Colloids and Surfaces A: Physicochem. Eng. Aspects 423 (2013) 178–187

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Experimental determination of the colloidal stability of Fe(III)-montmorillonite: Effects of organic matter, ionic strength and pH conditions

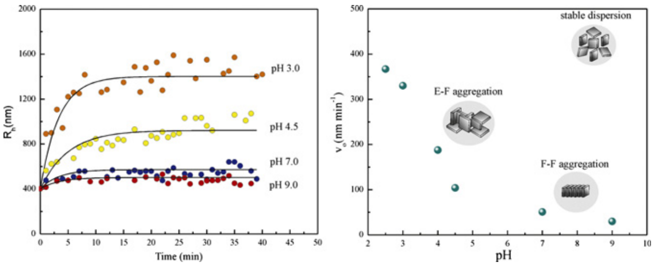
Laura Borgnino*

Centro de Investigaciones en Ciencias de la Tierra (CICTERRA). Instituto de Investigaciones en Físico-Química Córdoba (INFIQC). Departamento de Fisicoquímica, Facultad de Ciencias Químicas. Universidad Nacional de Córdoba. Ciudad Universitaria, 5000, Córdoba, Argentina

HIGHLIGHTS

- Low pH and high ionic strength may destabilize Fe-M suspensions.
- High concentrations of AH stabilize suspensions of Fe-M.
- For all pH, steric and electrostatic effects have an influence on Fe-M stabilization.
- The steric effects are more important at pH 4.5 and high ionic strength.
- The DLVO energy profiles support the experimental results.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 December 2012
Received in revised form 28 January 2013
Accepted 30 January 2013
Available online 14 February 2013

Keywords:
Aggregation
Humic acid
Fe(III)-montmorillonite
Colloidal stability

ABSTRACT

Aggregation and disaggregation of particle colloids are one of the most important surface-driven phenomena encountered in the aquatic and terrestrial environments and a key factor controlling a number of important environmental processes. This study investigates the effects of pH, ionic strength, and humic acid concentration on the stability behavior of Fe(III)-montmorillonite, a natural colloid commonly present in natural waters. Time-resolved dynamic light scattering was used to monitor the increase of the aggregate size over time in the aggregation kinetics experiments. Aggregation rate, stability ratio, and CCC (critical coagulation concentration) were calculated to quantify the experimental results, and the DLVO theory was employed to explain the observed behaviors. The effect of humic acid on the colloidal electrosteric stability was also investigated. This study demonstrates that low pH and high ionic strength may destabilize Fe(III)-montmorillonite suspensions, while increasing humic acid concentrations has the opposite effect, stabilizing the suspension at any pH. Comparing the steric and electrostatic effects on the Fe-M stabilization, both have an important influence for all pH levels studied, although steric is more pronounced at low pH and high ionic strength. DLVO energy predictions support the experimental results. The obtained results contribute to the understanding of the behavior of colloidal particles in saline or freshwater natural environments as well as the role of humic acid in the mobility of contaminants associated with natural colloids.

1. Introduction

The occurrence of natural colloids (particles with an effective diameter of less than 10 μm) is very common in natural aquatic media [1]. Both natural waters such as lakes and streams and pore water found in sediments and soils contain natural colloids and dissolved ions. A variety of organic and inorganic materials exist as colloids, including humic substances, “biocolloids” such as microorganisms, mineral precipitates, and weathering products. The occurrence of colloids may be detrital (contained in the original parent geologic material) or authigenic (formed *in situ* through geochemical alteration of primary mineral solids) [2]. Layer silicates,

---

* Corresponding author. Tel.: +54 351 4334169/4; fax: +54 351 4334188.
E-mail address: borgnino@fcq.unc.edu.ar

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.01.065

as well as iron and aluminum oxides, can be detrital in subsurface sediments, while secondary hydrous oxides, silica, calcite and other complex mixtures and solid solutions of theses phases are authigenic colloidal particles [2]. Regardless of their origin, dispersed colloids can remain a stable suspension in water. Due to their small size, they do not settle by gravitation. Furthermore, at the pH values of natural water, the particles are charged; so the electrostatic interactions, the van der Waals forces, and the steric forces maintain the stability of the colloidal suspension. Any changes in such a system with respect to pH, ion concentrations, or other factors may destabilize the suspension. Besides, colloids have a large specific surface area which makes them an important absorbent in natural waters. Hence, their potential to affect and modify the transport of many pollutants in natural aquatic systems is significant [1,2,3].

The colloidal mobility depends on its stability. To be mobile over a distance and thus facilitate contaminant transport, suspended colloidal material must be resistant to aggregation with other similar particles. Aggregation, the process of producing large aggregates by collisions induced by interparticle motion, is an important process which occurs among colloids. Although nanoparticles have been recently the focus of the aggregation studies [4–8] the importance of the aggregation process has been documented during decades [2,9–16]. Colloid stabilization is influenced by the particle mineralogy, surface charges, and by the extent of the electrical double layer. According to the theory proposed by Derjaguin and Landau, [17] Verwey and Overbeek [18], (DLVO theory), the stability of a homogeneous colloidal suspension is determined by the balance between van der Waals attractive forces that promote aggregation, and by electrostatic repulsive forces that drive particles apart. Studies have shown that aggregation causes rapid deposition of suspended sediments in rivers and may change the sediment transport properties, both in terms of the particle size and floc density [19,20]. Another consequence of aggregation is that fewer surface sites could be available for adsorption. Thus, aggregation and disaggregation also impacts the sorption–desorption of contaminants, and therefore in the transport in the aquatic media.

A number of studies have been conducted to evaluate the aggregation behavior of natural colloids particles via dynamic light scattering. Many of them involve experimental studies on the effect of ionic strength, pH and organic matter in the aggregation of oxide nanoparticles [5–8,21–25]. Fewer studies focused in the aggregation of clay minerals particles [26–30] and less in a theoretical and experimental approach of the effects of humic acid on the aggregation of clays [16,31,32] or Fe(III) modified clays.

The goals of this study are to investigate the stability of a Fe(III)-montmorillonite at different pH and ionic strength conditions, and the effect of humic acid on its stabilization using dynamic light scattering. A series of batch experiments were conducted to measure the hydrodynamic size of Fe(III)-montmorillonite via dynamic light scattering under a variety of experimental conditions. Aggregation rate, stability ratio, and critical coagulation concentration were estimated using the experimental results, and the DLVO theory was employed to explain the observed behaviors. Because sediment particle's composition is mostly clay minerals, Fe/Mn (hydr) oxide and organic matter which often exists as coating of clays, the system Fe(III)-montmorillonite employed in this work is used with the intention of representing the colloid behaviour of natural sediments particles. The obtained results may contribute to describe the behavior of colloids particles in saline or freshwater natural environments, as well as to understand the role that humic acid plays in the mobility of contaminants associated with natural colloids.

2. Material and methods

All solutions were prepared from analytical reagent grade chemicals and purified water (Milli-Q system).

2.1. Fe(III)-montmorillonite (Fe-M) and humic acid (HA) samples

The Fe-M sample employed was the same one used in previous research [33,34,35]. 550 mL of a clear fresh solution were mixed with 250 mL of a 2.2% Na-M dispersion in water, whose pH was adjusted to 3.5 before the mixing. After 2 h of vigorous magnetic stirring at this pH, a NaOH solution was added drop wise until pH 9. Once at pH 9, the dispersion was stirred for other 3 h and then the solid was washed with water and dried at 60 °C for 3 days. The chemical and mineralogical characteristics of the Fe-M obtained were described elsewhere [33]. The solid had an iron content of 77.3 mg g^{-1} and a specific surface area of 567 $m^2\,g^{-1}$, measured by the methylene blue adsorption method [36]. More than 60% of the total Fe(III) in this sample corresponded to interlayer/sorbed Fe(III) as XRD pattern and Mössbauer spectra indicated. The remaining fraction was already present in Na-M (structural Fe). If some ferrihydrite was formed as an associated phase, it has not been detected in the diffraction pattern [33].

HA suspensions were prepared from a Fluka humic acid (code: 1415-93-6), which had been previously purified according to the methodology proposed by the International Humic Substances Society [37]. Once the purification was completed, a concentrated stock solution of 2 g L^{-1} was prepared by dissolving a weighted amount of HA at pH 10 during 2 h. The HA stock solution was stored in dark conditions at 5 °C.

2.2. Aggregation kinetic measurements

The aggregation kinetics of the Fe-M and Fe-M-HA suspensions was investigated by the time-resolved dynamic light scattering (DLS) measurements (Delsa Nano 2.20, Beckman Coulter Inc.). The equipment was operated at a controlled temperature (25 ± 1 °C) and all light scattering experiments were conducted at 165° scattering angle. Using DLS, the average hydrodynamic radius R_h of the aggregates was measured as a function of time t. From the diffusion coefficient, the R_h could then be calculated using the Stokes–Einstein equation: $R_h = k_B T/6\pi\eta D$ where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the medium. The method of cumulants was used to extract the average diffusion coefficient from the intensity autocorrelation functions [31].

For the aggregation kinetics experiments, the increase of the R_h with time was recorded. The initial change in particle radius with time (the aggregation rate constant) is proportional to the particle concentration [38]. It is difficult to determine the absolute aggregation rate constants for the suspensions of nonspherical, polydispersed particles, such as montmorillonite. However, aggregation rates are often expressed in relative terms as the so-called stability ratio, W, by normalizing them to the rate of fast aggregation. Therefore, for a series of suspensions having the same mass concentration and the same initial particle sizes, W can be determined directly from the initial slopes of aggregation curves as:

$$W = \frac{[(dR_h/dt)_{t\longrightarrow 0}/C]^{(f)}}{[(dR_h/dt)_{t\longrightarrow 0}/C]} \tag{1}$$

where $(dR_h/dt)_{t\longrightarrow 0}$ is the initial change in particle radius with time (in nm $\min^{-1}$), C is the particle mass concentration (in mg L^{-1}), and (f) indicates the regime of fast aggregation, as explained below.

For each experiment, a dilute suspension containing 8.0–20.0 mg L^{-1} of Fe-M was prepared in a 0.01 M $NaNO_3$ electrolyte solution at the desired pH. The suspensions were agitated to maximize particle dispersion. A subsample was then quickly transferred into a glass cuvette; where R_h was monitored for 40 min and a complete autocorrelation function was recorded every 60 s. Aggregation rate constants were calculated from