Colloids and Surfaces A 554 (2018) 16–26

Contents lists available at ScienceDirect

Colloids and Surfaces A

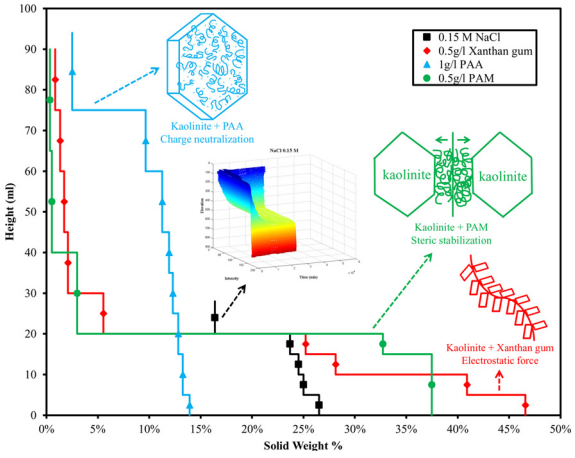
journal homepage: www.elsevier.com/locate/colsurfa

Microscopic and physicochemical studies of polymer-modified kaolinite suspensions

Cao J.[a], Kang X.[b], Bate B.[c,*]

[a] Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO, United States
[b] College of Civil Engineering, Hunan University, PR China
[c] Institute of Geotechnical Engineering, College of Civil Engineering and Architecture, Zhejiang University, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Biopolymers
Zeta potential
Microscopic particle size
Time-lapse

ABSTRACT

Sedimentation tests on kaolinite in biopolymers (xanthan gum, chitosan, polyacrylic acid and polyacrylamide) solutions were conducted and recorded with time-lapsed technique up to 35 days. Microscopic particle size, zeta potential, final volume and solid content were measured along the elevation of the graduated cylinder at the end of tests, and settling velocity and intensity calculated. Test results suggested that positive charged edges of kaolinite particles attached to negatively-charged xanthan gum (0.001 and 0.5 g/l) long chain via electrostatic force, exhibiting edge-to-edge (EE) fabric structure, and that charge neutralization was the primary interaction mechanism between kaolinite and either chitosan (0.05 and 5 g/l) or PAA(0.05 and 1 g/l),and that steric stabilization dominates the interaction between kaolinite and PAM molecules at 0.1 and 0.5 g/l PAM solutions.

1. Introduction

Grain size distribution (GSD) of the aggregates (or flocs) of a fine-grained soil in marine or lacustrine environments has been studied primarily in mesoscale (0.25 μm to 1 mm) due to its relevance to the macroscale mechanical or fluid dynamic behaviors [1]. At microscopic (sub-micron) scale, however, GSD and the physicochemical properties of fine-grained soils, which govern the fabrics and characteristics of

* Corresponding author at: Institute of Geotechnical Engineering, College of Civil Engineering and Architecture, Zhejiang University, PR China.
E-mail addresses: jcg83@mst.edu (J. Cao), kangxin@hnu.edu.cn (X. Kang), batebate@zju.edu.cn (B. Bate).

https://doi.org/10.1016/j.colsurfa.2018.06.019
Received 14 December 2017; Received in revised form 26 May 2018; Accepted 8 June 2018

flocs, are still not well understood. On the other hand, Stoke's law (Eq. (1)) predicted the terminal velocity of small particles in a suspension:

$$v = \frac{F_d}{6\pi\mu r} \quad (1)$$

Where F_d is the frictional force (unit: N) acting on the interface between fluid and particle, also known as Stokes' drag, μ the dynamic viscosity (unit: Pa), r (m) the radius of the spherical object, and v (m/s) the flow velocity relative to the object. However, the real sedimentation process is complicated by particle colliding [2,3], Coulombic interactions [4], van der Waals interactions [5–7], and Brownian motions [1,2], which render significant difficulties in simulating the sedimentation process of fine grain soils. Zeta potential, which is a good indicator of the inter-particle forces, yields insight into the interaction between the clay particles and the fluid phase [8,9].

Polymers emerged as new engineering materials in recent decades due to their environmental-friendly nature, minimal carbon footprint, and high efficiency. Polymer modification has been widely used in several disciplines, including chemical enhanced oil recovery [10–13], soil erosion control [14–18], dewatering of mine tailings [19–21], dredging of sediments [22–24], waste water treatment [25,26] and soil stabilizations [27–29]. Despite these applications, the interaction mechanisms between polymers and soil particles have not been fully explored. Polymer bridging and charge neutralization are the two major interaction mechanisms [30–32].Polymer bridging occurs when soil particles are brought together, sometimes forming flocculation, via hydrogen bonding between the end functional groups on the polymer chain and the sites on clay surfaces [7,21,33,34]. Charge neutralization, on the other hand, occurs when polymer chain with cationic functional groups adsorbed onto clay mineral surfaces and modified the particle fabrics [21]. Besides, depletion flocculation and stabilization are the less common mechanisms which are generated by dissolving nonionic polymer into the dispersions. The depletion interactions are induced by the unbalanced osmotic force caused by the exclusion of the free non-adsorbing polymer molecules from the space between the two approaching particles [35]. The effects of polymers on the clay particles behaviors are complicated, and the acting mechanisms often depend on solid concentration [36], cation exchange capacity [37], polymer dosage and molecular weight [38], adsorption density of polymer [7], types of polymer functional groups [30] and pH [39,40].

Time-lapse visualization of sedimentation process has been used for years in the study of glaciers [41], soil movement and erosions [42–44] and earth flow movement [45]. Time-lapse technique in monitoring the sedimentation process saves labor and provides turbidity information that linked to final volume, settling rate and maybe even solid content, even though the aqueous turbidity could be directly detected by Analytic Jena Specord S 600 BU machine [46].

This study aims at elucidating the fundamental mechanisms on the effects of sodium chloride (NaCl) and four polymers (xanthan gum, chitosan, polyacrylic acid and polyacrylamide) with kaolinite. To achieve this goal, the following tasks will be performed: First, a series of sedimentation tests for kaolinite and polymer mixtures with time-lapsed recording were performed. When final volume was reached, particle size, zeta potential and solid content were measured. Finally, the relationship between the microscopic/physicochemical properties and the macroscopic sedimentation behaviors (final volume, settling velocity and intensity) were proposed.

2. Materials and methodology

Georgia kaolinite (RP-2, properties are shown in Table 1) was homoionized with sodium cations before use. The homoionization process is similar to that in Bate and Burns [8], and a brief description was given below. 2 kg of kaolinite was added to 14 L of 2.0 mol/l NaCl solution. The resulting suspension was mechanically stirred for 15 min and allowed to stand for at least 24 h for gravity separation. The supernatant was then siphoned off, and the solids were rinsed with deionized water to remove any loosely bound cations. This process was repeated until the electrical conductivity of the supernatant was below350μS/cm.

Table 1
Properties of Geogia kaolinite used in this study.

Source	Active Minerals International, Hunt Valley, MD, USA
Trade name	ACTI-MIN RP-2
Color	Cream[a]
Specific gravity	2.60[a]
d_{50}	0.36 μm[a]
Chemical composition	SiO_2 45.60%, Al_2O_3 38.40%, Fe_2O_3 0.88%, TiO_2 1.69%, CaO 0.05%, MgO 0.02%, K_2O 0.15%, Na_2O 0.21%, LOI 13.70%[a]
Cation exchange capacity (CEC)	CEC = 7.9 meq/100 g[b]
Isoelectric point (IEP)	Face pH ≈ 4, edge pH ≈ 7.2[c]
Point of zero charge (PZC)	4.6[d]

[a] From ACTI-MIN RP-2 data sheet, Active Minerals International [62].
[b] From Hazen Research Inc.
[c] From Palomino and Santamarina [6].
[d] From Stumm [64].

Traditional method of oven-drying a slurry and mechanical grounding to obtain the solid powder will break kaolinite plates [47], and therefore was not adopted in this study. Instead, after Na-homoionization, the slurry was manually stirred for 5 min to obtain a uniform suspension, which was siphoned into graduated cylinders for the sedimentation tests. In order to obtain consistent solid content, suspension volume calibration tests were performed. It was found out that 85 ml of uniform suspension contained consistently 10 ± 0.1 g of solids. Therefore, 85 ml of uniform suspension was extracted for each 100 ml graduated cylinder, and approximately 15 ml of solutions with prescribed chemical concentrations was added to reach the full volume of 100 ml. The resulting chemical concentrations of different chemicals (NaCl, Xanthan gum, Chitosan, polyacrylic acid or polyacrylamide) in 100 ml kaolinite slurries were summarized in Table 2. The molecular structures of xanthan gum (Pfaltz&Bauer, CAS#: 11138-66-2), chitosan (Alfa Aesar, CAS#: 9012-76-4. 85% deacetylated), polyacrylic acid (PAA) (Polysciences, Inc., Lot#: 541449) and polyacrylamide (PAM) (Acros Organics, CAS#: 62649-23–4) used in this study were shown in Fig. 1. Molecular weights of above polymers are given in Table 3.

A 360° rotational sedimentation panel (Fig. 2) was developed in this study to simultaneously measures lurries in up to 28graduated cylinders. Graduated cylinders were locked onto the shelves of the panel. After slowly rotating the sedimentation panel for 5 min to ensure uniform slurries, the panel was locked, graduated cylinders stood upright, and the sedimentation process started. Time-lapse photos were taken for all the tested graduated cylinders with high resolution digital camera (Canon EOS 5d Mark II, Canon, Japan). The time intervals are as follows: 1 min interval in the first 1 h, 30 min interval in the following 19 h, 2 h interval in the following 11 days, 4 h interval in the following 8 days, and then 24 h interval for another 15 days (total of 35 days). No further changes were observed in all the graduated cylinders after 35 days. The interface between supernatant and suspension, and

Table 2
Chemical concentrations in kaolinite slurries.

Chemical Name	NaCl (mol/l)	Xanthan gum (g/l)	Chitosan (g/l)	PAA (g/l)	PAM (g/l)
Concentration	0.003	0.001	0.05	0.05	0.1
	0.006	0.01	0.5	0.5	0.5
	0.015	0.1	1	0.25	–
	0.15	0.5	5	1	–