Applied Clay Science 151 (2018) 140–147

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Comparison of methylene blue adsorption on bentonite measured using the spot and colorimetric methods

Youko Miyoshi*, Katsuhiro Tsukimura, Kazuya Morimoto, Masaya Suzuki, Tetsuichi Takagi

Research Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology (AIST), Central-7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

A R T I C L E I N F O

Keywords:
Bentonite
Methylene blue adsorption
Spot method
Colorimetric method
JBAS-107-91

A B S T R A C T

The maximum amount of methylene blue (MB) adsorbed on montmorillonite in bentonite can be determined using a spot or colorimetric method to evaluate the quality of bentonite. The spot method differs from the colorimetric method in terms of the procedure used to add MB solution to a bentonite dispersion and the procedure to determine the maximum amount of MB. In the spot method, MB solution is added in a step-by-step process and the maximum amount is determined by observing a spot of MB and bentonite on filter paper. In the colorimetric method, MB is added only once and the maximum amount is determined using a spectrophotometer. This study revealed that the maximum amount of MB adsorbed onto bentonite measured using the spot method differs from that measured using the colorimetric method. The maximum amount measured using the colorimetric method can be estimated by multiplying the amount measured using the spot method by 0.937. To ascertain why the maximum amounts measured using the two methods differ, we examined bentonites using a newly proposed method (a step-by-step colorimetric method), in which MB is added in a step-by-step manner and the maximum amount is determined using a spectrophotometer. The maximum amount measured using the step-by-step colorimetric method showed that step-by-step addition of MB decreases the maximum amount. The decrease can be explained by the re-flocculation of montmorillonite particles in bentonite.

1. Introduction

Bentonite, a clay containing a large amount of montmorillonite, has been adopted for various applications because it has useful characteristics such as low water permeability, high degree of swelling, high viscosity, high plasticity, gelation property and high cation exchange capacity. A mixture of bentonite and sand is used as an artificial barrier at disposal sites of radioactive wastes from nuclear power stations because bentonite has low permeability and high degree of swelling (e.g., Komine and Ogata, 1999). This mixture is also used as molding sand because the addition of bentonite to sand increases the material's bonding strength and plasticity (e.g., Clem and Doehler, 1963; Murray, 1991). Bentonite slurry is used as drilling mud because water containing bentonite strengthens the wall of the drill hole (e.g., Clem and Doehler, 1963). Bentonite is also used as pet litter (e.g., Murray, 1991) because it absorbs the odor and surrounds the feces.

The amount of montmorillonite in bentonite, which is positively correlated with the degree of the useful characteristics of bentonite, can be determined using the methylene blue (MB) test. The test measures the maximum amount of MB cation that can be adsorbed onto the surface of montmorillonite in the bentonite. When MB cations are adsorbed onto the montmorillonite surface, the MB cations replace cations at montmorillonite exchange sites. Therefore, the maximum amount of MB adsorbed onto the surface of montmorillonite is proportional to the specific surface area and cation exchange capacity of the montmorillonite (Nevins and Weintritt, 1967; Brindley and Thompson, 1970; Hang and Brindley, 1970; Kahr and Madsen, 1995; Wang et al., 1996; Yukselen and Kaya, 2008; Sarkar and Haldar, 2009).

In most bentonite companies, the maximum amount of MB adsorbed onto bentonite is measured using the spot method, because this method is simple and quick (Miyoshi et al., 2015). Standard spot methods have been proposed by the Japan Bentonite Manufacturers Association (Japan Bentonite Manufacturers Association, 1991), the American Society for Testing and Materials (American Society for Testing and Materials, 2014), and the American Foundry Society (American Foundry Society, 2015). In the spot method, MB solution is added to a bentonite dispersion in a step-by-step manner and a drop of the solution is placed on filter paper to form a dark blue spot. When a sufficient amount of MB solution has been added, a light blue halo appears around the spot. The halo is attributable to MB that is not adsorbed onto

* Corresponding author.
E-mail address: youko-miyoshi@aist.go.jp (Y. Miyoshi).

http://dx.doi.org/10.1016/j.clay.2017.10.023
Received 7 February 2017; Received in revised form 19 October 2017; Accepted 20 October 2017

bentonite. When the halo appears around the spot, it may be assumed that all of the exchangeable sites of the montmorillonite are occupied by MB and that a small amount of MB remains in the solution. However, deciding whether or not the halo has appeared is difficult because the halo is not always clearly observed, which causes large differences in results among examiners (Yukselen and Kaya, 2008; Miyoshi et al., 2015).

The maximum amount of MB adsorbed onto bentonite can also be measured by the colorimetric method, which is used mostly for academic research (Brindley and Thompson, 1970; Hang and Brindley, 1970; Rytwo et al., 1991; Kahr and Madsen, 1995; Santamarina et al., 2002; Yukselen and Kaya, 2008); this is because the method is rarely associated with human error. In the colorimetric method, MB solution is added to a bentonite dispersion in one step, and the concentration of MB that is not adsorbed onto bentonite is measured using a spectrophotometer. The maximum amount of MB that can be adsorbed onto the bentonite is determined by subtracting the amount of MB that was not adsorbed from the amount of MB added to the bentonite dispersion. However, the colorimetric method is not used by many bentonite companies (Miyoshi et al., 2015) because it requires a spectrophotometer, which is relatively expensive, and some knowledge of relevant technical operations.

The main problem using the MB test is that the maximum amount of MB adsorbed onto bentonite may differ between the spot and colorimetric methods. One reason for this difference is that the spot method may overestimate the amount of MB adsorbed. The spot method assumes that the amount of MB adsorbed onto bentonite is equal to the amount added to the bentonite dispersion at the time when the halo appears. However, the appearance of the halo indicates the presence of MB in solution that is not adsorbed onto bentonite. Another reason is that the spot method differs from the colorimetric method in terms of the procedure used to add MB to the bentonite dispersion. In the spot method, MB solution is added to the bentonite dispersion in a step-by-step process (Nevins and Weintritt, 1967; Kahr and Madsen, 1995; Wang et al., 1996; Santamarina et al., 2002; Chiappone et al., 2004; Sarkar and Haldar, 2009), but in the colorimetric method, it is added in one step (Soderling and Neltner, 1983; Brindley and Thompson, 1970; Hang and Brindley, 1970; Kahr and Madsen, 1995; Santamarina et al., 2002; Yukselen and Kaya, 2008). The procedure for adding MB may affect the maximum amount of MB adsorbed onto the bentonite. In fact, Miyoshi et al. (2016) reported that the maximum amount of MB adsorbed onto bentonite measured using the spot method increased as the initial amount of MB added to the bentonite dispersion increased. Almeida et al. (2009) also reported that the amount of MB adsorbed onto montmorillonite increased with increasing initial MB concentration.

One of the goals of this study was to identify a method to convert the maximum amount of MB adsorbed onto bentonite measured using the spot method to the amount measured using the colorimetric method. We found systematic differences between the spot and colorimetric methods with respect to the measured maximum amount of MB adsorbed onto bentonite. It is important to develop the method to convert the maximum amount measured using the spot method to the amount measured using the colorimetric method. This is because the spot method, which is used in most bentonite companies, may give the result that differs from the result given by the colorimetric method. We can compare the results given by the different methods by using the conversion method.

The other goal of this study was to clarify why the maximum amount of MB adsorbed onto bentonite measured using the spot method differs from that measured using the colorimetric method. To examine this, we measured the maximum amount of MB adsorbed onto bentonites using a novel colorimetric method. In this new method, MB solution was added in a step-by step process, as in the spot method, but the maximum amount of MB that could be adsorbed onto bentonite was determined with a spectrophotometer, as in the colorimetric method. We call this new method the step-by-step colorimetric method. We developed the step-by-step colorimetric method to show how the procedure for adding MB affects the results. We discuss the effect by comparing the maximum amounts of MB measured using the colorimetric and step-by-step colorimetric methods. Additionally, the step-by-step colorimetric method will give information on the suitable halo-size of the spot method. We discuss the halo size by comparing the maximum amounts measured using the spot and step-by-step colorimetric methods.

2. Materials and methods

2.1. Samples

We used three bentonites from three different locations: Mikawa, Tsukinuno, and Wyoming. The Mikawa bentonite was obtained from the Mikawa deposit (Niigata region of Japan), which is a Na or Na-Ca bentonite deposit (Takagi, 2005). The Mikawa bentonite is one of the reference samples of the Clay Science Society of Japan (JCSS-3102 Montmorillonite; Mikawa, Japan) (Miyawaki et al., 2010). The Tsukinuno bentonite was obtained from the Tsukinuno deposit (Yamagata Prefecture, Japan), which is a representative Na-bentonite deposit in Japan (Takagi, 2005). The Wyoming bentonite was obtained from the Wyoming deposit (Wyoming, USA), which is a Na-bentonite deposit (Hosterman and Patterson, 1992).

2.2. Mineralogical and chemical analysis

Minerals in the bentonites were identified using an X-ray diffractometer (RINT-2500V; Rigaku, Tokyo, Japan). The incident beam was Cu-Kα radiation (λ = 1.5418 Å) from a rotating X-ray anode at 40 kV and 100 mA. The instrument was equipped with a diffracted beam monochromator. The divergence slit was 1/6°, the scan speed was 3°/min (step width of 0.05°2θ and time for one step of 1 s), and the scan range was 2–64°2θ. The bentonites were placed in a flat glass sample holder.

The chemical compositions of the bentonites were analyzed using a wavelength dispersive X-ray fluorescence spectrometer (ZSX Primus III +; Rigaku). After drying at 1000 °C for 2 h, 0.5 g of bentonite was weighed and mixed with 5 g of lithium tetraborate ($Li_2B_4O_7$) powder, and the mixture was melted at 1250 °C to form a glass bead. Calibration curves were determined on the basis of Morita et al. (2015).

2.3. Methylene blue test

2.3.1. Preparation of bentonite dispersion

We prepared the bentonite dispersion following the Japan Bentonite Manufacturers Association Standard (JBAS) (Japanese spot method; JBAS-107-91) (Japan Bentonite Manufacturers Association, 1991). Bentonite was dried at 105–110 °C for > 18 h. The dried bentonite (0.500 g) then was placed in a conical beaker with 50 mL of 2% tetrasodium pyrophosphate (TSPP) solution. The bentonite grains in the solution were dispersed by ultrasonic treatment for 10 min. After preparing the bentonite dispersions, the maximum amount of MB adsorbed onto the bentonites was measured using the following three methods.

2.3.2. Spot method

We used a procedure based on JBAS-107-91 (Japan Bentonite Manufacturers Association, 1991). First, we added about 65–75% of the estimated maximum amount of MB that could be adsorbed onto the bentonite to the bentonite dispersions in a single step and stirred the MB–bentonite solution using a magnetic stirrer for 2 min. Then, MB solution (0.01 mol/L) was added step-by-step in 1 mL increments. After every addition, the bentonite–MB solution was stirred for 30 s and a drop of the solution was dropped on filter paper (back side of No. 131; Advantec Toyo Kaisha Ltd., Tokyo, Japan) using a pipette to form a