Colloids and Surfaces A 525 (2017) 1–6

Contents lists available at ScienceDirect

Colloids and Surfaces A

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

Correlation of electrophoretic mobility with exfoliation of montmorillonite platelets in aqueous solutions

Tianxing Chen[a,b,c], Yunliang Zhao[a,b,c], Shaoxian Song[a,b,c,*]

[a] School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China
[b] Hubei Provincial Collaborative Innovation Center for High Efficient Utilization of Vanadium Resources, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China
[c] Hubei Key Laboratory of Mineral Resources Processing and Environment, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China

ARTICLE INFO

Keywords:
Montmorillonite
Electrokinetic property
Exfoliation
Electrophoretic mobility distribution

ABSTRACT

In this work, the effect of the exfoliation degree of montmorillonite (MMT) platelets on their electrophoretic mobility distributions in aqueous suspensions was investigated in order to approach into the correlation of MMT exfoliation with electrokinetic property. The experimental results have shown that the negative mobility increased with the increase of exfoliation degree or with the decrease of MMT thickness. This observation might be attributed to the "exposing" of permanent layer negative charge during the exfoliation processing and the "spillover" of electrostatic potential from basal surfaces onto edges. The former would increase the permanent negative charge of the MMT platelets because of the large amounts of layer charge; the latter would decrease the positive edge charge. It is demonstrated that MMT exfoliation would change the electrokinetic property, which might be helpful of the applications of MMT in the related industries.

1. Introduction

Montmorillonite (MMT), a smectite type clay mineral, has been used in many industries and has received many interests in terms of practical application due to its swelling, colloidal, rheological, and electrical properties [1–3]. It is known that a unit of this clay (a primary particle) consists of a quite thin platelet of thickness of 10 Å. The platelet consists of two kinds of sheets: two tetrahedral layers of silicon oxide between which one octahedral layer formed by aluminum, magnesium, or iron oxide is sandwiched. (Fig. 1). Its general formula is $(Na)_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4.nH_2O$.

MMT has very small particle size, a high specific surface area and a cation exchange capacity values. The particles have permanent negative charges on their faces due to isomorphic substitutions which are Al^{3+} for Si^{4+} substitution in tetrahedral sites and Mg^{2+} for Al^{3+} substitution in octahedral sites. The broken bonds located at the edges of the platelet (alumina sheet) have a capacity to adsorb H^+ or OH^-, depending on pH value [4]. Due to these characteristics, MMT can show complex electrokinetic properties when they are dispersed in aqueous media, especially with electrolyte species.

Electrokinetic properties govern the flotation, coagulation and dispersion properties in suspension systems and also identify the optimal conditions of a well dispersed system [5,6]. The first step in obtaining clay-based products with homogeneous structure is the preparation of stable suspensions [7]. Clay suspensions are the first step to obtain commercial products which are diverse size, shape, material composition and cost. The stability properties of clay suspensions are very important in the manufacture of various products, since the final property and formulation of product, economic aspects of the process and storage stability of product depend on these properties [8,9].

In recent years, great attention has been paid to exfoliation of MMT minerals. The delamination nature of MMT induces the production of a large amount of slimes. The presence of slimes has a negative impact on slurry rheology, with detrimental effects on both flotation and comminution [10–12]. Moreover, after exfoliation of lamellar MMT, the specific surface area and cation exchange capacity (CEC) values will increase by a substantial margin, providing the fundament of for syntheses and applications of layered silicate nanocomposites [13,14]. Despite the importance of exfoliated MMT for the mineral processing and the synthesis of successful polymer nanocomposites, very little work has been done to directly quantify of their physical characteristics. Therefore, it is necessary to investigate the property of exfoliated MMT, especially the electrokinetic property.

There are some studies published in the literature related with the electrokinetic properties of MMT suspensions. Duman et al. [15]

* Corresponding author at: School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China.
E-mail addresses: shaoxian@uaslp.mx, ssx851215@whut.edu.cn (S. Song).

http://dx.doi.org/10.1016/j.colsurfa.2017.04.057
Received 14 March 2017; Received in revised form 19 April 2017; Accepted 25 April 2017
Available online 02 May 2017
0927-7757/

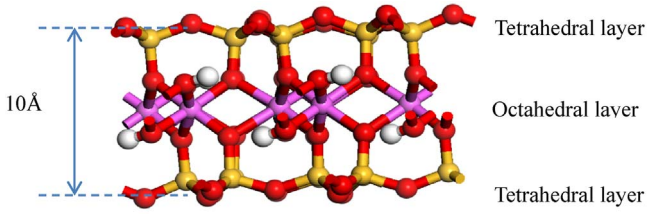

Fig. 1. Schematic MMT platelet structure.

performed a series of systematic zeta potential measurements to determine the effect of various electrolyte solutions on the zeta potential of Na-bentonite. They reported that divalent cations (Cu^{2+}, Mn^{2+}, Ca^{2+}, Ba^{2+} and Ni^{2+}) and trivalent cation (Al^{3+}) were potential determining cations for the Na-bentonite suspensions. Monovalent counter-cations and mono-, di- and tri-valent anions were indifferent ions for the Na-bentonite suspensions. Durán et al. [16] studied that the zeta potential of sodium MMT is based on the assumption of constant surface charge of faces and pH-dependent charge of edges. They assumed that surface properties of edges can be considered as a weighted average of that of silica and alumina, this yielding an isoelectric point of edges at pH ~ 7. Thomas et al. [17] determined the effect of the layer charge on the electrophoretic mobility of smectites, using electrophoresis measurements. Tsujimoto et al. [18] investigated the electrokinetic properties of MMT suspensions at different volume fractions. They noted that the acoustic zeta potential is extremely dependent on volume fraction around the volume fraction (2% and 4% volume fractions). The question remains, however, how the electrokinetic property of particles MMT behaves after exfoliation.

In this study, an attempt has been made to investigate the effect of exfoliation on the electrokinetic property of MMT platelets. The objective is to establish the relationship between electrokinetic characteristics and the thickness of lamellar MMT in aqueous solutions, in order to obtain more understandings of the electrokinetic property of the exfoliated MMT platelets.

2. Experimental

2.1. Materials

The original MMT used in the present study was obtained from Sanding Technology Co., Ltd, Zhejiang province, China. A common method for obtaining purified colloidal MMT is fractionation by sedimentation after removal of carbonates, oxides, and organic materials and smashed by the ultrasonic grinder. Fig. 2 gave the X-ray diffraction (XRD) image of the sample, showing that the colloidal MMT particles were very high grade and contained negligible impurities.

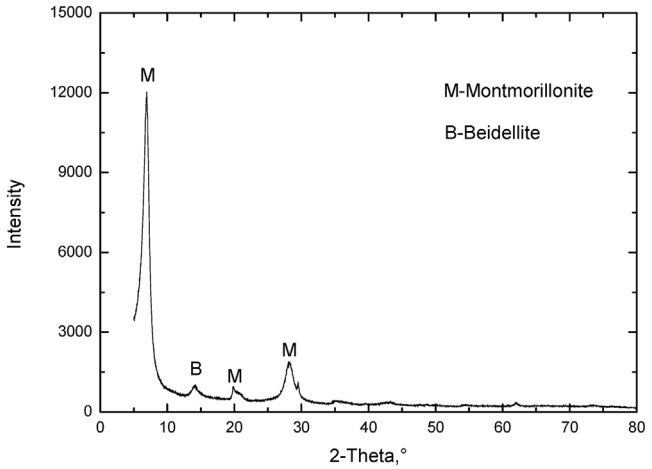

Fig. 2. XRD trace of the MMT.

Sodium hydroxide (NaOH) and hydrochloric acid (HCl) for adjusting pH were from the Sinopharm Chemical Reagent Co., Ltd (China). All of them were of analytical purity. The water used in this work was produced using a Millipore Milli-Q Direct 8/16 water purification system with 18.2 MΩ.

2.2. Preparation of exfoliated MMT platelets

The exfoliated MMT platelets were got according to a ultrasonic process rather similar to that indicated by Song et al. [19] 0.7 g Na-MMT was added into 70 mL liquid medium (water) in a beaker and then mixed for 30 min with a magnetic stirrer. The supernatant was treated by a Vernon Hills Illinois CP505 ultrasonic dispersion instrument (40 kHz) at different ultrasonic intensity for 4 min separately. Then a Fluko FA25 high speed mixer was used to disperse the supernatant with 10000 r/min for 3 min. The ultrasonic and shearing treatment was done to exfoliate the MMT.

2.3. Measurements

The Stokes size distribution of the MMT platelets was estimated by using centrifugal sedimentation with a Thermo Fisher Sorvall ST16 centrifuge. Sample aliquots were placed in an ultrasonic bath for 1 min before measurement. After the centrifugation, the supernatants and sediments were dried at 60 °C and then weighed. The weight of supernatant divided by the total weight was the percentage of correspondent particles.

The atomic force microscope (AFM) images of MMT platelets were obtained by using a Bruker MultiMode 8 AFM with peak force tapping-mode. The sample for AFM measurement was prepared by dropping MMT dispersion on a freshly cleaved mica surface. The mica substrate with MMT sample was dried at 60 °C for 2 h in an automatic thermostatic blast air oven. In order to obtain the distribution of sheet thickness, 50 sheets of each MMT sample in the AFM images were determined for the topographic height.

A Malvern Zetasizer Zeta-Nano was used to determine the electrophoretic mobility of the MMT platelets in aqueous solutions. This instrument works with the technique of laser doppler electrophoresis. Then, the suspension was poured into the measuring cell of zeta meter. The temperature was kept at 25 ± 1 °C throughout the measurement. Every individual measurements can get the distribution of electrophoretic mobility. All the measurements were performed with 1 mM KCl background electrolyte concentration.

The determination of the cation exchange capacity (CEC) of clays were performed by exchange with the cationic copper complexes [Cu(trien)]$^{2+}$ according to the procedure described previously [20]. The 0.02 M solution of [Cu(trien)]$^{2+}$ was prepared by dissolving 0.02 mol of triethylenetetramine (2.926 g) and 0.02 mol of $CuSO_4$ (3.192 g) in water and filling up to 1 L (pH = 8.4). For the CEC determination, 4 mL MMT suspension (25 g/L) were added in 25 mL centrifugal tubes and 4 mL of the 0.02 M complex solution [Cu(trien)]$^{2+}$ were added. The samples were shaken for at least 30 min and then centrifuged at a relative centrifugal field of 3000*g* for 10 min 3 mL of the supernatant were transferred into cuvettes, and the absorption was measured at 577 nm for [Cu(trien)]$^{2+}$ using calibration curves. The amount of copper complex adsorbed was calculated from the concentration differences. Every determination was carried out with at least three parallel samples.

The titration curves were recorded by using a computer-controlled titrator (907 Titrino, Metrohm) and a low-temperature thermostat bath to maintain the constant temperature. All titration were conducted under nitrogen atmosphere on 50 mL clay suspensions and at a constant temperature of 25 °C. The MMT suspension (50 mL, 4 g/L) diluted in