of different density with slight contours of separate particles. The dimensions of primary particles in this case does not exceed 30 nm. Montmorillonites with calcium cation in the exchange complex on the microphotographs demonstrate large dense micro-aggregates of various configuration, usually with distinct contours. The specific surface of a montmorillonite is extremely large: it usually amounts to 700–840 m^2/g . However, the value of the specific surface of external edges of crystals amounts to 50–120 m^2/g . The formation of residual surface of the crystals occurs

owing to intracrystalline planes that can be wetted by water and other polar liquids [10].

Chemical, structural and mechanical properties of bentonites and peculiarities of its structure mainly depend on the degree of crystalline structure order, number of substituted cations in the layer and character of the interlayer complex [11]. A particular role in the exhibition of properties is played by the nature of exchange cations.

An important property of bentonite clays is their ability of self-dispergation. The process of dispergation leads to manifestation of some incomplete structural elements. These structural elements can be represented as a variant of nanoparticles or a peculiar kind of platelet. The width and length of elementary platelets can vary from several dozens to several hundreds of nanometers, while their thickness can reach 1–1.5 nm. The thickness depends on the number of adsorbed water molecules. Elementary platelets have negative charge which value depends on isomorphous substitutions in octahedral and tetrahedral layers of the mineral. The neutralization of the negative platelet charge occurs during exchange by cations with one or two same-name layers of water located in the interlayer space between elementary platelets.

The groups of elementary platelets form a clay particle. After submersion of these particles in water, the water penetrates the interlayer space, which leads to swelling of the clay particles. Thus, with the help of water clay particles comprised of a number of differently oriented elementary platelets transform into water suspension.

Bentonites, similarly to other clays, are represented by three-component systems comprised of mineral skeleton, air and water. The mineral particles of bentonites take only part of the volume (55–68%), the rest of the volume is taken by pores filled with water and small amount of air (2%).

The micro- and meso-porosity of bentonite can be increased by introduction of pillars into the interlayer structure of aluminosilicates. The obtained complexes can be classified into three main types:

1. Complexes with water and inorganic cations. They are specific for the influence of cations on the interlayer distance and presence of mixed structures.
2. Complexes with large organic cations. They are characterized by large interplane distances that do not depend on the water content.
3. Complexes with organic molecules. They are characterized by the perfection of the structure, and that is why the complexes with polyatomic alcohols are used to identify montmorillonites.

In current work, the third variant of complex production with the use of glycerol was chosen. The choice was conditioned by the environmental friendliness and inexpensiveness of implemented organic substance. The concentration of the organic reagent was from 2 to 15 vol.% of water solution.

The production of bentonite gel was performed as follows.

The quality of product milling by the producer was checked. If necessary, the initial batch of bentonite was subjected to milling in a ball mill to obtain particles of no larger than 50 μm . A lightly alkaline water-glycerol solution was prepared. Under intense mixing, bentonite was added into the solution. The rate of powder pouring was not high and determined by the geometrical parameters of the reactor, intensity of mixing and temperature of the solution. To prepare the uniform gel with increased content of bentonite, the suspension after the mixing in the reactor was processed in an ultrasound reactor (Fig. 2). Ultrasound intensifies the dispergation of swollen bentonite particles in the solution, which appreciably reduces the time of gel formation.

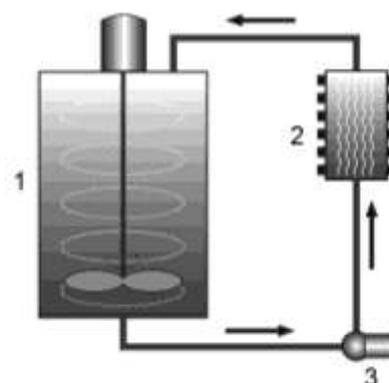


Fig. 2. Scheme of testbed for bentonite gel production: 1) vessel with mixer, 2) ultrasound reactor; 3) pump.

To form granules, the bentonite gel was dried up to preset moisture (15–30%). The granules were extruded. The cylindrical granules were of 0.5–2 mm in diameter and no more than 2 mm in height. The annealing temperature was 550–600 °C.

The granulated non-modified (a) and modified by glycerol (b) bentonites are shown in Fig. 3.



Fig. 3. Bentonite granules: a) non-modified; b) modified by glycerol.

The surface of granulated non-modified and modified bentonite was studied by the method of low-temperature adsorption of nitrogen on a Quantachrome NOVA 4200e gas sorption analyzer.

III. RESULTS

During the investigation of the morphology of natural bentonite by microscopy, the specimens demonstrated the formation of montmorillonite, round quartz grains, micaceous

fragments, residues of siliceous skeleton of microorganisms (single specules of sponges), fragments of opal in the form of diatoms of poor preservation. On electronic microphotographs of bentonite (Figs. 4–5), the particles of montmorillonite are represented by large and small scales in the form of leaf aggregates. There are aggregates with flake-like contours and folded formations. There are particles with different shape and size combined into ultramicro-aggregates and aggregates with poorly and highly-oriented into micro-blocks arrangement. In line with the type bound with composition and formation conditions, as per the classification of E.M. Sergeev [12], the microstructure of studied specimens relates to cellated one that is characterized by the formation of large micro-aggregates contacting with each other in terms of basis-basis and basis-chip. The types of pores are as follows: interparticular formed by the sparsity between initial particles; inter-microaggregate, mostly slit-shaped with various size.

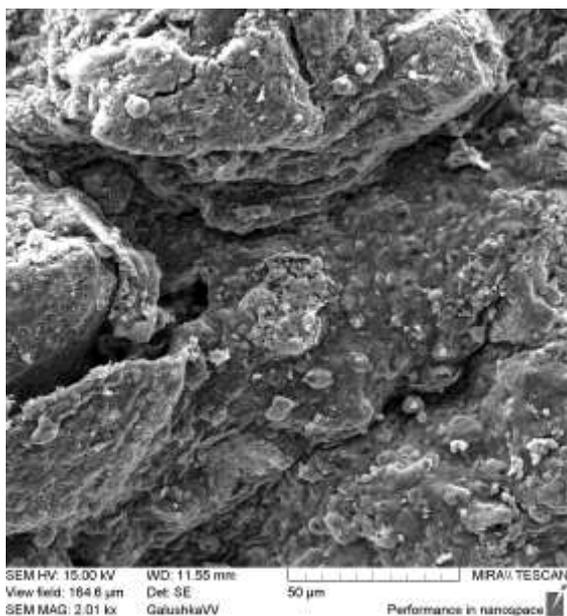


Fig. 4. Magnification – 2kx. Bentonite surface

The elemental composition of the specimens was studied using an energy dispersive spectrometry of bentonite granules, which allowed getting into the mechanism of sorption material formation in more details.

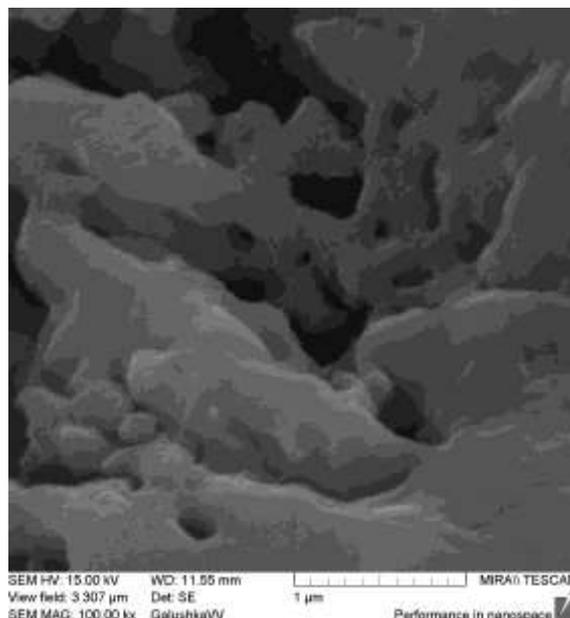


Fig. 5. Magnification – 100kx. Bentonite surface

The electronic microphotographs of the side face and side surface of the granule of annealed specimen of modified bentonite are presented in Figs. 6 and 7, respectively. Point 1–9 denote the locations where elementary analysis was performed. The results of the elementary analysis are presented in Tables 1 and 2.

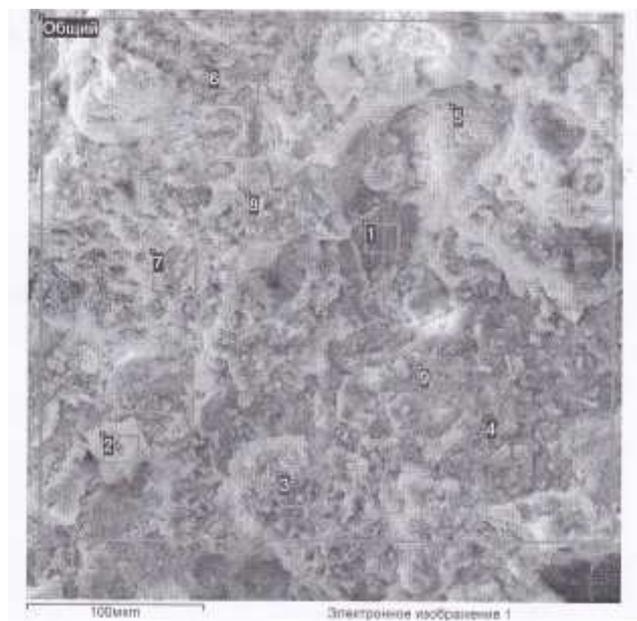


Fig. 6. Electronic microphotograph of the side face of annealed granule.



Fig. 7. Electronic microphotograph of the side surface of annealed granule.

IV. CONCLUSION

The developed method of bentonite modification allows easy-to-use sorption material for adsorption filtering systems used in water treatment stations.

The investigation results confirmed that the bentonite granules during the annealing are modified by pyrolysis carbon formed after decomposition of glycerol in oxygen-free environment. The granules have the specific surface area of 96.7 m²/g, which considerably exceeds that of granules from non-modified bentonite (29.8 m²/g).

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TABLE I. ELEMENTARY ANALYSIS OF POINTS ON THE GRANULE SIDE FACE

| Point | C | O | Na | Mg | Al | Si | S | K | Ca | Ti | Fe | Σ |
|-------|-------|-------|------|------|------|-------|------|------|------|------|-------|-----|
| 1 | 18.55 | 52.16 | | 1.23 | 4.44 | 14.86 | | | 3.42 | | 5.33 | 100 |
| 2 | 7 | 34.48 | | 2.26 | 6.62 | 31.26 | | 1.96 | 1.34 | 0.56 | 14.51 | 100 |
| 3 | 14.14 | 41.37 | 0.63 | 1.28 | 5 | 25.65 | | 1.11 | 2.08 | 0.72 | 8.02 | 100 |
| 4 | 5.11 | 48.84 | 0.58 | 1.83 | 6.58 | 28.28 | | 0.91 | 2.07 | 0.54 | 5.27 | 100 |
| 5 | 11.06 | 43.01 | 0.53 | 1.82 | 6.36 | 26.07 | | 0.94 | 2 | 1.54 | 6.78 | 100 |
| 6 | 26.97 | 33.45 | | 0.94 | 3.45 | 10.34 | | | 0.92 | | 23.93 | 100 |
| 7 | 9.83 | 46.07 | 1.25 | 1.38 | 7.67 | 24.20 | | 1.04 | 3.39 | 0.39 | 4.78 | 100 |
| 8 | 8.51 | 45.01 | 0.76 | 1.57 | 6.45 | 26.38 | 1.15 | 1.36 | 3.16 | 0.65 | 5.01 | 100 |
| 9 | 5.71 | 49.16 | 0.62 | 2.08 | 7.25 | 27.23 | | 0.78 | 1.37 | 0.39 | 5.41 | 100 |

TABLE II. ELEMENTARY ANALYSIS OF POINTS ON THE GRANULE SIDE SURFACE

| Point | C | O | Na | Mg | Al | Si | Cl | K | Ca | Ti | Fe | Σ |
|-------|-------|-------|------|------|------|-------|------|------|------|------|-------|-----|
| 1 | 14.26 | 35.68 | 0.68 | 1.73 | 6.47 | 27.22 | | 2.53 | 1.93 | 0.65 | 8.85 | 100 |
| 2 | 6.76 | 41.01 | 0.83 | 1.36 | 6.20 | 26.12 | | 1.31 | 4.08 | 1.55 | 10.79 | 100 |
| 3 | 3.34 | 47.06 | 0.83 | 1.59 | 5.85 | 31.30 | 0.54 | 1.73 | 1.61 | 0.47 | 5.70 | 100 |
| 4 | 6.87 | 43.21 | 2.30 | 0.52 | 5.98 | 33.42 | | 2.21 | 0.82 | 0.40 | 4.27 | 100 |
| 5 | 6.42 | 43.26 | 1.12 | 1.66 | 7.40 | 29.77 | | 1.37 | 2.67 | 0.43 | 5.91 | 100 |
| 6 | 9.87 | 40.96 | 1.14 | 1.51 | 7.52 | 27.32 | | 1.76 | 2.46 | | 7.45 | 100 |
| 7 | 6.90 | 40.48 | | 1.97 | 7.15 | 29.06 | | 1.86 | 3.35 | 1.10 | 8.13 | 100 |
| 8 | 9.04 | 47.06 | 0.53 | 1.64 | 5.04 | 30.70 | | 0.74 | 1.66 | | 3.59 | 100 |
| 9 | 8.41 | 46.98 | 0.69 | 2.36 | 6.58 | 26.58 | | 1.16 | 1.24 | 0.29 | 5.70 | 100 |