Research paper

Effects of exchanged cation, acid treatment and high shear mechanical treatment on the swelling and the particle size distribution of vermiculite

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ABSTRACT

The objective of the present work is the study of the effect of three different chemical treatments on the swelling and the particle size distribution of a vermiculite sample from of the State of Goiás, central-west Brazil, by using inorganic solutions of LiCl, NaCl, and HCl, accompanied by a high shear mechanical treatment. X-ray diffraction and X-ray fluorescence were used to characterize the as-received material. The effect of the chemical/mechanical treatment on the swelling and the particle size distribution of the vermiculite were investigated by Foster swelling test in water, cation exchange capacity, and particle size distribution by laser diffraction. Results showed an increase in swelling and a reduction in particle size for all the samples after the chemical treatments. The highest rates of swelling in water were obtained after the chemical treatment and the high shear homogenization process, following the order: HCl > LiCl > NaCl. These results stimulate further research exploring the acid treatment combined with a high-shear mechanical treatment to modify the characteristics of vermiculites, in order to produce high rates of dissociation/dispersion of vermiculite particles in water, thus broadening the potential applications for this material.

1. Introduction

Vermiculite is a clay mineral of considerable commercial importance (Souza Santos, 1975; Harben, 2002; Hindman, 2006). Vermiculites are commonly used in lightweight concrete aggregate applications, heat insulation and sound dissipation; it is also used as a carrier or a bulking agent in horticulture, as thermal protecting and shock-proof-filling material, as protection agent against breaking containers, and in metallurgy, as thermal protection of the surface of molten metals (e.g. Bergaya et al., 2006b; U.S. Geological Survey, 2010). In recent years, vermiculites have been extensively studied for other potential applications, such as immobilizing toxic compounds or pollutants, such as heavy metal cations, as sorbents (e.g. Brigatti et al., 2005; Santos and Masini, 2007; Zheng et al., 2007; Mulange and Garbers-Craig, 2012), as simple and effective support for catalysts (e.g. Suquet et al., 1991; Suquet et al., 1994; Rey-Perez-Caballero and Poncelet, 2000; Temuujin et al., 2003); and particularly in the synthesis of clay polymer nanocomposites (e.g. Tjong et al., 2002; Osman, 2006; Shao and Wang, 2006; Valášková et al., 2013), due to their potential to generate platelike aluminosilicate layers with high aspect ratios (e.g. Wiewióra et al., 2003; Osman, 2006; Prakash, 2007).

Vermiculite exhibits a crystalline structure 2:1, and is in the same group of the smectites, including montmorillonite, beidellite, hectorite, saponite, and other varieties. Vermiculite is differentiated from other expandable 2:1 clay minerals by a high negative electrostatic layer charge, due to a higher substitution of Si^{4+} for Al^{3+} in tetrahedral sites (Rausell-Colom et al., 1989; Brigatti et al., 2006; Tjong, 2006). This characteristic gives vermiculites a high thermal stability and high CEC. The layer charge is perhaps the single most significant characteristic of 2:1 layer clay minerals (Mermut and Lagaly, 2001; Czímerová et al., 2006). Layer charge significantly influences several physicochemical properties of clay minerals, such as cation-retention capacity, in addition to the adsorption of water and various polar organic molecules; swelling or sedimentation volumes; rheology, and others (e.g. Madsen and Müller-Vonmoos, 1989; Mermut and Lagaly, 2001; Christidis et al., 2006; Laird, 2006; Zemanová et al., 2006; Dultz et al., 2012).

Clay swelling is the term generally used to describe the phenomenon of the increase in volume of an aggregate of clay mineral particles.

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This phenomenon is associated with the increase in the interlayer space of the clay structure and it is commonly observed in the presence of water. However, other polar molecules, such as alcohols, can also induce swelling (Michot and Villiéras, 2006). Clay swelling occurs when the clay is dispersed in a solvent or when it is in direct contact with an atmosphere having a high vapor pressure of solvent. Clay swelling also occurs when small interlayer cations are replaced by larger organic cations or by larger polymeric hydroxyl-metal cations (Laird, 2006).

The swelling of clays in the presence of water may occur by two processes: crystalline swelling and inter-crystalline or osmotic swelling (Norrish, 1954; Madsen and Müller-Vonmoos, 1989; Laird, 2006; Anderson et al., 2010). All clay minerals exhibit crystalline swelling and it occurs by the formation of molecular water layers in the interlayer position of the clay mineral, due to the hydration of the interlayer cations. Crystalline swelling results in discrete increases of basal spacing until about 20 Å (Slade et al., 1991; Laird, 1996; Hensen and Smit, 2002; Seppälä et al., 2016). On the other hand, osmotic swelling occurs by the formation of a diffuse electrical double layer on the surface of the clay mineral. This phenomenon creates repulsive forces that keep the clay particles apart and results in volume increases (up to 20 Å) significantly greater than the one verified for crystalline swelling (Norrish, 1954; Madsen and Müller-Vonmoos, 1989; Fink, 2003; Laird, 2006; Anderson et al., 2010). Osmotic swelling may lead to almost a complete separation of the particles into individual silicate layers. However, it occurs only in certain smectite clay minerals (especially montmorillonites) saturated with strongly hydrated monovalent cations, e.g. Na^+ and Li^+. Crystalline swelling depends on the hydration energy of the interlayer cations, the magnitude of the layer charge and the charge distribution. An increase in layer charge results in a decrease in crystalline swelling (Slade et al., 1991; Michot et al., 2002; Laird, 2006). On the other hand, the specific influence of the layer charge in the osmotic swelling is not clearly defined yet (Laird, 2006), although it is well known that the layer charge dictates the aggregation/dispersion behavior of clay particles (Thomas et al., 1999).

Naturally occurring vermiculites exhibit crystalline swelling, but not osmotic swelling (Bleam, 2011). However, despite the high layer charge, vermiculites can exhibit a considerable osmotic swelling, similar to smectites, when saturated with Li^+ or with certain organic cations (Garret and Walker, 1960; Walker, 1960; Vieira Coelho, 1986; Rausell-Colom et al., 1989; Braganza et al., 1990). Vermiculite is characterized by plate-like crystals with a considerable large particle size and a potential to generate plate like aluminosilicate layers with high aspect ratio (Osman, 2006). Unfortunately, the high charge of the layer prevents their swelling, thus making the dispersion of their particles in solvents difficult. In the present work, the as-received material was characterized in terms of CEC, phase (XRD) and chemical (XRF) compositions. After, the effects of three different chemical treatments, using inorganic solutions combined with a high shear mechanical treatment, on the swelling and the particle size distribution of a Brazilian vermiculite, are presented. The Foster swelling method (Foster, 1953) and the particle size distribution by laser dispersion were used to evaluate the extent of the chemical and mechanical treatments.

2. Experimental

2.1. Materials

The origin of the raw material used in this study is the State of Goiás, Central-West Brazil. This mineral is associated with a ultramafic complex and contains Mg^{2+} and K^+ as the principal cations in the interlayer space (Marcos et al., 2009). The starting material was supplied by Eucatex Química e Mineral Ltda. (São Paulo, Brazil) with mean particle size of about 300 μm. The raw material was pulverized in a rotary knife mill to reduce the particles into a relatively small size. The grain-size fraction range of particle size used for the chemical treatments, obtained by sieving, was from 63 μm (250 mesh) to 150 μm (100

mesh). The treatment solutions were prepared from analytical-reagent grade materials with distilled water.

2.2. Samples treatments

The vermiculite samples were treated separately with three aqueous solutions of lithium chloride, sodium chloride, and hydrochloric acid. The procedure was as follows: (1) samples were saturated with 0.8 M LiCl and 0.2 M NaCl solutions according with the procedure outlined in previous work (Vieira Coelho, 1986; Chambi et al., 2009); (2) 5 g of vermiculite was dispersed into 25 mL of chloride solution; (3) the resulting dispersion was then placed in an furnace at 90 °C, for enough time to allow the complete drying of the solution (times of up to 144 h); (4) the dried material was washed with distilled water, furnace dried at 60 °C and finally ground.

The treatment with hydrochloric acid was carried out according with a reported patent (Rittler, 1990): (1) the sample (25 g) was added to 1000 mL of a 2 M HCl solution and magnetically stirred for different times (2, 4, 5, 6, 8, and 10 h) at room temperature; (2) the content was then filtered, repeatedly washed with distilled water to remove any residual acid, oven dried at 60 °C and ground.

2.3. High shear mechanical treatment

After the chemical treatments, the samples were subjected to high shearing forces by using a conventional homogenizer (Heidolph DIAX 900). The sample (5 g) was suspended in 300 mL of distilled water and stirred using a high shear homogenizer at 24000 rpm for 10 min. The resultant dispersion was centrifuged, washed for several times with distilled water and ethanol, and then dried at 60 °C in a furnace.

2.4. Characterization

2.4.1. X-ray diffraction

X-ray diffraction (XRD) was used to determinate the mineral components in the samples. The XRD patterns were obtained from the oriented specimens by using a BRUKER D8 Advance diffractometer, CuKα radiation and 2θ step scans of 0.02° and a scan speed of 0.2 s per step. The oriented specimens were prepared by deposition of a dilute dispersions of samples onto glass slides, allowed to air dry and then subjected to treatments according with the commonly procedures used in the study of clay minerals (Brown and Brindley, 1980), i.e., solvation in ethylene glycol vapor and heating at 500 °C for 4 h.

2.4.2. Chemical analysis

The chemical composition of the raw clay sample and the treated samples were determined by X-ray fluorescence using a Panalytical (Philips) PW2404 X-ray spectrometer. The loss on ignition was determined at 1050 °C and the results were expressed in weight percentage of oxides.

2.4.3. Laser diffraction analysis

The particle size distribution and average diameter of the samples were measured by light scattering technique, using a Malvern Mastersizer E equipment, at 2000 rpm and ultrasound speed at 10. Distilled water and sodium pyrophosphate were used as dispersant and pre-dispersant agents, respectively.

2.4.4. Cation exchange capacity (CEC)

The cation exchange capacity (CEC) of the treated samples was determined based on an ammonium acetate method (Chapman, 1965): 5 g of sample were added to a beaker containing 200 mL of 3 M ammonium acetate solution, magnetically stirred for 15 h, then the suspension was centrifuged for 3 min at 3000 rpm and the sediment was collected, washed three times with ethanol and dried at 60 °C. Finally, the amount of NH_4^+ adsorbed by the dried samples was analyzed using