



Research paper

Determination of the specific surface area of layered silicates by methylene blue adsorption: The role of structure, pH and layer charge



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ARTICLE INFO

Keywords:

Methylene blue adsorption
Specific surface area
Langmuir isotherm
Surface orientation
pH
Adsorption mechanism

ABSTRACT

The specific surface area of three layered silicates was determined by three independent methods; it was estimated from the average dimensions of individual silicate layers, determined by nitrogen adsorption using the BET model and calculated from the adsorption of methylene blue on their surface in aqueous sol. The BET model gave smaller surface areas than expected, because nitrogen molecules cannot penetrate freely into the interlayer space of the silicates. Geometric calculations and the methylene blue approach yielded very similar values for two different types of Laponite when the pH of the dispersion was adjusted to 6.5 or the edges of the silicate were modified with tetrasodium pyrophosphate dispersing agent. The measurement of surface area in water without the control of pH yielded smaller surface area, because methylene blue decreased the pH of the solution resulting in the competitive adsorption of methylene blue cations and protons at the basal surface. The methylene blue approach resulted in larger surface area than expected for the silicate with large ion exchange capacity, because of the tilted orientation of the adsorbed methylene blue molecules. All these factors must be considered during the use of the methylene blue method for the determination of the specific surface area of smectites.

1. Introduction

Methylene blue (MB) is routinely used for the determination of the specific surface area of materials in aqueous medium (Cenens and Schoonheydt, 1988; Gürses et al., 2004; Kipling and Wilson, 1960; Ruiz-Hitzky, 2001; Schoonheydt and Heughebaert, 1992). The planar molecule has a rectangular shape with the area of approximately 1.7 nm × 0.76 nm and a thickness of 0.325 nm (Ruiz-Hitzky, 2001), thus one molecule covers 1.30 nm² area (Santamarina et al., 2002). Methylene blue can interact with the surface of layered silicates both through ionic and secondary, van der Waals forces, since in water MB dissociates into a cation with one positive charge (MB⁺) and an anion (chloride) (see Fig. 1). The specific surface area and cation exchange capacity (CEC) of smectites are often determined simultaneously by the adsorption of MB on their surface (Hang and Brindley, 1970; Kahr and Madsen, 1995; Yener et al., 2012). The isotherm obtained can be divided into two sections in which different interactions dominate. Below the optimum flocculation point (OFP) mainly ionic interactions develop between the silicate surface and methylene blue. Above this concentration the permanent negative charges of the silicate are neutralized by MB cations thus adsorption occurs mainly by physisorp-

tion (Kahr and Madsen, 1995). In the case of smectites, the amount of MB necessary to reach the optimum flocculation point is regarded as their cation exchange capacity (Hang and Brindley, 1970) and below this point methylene blue is irreversibly bonded to the surface (Bergmann and O'Konski, 1963). In the second part of the isotherm, the adsorption of MB molecules is in dynamic equilibrium. The various aspects of the adsorption of methylene blue on the surface of smectites have already been investigated in detail (Arab et al., 2015; Chang et al., 2016; Cottet et al., 2014; Gao et al., 2016). The type of the counter ion influences the extent of cation exchange, contrary to sodium ions, calcium ions cannot be completely exchanged to MB⁺ ions resulting in smaller apparent specific surface area values (Hang and Brindley, 1970).

In spite of the frequent use of the methylene blue technique for the determination of the specific surface area of layered silicates, a number of factors have not been paid attention to or have not been investigated sufficiently thoroughly yet. Up to now, only a few attempts have been made to determine the influence of cation exchange capacity and layer charge on the measured specific surface areas. Yener and co-workers, for example, studied the effect of cation exchange capacity on the surface area measured, but the CEC values used were quite small

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<http://dx.doi.org/10.1016/j.clay.2017.05.007>

Received 30 January 2017; Received in revised form 27 March 2017; Accepted 8 May 2017
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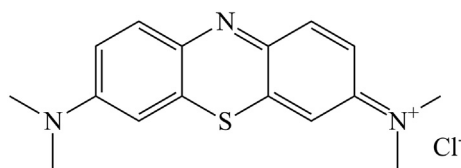


Fig. 1. The chemical structure of methylene blue.

(smaller than 0.34 meq/g clay) (Yener et al., 2012; Gürses et al., 2006). At small ion exchange capacity methylene blue molecules orient parallel to the surface and the surface area determined is proportional to the number of adsorbed molecules.

On the other hand, large layer charge was shown to lead to the tilted orientation of surfactants used for the modification of the clay (Lagaly and Weiss, 1970) with increasing tilting angles at larger surface coverages (Pozsgay et al., 2004). Sponza et al. (Sponza et al., 2015), for example, measured very large, 1295 m²/g, specific surface area, but they did not characterize their silicate sufficiently (cation exchange capacity and the size of the platelets are missing) and the authors did not give any explanation for the unrealistically large value. Tilting may occur also during the adsorption of methylene blue, but sufficient attention has not been paid to the structure of the adsorbed layer including its effect on the adsorbed amount from which the specific surface area of the silicate is derived. Moreover, large layer charge leads to the aggregation of MB molecules, but its effect on the surface area measured has not been studied either (Bujdák and Komadel, 1997; Gessner et al., 1994; Neumann et al., 2002; Pentrák et al., 2012), and especially not at adsorption levels exceeding the cation exchange capacity of the silicate (Beltrán et al., 2014).

The pH dependent charge of the edges of the silicate may also influence adsorption by electrostatic attraction or repulsion. Since the addition of MB into an aqueous dispersion results in the decrease of pH, the edges of the silicate platelets become positively charged below a certain pH value. Positively charged edges repulse MB⁺ cations, thus adsorption capacity decreases resulting in smaller apparent specific surface area. According to our knowledge, the effect of pH on the measured surface area of smectites has not been studied in sufficient detail yet. Although Amrhar et al. (Amrhar et al., 2015) observed the dependence of the adsorbed amount of MB on pH for illite, adsorption was very limited and the structure of the mineral differs considerably from that of the clays studied in this work.

The goal of our work was to study questions related to the determination of the specific surface area of smectites, which have not been explored sufficiently yet. The structure of the adsorbed methylene blue layer was studied for a smectite with large CEC value to determine the effect of the orientation of MB molecules on the surface area obtained. We investigated the effect of measurement conditions, and specifically that of pH, on the adsorption isotherm of methylene blue on various layered silicates. The influence of the edge charge of the silicate platelets on their surface area was determined in measurements carried out with and without the control of pH. Smectites with small diameter were used in the experiments, for which the ratio of the surface of the edges is not negligible compared to the total surface area of the silicate (~7%). A silicate modified at the edges was also used as reference to obtain further information about the role of edge charges in MB adsorption.

2. Materials and methods

2.1. Materials

Sodium montmorillonite (Nanofil 116, NaMt; density (ρ) = 2.86 g/cm³, CEC = 1.16 meq/g, diameter (d) = 240 nm, height (h) = 0.96 nm) was obtained from Rockwood Clay Additives GmbH, while Laponite XLG (ρ = 2.53 g/cm³, CEC = 0.55 meq/g, d = 25–30 nm,

h = 0.92 nm) and Laponite XLS (ρ = 2.53 g/cm³, CEC: no data, d = 25.0 nm, h = 0.92 nm) were purchased from Byk Additives and Instruments. Laponite XLS is prepared from XLG by modification with pyrophosphate to obtain edges with negative charges in aqueous medium. All three smectites were fine powders and were used as received; they will be abbreviated as NaMt, XLG and XLS, respectively, in the further part of the paper. The chloride salt of methylene blue (MB) trihydrate (> 98.5%) and sodium chloride (NaCl, analytical grade) was obtained from Sigma-Aldrich. Phosphoric acid (85 wt%) and sodium hydroxide (NaOH, a.r.) were purchased from Reanal, Hungary. De-ionized water (MilliQ reagent grade, resistance larger than 18.2 M Ω cm, Millipore, USA) was used for sample preparation. All experiments were done at 25 °C unless otherwise indicated.

2.2. Methods

The specific surface area of the silicates was determined by nitrogen adsorption using a Quantachrom Nova 2000 apparatus. Samples were degassed at 200 °C in vacuum for 24 h before the measurement. The specific surface area was obtained from the Brunauer-Emmett-Teller (BET) model (Brunauer et al., 1938) using 0.162 nm² as the area occupied by one nitrogen molecule.

The adsorption isotherm of MB on the silicates was determined in aqueous medium. 1.2 g silicate was dispersed in 100 ml MilliQ water with 10 min ultrasonication. 100 μ l of the aqueous silicate sol with the concentration (c) of 12 g/l was diluted with 10 ml 10 mM NaCl or 10 ml phosphate buffer (10 mM, pH = 6.5) to keep the ionic strength constant during the experiments. Various amounts (0–1200 μ l) of aqueous MB solution (c = 1.95 mM) was added to the sol and the samples were stirred intensively at 25 °C for 24 h to reach equilibrium. Subsequently the dispersion was centrifuged at 13500 rpm for 10 min and the absorbance of the supernatant was determined in a glass cuvette (path length = 1 cm) using a Unicam UV 500 UV-Vis spectrophotometer. MB concentration was calculated after calibration with aqueous solutions (λ = 665 nm, ϵ = 6.24·10⁵ M⁻¹ cm⁻¹). As the silicates were not dried before the adsorption measurements, water content had to be determined to obtain the amount of dry silicate. Water content was deduced from thermogravimetric analysis (TGA6, Perkin Elmer). The weight change of samples of 10–15 mg were measured in nitrogen atmosphere in the temperature range of 30–800 °C with 10 °C/min heating rate. The pH of buffer solutions was checked with a pH/ion analyzer (Radelkis OP-271/1). All adsorption experiments were done in polyethylene centrifuge tubes to avoid the adsorption of MB on the surface of the container. The amount of adsorbed MB was determined by thermogravimetric analysis as well. Solid MB was added to aqueous silicate sols (c = 10 g/l) and left standing for 24 h. The dispersions were centrifuged, precipitates were dried at 60 °C and then characterized by TGA. Measurements were carried out in oxygen atmosphere in the temperature range of 30–800 °C with 10 °C/min heating rate (TGA6, Perkin Elmer). After MB adsorption and drying the gallery structure of the silicates was characterized by X-ray diffraction using a Philips PW 1830/PW 1050 equipment with CuK α radiation (0.154 nm) at 40 kV and 35 mA anode excitation with 0.04 step size and 4 s counting time. Zeta potential was determined in the same supernatant solutions used also for the measurement of the concentration of methylene blue in the adsorption experiments by using a ZetaPALS analyzer (Brookhaven Instruments Co.) at 30 °C in polystyrene cuvettes. The Smoluchowski equation (Eq. 1) was used for the calculation of zeta potential:

$$\xi = \frac{\mu_E \eta}{\epsilon} \quad (1)$$

where ξ is zeta potential, μ_E is electrophoretic mobility, while η is the viscosity and ϵ the permittivity of water (Wall, 2002). Five parallel runs were done on each sample and each run consisted of 10 cycles.

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