



Structural, textural and adsorption characteristics of bentonite-based composite



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ABSTRACT

An application of coatings composed of mixed (hydr)oxides over bentonite particles in aqueous suspension, in narrow range of pH, has been proven as a useful method for obtaining bentonite based composite with a developed, specific surface area and pronounced adsorption features toward cationic pollutants. This paper deals with detailed characterization of structure as well as textural and adsorption properties of bentonite based composite. The structure of the composite was examined by using XRD technique providing results that confirm changes in orientation of layered quasi-crystalline particles of montmorillonite, which is the most common component of bentonite clay. Surface area and pore volumes were determined by N₂ adsorption at –196 °C using BET, *t*-plot, α_s -plot, Dubinin Radushkevich and Dollimore–Heal method. The results have revealed that the specific surface area for composite is about two times higher than for starting bentonite. Moreover, modification of bentonite leads to significant changes in the meso- and microporosity. Adsorption properties of the composite were studied by analyzing the adsorption of dye methylene blue which was used in this study as a model of cationic pollutant in water. The most prominent role in the mechanism of dye molecules retention on the surface, interlayers and in the pores of the adsorbent is ascribed to establishing of electrostatic, van der Waals and hydrogen bonds. The shape of adsorption isotherm indicates that methylene blue can be adsorbed onto composite in more than one layer.

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1. Introduction

Bentonite is a natural, colloidal, hydrated aluminosilicate, which occurs as the clay sediment with a high content of minerals from the smectite group. It was named after Fort Benton, United States, where a large deposit of this raw material was found for the first time. In addition to smectite, natural bentonite contains other minerals such as: illite (mica), kaolinite, quartz, cristobalite, dolomite, calcite, plagioclase and others.

Smectite belongs to the 2:1 group of clay minerals, in which isomorphous substitution of Si⁴⁺ ions in the tetrahedral layer with aluminum ions and Al³⁺ ions in octahedral layer with Mg²⁺, Fe²⁺, Zn²⁺ etc., leads to a permanent positive charge on the clay surface [1]. Apart from permanent charge, there is a pH dependent charge on the surface of bentonite originating from hydroxyl groups, which protonation and deprotonation with the changing of pH value determines the type and amount of surface charge. Binding

of pollutants from water on the surface of smectite can be established through electrostatic attraction as well as forming of surface complexes. For the already stated reasons, bentonite is widely used in the environmental protection, for detoxification of drinking water, wastewater treatment etc. [1–7]. In recent years, a number of procedures for modification of clays and clay minerals have been developed including physical, chemical and thermal treatment, in order to improve their adsorption capacity for certain harmful substances in water. The adsorption of heavy metals and other pollutants onto natural [8], Na⁺-exchanged [4,9], pillared [10,11], acid activated [12,13], or iron, aluminum and manganese oxide-coated bentonites [14] has received wide attention. However, there is a lack of information on impact of mixed iron/magnesium (hydr)oxide coatings on structure, texture and adsorption characteristics of bentonite.

Colloidal behavior of clay-(hydr)oxide dispersion is very complex. Interactions between suspended particles of clay and (hydr)oxides in the system, under certain conditions may lead to hetero coagulation between positively charged (hydr)oxides and negatively charged clay at pH values that are between the PZC (Point

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of Zero Charge) of (hydr)oxides and clay PZC [15]. Thus, in the dispersion consisting of clay and (hydr)oxide mixture, there comes to composite particle formation, i.e. (hydr)oxide is being distributed as a coating over the clay particles, which serve as the nuclei.

In this paper, it is examined how the application of coatings, consisting of mixed hydrolysis products of Mg^{2+} and Fe^{3+} , onto the suspended bentonite particles influences the structure, texture and adsorption properties of bentonite. Thus, the aim of the research is to characterize, in details, the composite with a developed specific surface and high adsorption capacity for cationic pollutants in water. Crystal structure of composite was analyzed by XRD technique while specific surface area and textural parameters were determined using the results obtained from the N_2 adsorption at $-196^\circ C$. Adsorption properties of the composite were investigated for the removal of cationic dye methylene blue (MB), which was used as a model of cationic pollutant in water. The results have shown that the composite has about twice the size of specific surface area compared to the native bentonite and a high capacity for methylene blue dye. It was noticed that after the completion of MB monolayer on the composite the formation of a new layer begins, which indicates that it is a multilayer adsorption. Adsorption in this study was described by three adsorption isotherms: Langmuir, Freundlich and BET (Brunauer–Emmett–Teller).

2. Experimental

2.1. Materials

Bentonite used in this research for the synthesis of the composite has the following chemical composition: 57.92% SiO_2 , 11.49% Al_2O_3 , 1.34% Fe_2O_3 , 1.46% MgO , 1.21% CaO , 2.23% K_2O and 1.01% Na_2O . Bentonite was transferred into a Na-bentonite by suspending in 1 M NaCl solution and stirring for a period of 24 h. After separating solid phase and rinsing with deionized water, Na-bentonite was dried at $60^\circ C$, crushed in agate mortar and used for the synthesis of the composite. The composite was synthesized by applying of Mg^{2+} and Fe^{3+} (hydr)oxide coatings onto bentonite particle in aqueous suspension in narrow range of pH, according to procedure described in the [Supplementary file](#) as well as in our previous publication [16]. The final product was separated by filtration, washed with plenty of deionized water, dried at $105^\circ C$ and finally heat-treated at $225^\circ C$ for 2 h. The resulting composite was then crushed in agate mortar, sifted through a 120 mesh sieve (particle sizes less than 0.125 mm) and thus used for adsorption experiments and further investigations.

2.2. Characterization

X-ray structural analysis was performed on the diffractometer Siemens D500, recording diffraction patterns of bentonite and composite. Adsorption–desorption isotherms of N_2 were obtained at liquid nitrogen temperature ($-196^\circ C$) on the instrument Thermo Scientific Sorptomatic 1990. Before recording the isotherms, the samples were degassed for 4 h at room temperature, and then another 18 h at $110^\circ C$. All the calculations were performed taking into account that the surface of N_2 molecule is 0.162 nm^2 . The total pore volume (Gurvich) was determined from nitrogen adsorption data at relative pressure of 0.999. Microporosity was examined using Dubinin–Radushkevich method, while mesopore size distribution was calculated using the Dollimore and Heal method. Surface area was estimated by using the following comparative methods: BET (two and three parameters fit), t -Plot (Lippens and de Boer) and α_S -Plot (Sing). Field emission scanning electron microscopy was performed on a SUPRA 35VP Carl Zeiss. The PZC

of composite was determined by pH drift method as described elsewhere [17].

2.3. Examination of the MB adsorption onto composite

All batch adsorption experiments were carried out in the Erlenmeyer flasks of 100 cm^3 , with 50 mg of adsorbent and 50 cm^3 of MB solution at room temperature ($25^\circ C$). After phase separation, spectrophotometric determination of dye was carried out on a UV/Vis spectrophotometer Shimadzu UV-1650 pc at $\lambda_{\text{max}} = 665\text{ nm}$.

Kinetic data of MB adsorption on the composite were analyzed for initial dye concentration of 150 mg/dm^3 and $\text{pH } 5.0 \pm 0.1$ using pseudo first-order, pseudo second-order and intraparticle diffusion models. The initial concentrations of MB for equilibrium studies were in range from 100 to 525 mg/dm^3 . The samples were stirred for 120 min in order to achieve equilibrium. Obtained adsorption data were analyzed using non-linear fitting by three well known adsorption isotherms: Langmuir, Freundlich and BET (Brunauer, Emmeth and Teller) in the mathematical form as described elsewhere [18,19]. In addition to adsorption isotherms and kinetics studies, MB uptake was examined at different pH values and ionic strengths. All the adsorption experiments were performed of $25^\circ C$.

3. Results and discussion

3.1. XRD and FE-SEM analysis

At a temperature of $225^\circ C$, dehydration of composite and the removal of adsorbed water occurred, which enhanced the interaction between the bentonite and the products of controlled hydrolysis of Fe^{3+} and Mg^{2+} , which are in the form of aggregates and layers of non-uniform thickness distributed on the bentonite particles. X-ray diffraction patterns of (a) native bentonite, (b) composite and (c) mixed Fe/Mg (hydr)oxides heat-treated at $225^\circ C$ for 2 h are shown in [Fig. 1](#). The following crystalline phases were identified in bentonite and composite: montmorillonite (M), quartz (Q) and cristobalite (K). Montmorillonite is the most abundant mineral in bentonite, and its presence was confirmed by identification of peaks at certain values of 2θ ([Fig. 1](#)).

Main structural changes were reflected in changing d_{001} crystallographic spacing between montmorillonite layers. The d_{001} peak position of montmorillonite in native bentonite is at $5,74\ 2\theta$ which corresponds to a layers distance of 1.54 nm, calculated using Bragg's equation ($n\lambda = 2d \sin\theta$). For the sample of composite, peak arising from the d_{001} reflections at $6.90\ 2\theta$, corresponding to a layers distance of 1.28 nm, has a lower intensity, which is explained by partial delamination and collapse of the layered structure of montmorillonite particles and the fact that particles of crystalline phase in the composite covered with amorphous layers of the chemical species formed by hydrolysis of iron and magnesium salts (hydrated oxides and basic salts). Change of d_{001} distance is a consequence of the fact that the spacing between the smectite layers is very sensitive to the type of cations in the interlayers, and the degree of hydration of cations. The structural changes that occurred during the chemical and thermal modification of the native bentonite include delamination as well as the decrease of the distance between the layers of montmorillonite particles, because the interlayer water was lost due to heating. The loss of interlayer water upon heating of composite results in compressed structure which is accompanied by decrease of d_{001} value. Other peaks were without a significant shift. In addition to layers distance calculation, the full width at half maximum (FWHM) measured on the main reflection peak (001) was used to determination of the crystallite size of the bentonite and composite

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