



## Research paper

# Effects of humic acid release from sepiolite on the interfacial and rheological properties of alkaline dispersions



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## ABSTRACT

Humic acid (HA) is a major extractable and soluble component of soil organic matter that can play an important role in the stability of environmental colloidal dispersions. This study suggests that HA content of sepiolite is one of the essential reasons for non-Newtonian behaviour of sepiolite dispersions in alkaline media. Releases of HA from sepiolite matrix dramatically changed their rheological properties (thixotropy, apparent viscosity and yield stress), and interestingly, the level of sepiolite surface hydrophobicity. Alkaline environments also increased the release of  $Mg^{2+}$  ions from the sepiolite matrix and, thus, caused to a stable complex formation with HA macromolecules. This colloidal solid phase was directly observed and imaged by atomic force microscopy (AFM) which revealed a spherical shape of complexes between  $Mg^{2+}$  ions and HA in the size range of  $18\text{--}63 \pm 8$  nm at pH 11.5.

Alkaline environments also led to significant changes in the surface properties of sepiolite; after HA release, acid/base components of the surface free energy of sepiolite were determined as  $\gamma_s^-/\gamma_s^+ = 1.49$  and defined as having a highly hydrophobic character like natural hydrophobic minerals, e.g. talc. The major soil organic matter component, HA, was also found to be responsible for the changes in the sepiolite surface hydrophilicity.

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## 1. Introduction

Sepiolite (Sep) is one of the most important industrial magnesium-rich 2:1 clay minerals, and it differs from other layer silicates because of the lack of continuous octahedral sheets (Brigatti et al., 2013). Discontinuous octahedral sheets extend only in one direction and tetrahedral sheets divided into ribbons form a chain-layer molecular structure with  $3.6 \times 10.6$  Å of very large open channels or tunnels and  $320$  m<sup>2</sup>/g of corresponding high surface areas (Sabah et al., 2002).

A unique fibre structure exactly determines the hydrophobicity and anisotropic characteristics in half-cell formula  $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ . Electron acceptor and donor components of Sep fibres were previously calculated as  $\gamma_s^+ = 0.149$  and  $\gamma_s^- = 20.09$  (Benli et al., 2012). Sep was also identified as either hydrophobic or hydrophilic, and then it was found that hydrophilic repulsion is dominant according to van Oss's (1994) classification. However, computational molecular simulation results of the same study clearly showed that Sep basal surfaces, even talc-like surfaces, are hydrophobic (Benli et al., 2012). The results were also compared with contact angle measurements via the capillary rise technique. The implications behind hydrophobic material are not enough to explain why the electron donor component of Sep surfaces is much greater than its electron acceptor component. A possible explanation for the larger  $\gamma_s^-$  value of Sep could be attributed to

extractable components such as soil organic matter because HA have a large number of free and bound phenolic –OH and carboxylic –COOH groups arising from the natural environment and groundwater (Arnarson and Keil, 2000; Wall and Choppin, 2003; Tombacz et al., 2004; Feng et al., 2005).

Soil organic matter adsorption on clay mineral surfaces and their influence on the solution chemistry (e.g. ionic strength, pH, and soluble cations) have been extensively explored (Arnarson and Keil, 2000; Feng et al., 2005). However, direct measurements focusing on the relationships between viscosity and HA content are scarce; only a study on the effect of grinding on the rheology of Sep dispersions in acid and alkaline media (Çınar et al., 2009) and a few observations on the macromolecular structures of HA (Caceci and Billon, 1990; Pokorna et al., 2001; Zhao et al., 2013) are available. Çınar et al. (2009) showed that Sep dispersions exhibit viscosities practically close to zero at pH 12. This kind of change in viscosity was ascribed to the disruption of the particle network. On the other hand, Pokorna et al. (2001) suggested that carboxylic groups in HA with acidic pH are largely nonionic (R-COOH), whereas with alkaline pH carboxylic R-COO<sup>−</sup> groups are more dominant. Various groups ionised in HA and relatively more negative charges could lead to more hydrophilic Sep surfaces. Such interesting behaviour led us to investigate the role of HA in the flow behaviour of Sep with alkaline and highly alkaline pH values.

The aim of this study was therefore to show if HA content in the Sep matrix can modify the rheological and interfacial properties of

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**Table 1**  
Mineralogical analysis of natural sepiolite samples.

Samples	SiO <sub>2</sub> mass%	MgO mass%	Sepiolite content %	Mineral	Formula
SepTT	49.85	20.15	85	Sepiolite	Mg <sub>4</sub> Si <sub>6</sub> O <sub>15</sub> (OH) <sub>2</sub> · 6H <sub>2</sub> O
				Dolomite	CaMg (CO <sub>3</sub> ) <sub>2</sub>
				Albite	(Na, Ca) Al (Si, Al) <sub>3</sub> O <sub>8</sub>
				Quartz	SiO <sub>2</sub>
				Calcite	CaCO <sub>3</sub>
SepKS	52.66	21.76	60	Sepiolite	Mg <sub>4</sub> Si <sub>6</sub> O <sub>15</sub> (OH) <sub>2</sub> · 6H <sub>2</sub> O
				Quartz	SiO <sub>2</sub>
				Dolomite	CaMg (CO <sub>3</sub> ) <sub>2</sub>
				Calcite	CaCO <sub>3</sub>
				Albite	(Na, Ca) Al (Si, Al) <sub>3</sub> O <sub>8</sub>
SepSG	51.84	20.06	50	Sepiolite	Mg <sub>4</sub> Si <sub>6</sub> O <sub>15</sub> (OH) <sub>2</sub> · 6H <sub>2</sub> O
				Dolomite	CaMg (CO <sub>3</sub> ) <sub>2</sub>
				Albite	(Na, Ca) Al (Si, Al) <sub>3</sub> O <sub>8</sub>
				Quartz	SiO <sub>2</sub>
				Calcite	CaCO <sub>3</sub>
				Montmorillonite	Na <sub>0.3</sub> (Al, Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> · 4H <sub>2</sub> O

Sep dispersions in highly alkaline media. The understanding of the mechanisms controlling clay mineral response to pH changes is important for evaluating the rheological and interfacial behaviour of the surrounding media: in this case, controlling the viscosity of Sep dispersions depending on the extent of hydrophobicity or wettability in industrial applications.

## 2. Materials and methods

### 2.1. Materials

All Sep samples were obtained from the AEM Company in the Sivrihisar region of Turkey and labelled SepTT, SepKS and SepSG for Turktaciri, Kurtseyhi and Sıgırcık, respectively. Quantitative chemical analyses were carried out by ICP (inductively coupled plasma) spectrophotometry in the ACME Analytical Lab., Canada. Table 1 represents the main constituents of chemical analysis and mineralogical characterization of the Sep samples with a Shimadzu XRD-6000 (Shimadzu Corp., Tokyo, Japan) equipped with a Cu X-ray tube ( $\lambda = 1.5405 \text{ \AA}$ ). Analytical grade sodium salt of humic acid (HA) was purchased from Sigma-Aldrich Inc., MO, USA. The stock solution of HA was prepared by dissolving 25 mg of dry HA in 1000 mL of deionised water. After stirring overnight, the prepared solution was then pre-filtered through 0.22  $\mu\text{m}$  nitrocellulose filter membranes (Millipore Corp., MA, USA) under the applied pressure of an N<sub>2</sub> gas cylinder. Systematic studies on pH were enabled with the addition of dilute HCl and 0.01 M KOH. Bi-distilled water was also used throughout the study.

### 2.2. Rheological measurements

First, 5 mass% of Sep dispersion was stirred for 15 min via a magnetic stirrer at the desired pH. Prepared dispersion was then re-agitated for 2 min at 20,000 $\times g$  with an Arcelik brand mixer to obtain highly dispersed fibres. Flow behaviour (thixotropy, viscosity and yield stress) was measured by the R/S plus Soft Solids Tester in a controlled stress rotational rheometer featuring a CC458 model R/S coaxial spindle (Brookfield Engineering Laboratories, Inc., MA, USA) under laboratory conditions. All rheological measurements were conducted at 25 °C. Collection and evaluation of rheological data were accomplished with Brookfield Rheo-2000 V2.8 software (Brookfield Engineering Co., MA, USA) with a three-step program contains: The shear rate was increased from 0 to 1000 s<sup>-1</sup> over for 400 s, held at 1000 s<sup>-1</sup> for 1 min and then ramped down from 1000 to 0 s<sup>-1</sup> for another 400 s. Finally, each sample was performed a hysteresis loop.

### 2.3. Preparation of alkaline modified sepiolite

Sep dispersions (5 mass%) were shaken for 30 min under alkaline conditions (pH 8.5–11.5) and centrifuged at 6000 $\times g$  for 2 min. The supernatant was then filtered using with 0.45  $\mu\text{m}$  syringe membrane filters (Millipore, Corp., MA, USA) and analysed according to method 5910B (Eaton and Franson, 2005) by a UV-visible spectrophotometer (UV-160A, Shimadzu, Japan) at 254 nm ultraviolet wavelength (UV<sub>254</sub>). UV<sub>254</sub> also known as a water quality test parameter, which utilizes light at the 254 nm wavelength to be able to detect organic matter in water and wastewater. This is due to the fact that most organic compounds absorb light at the UV wavelength 254 nm. Mohammadi et al. (2012) shows that there is a significant linear relationship between humic acid concentration and UV<sub>254</sub> absorbance. Hence, the corresponding UV<sub>254</sub> absorbance values can be taken as an indication of the level of HA concentration. When UV<sub>254</sub> increases, the humic acid content increases.

Changes in the level of free Mg<sup>2+</sup> ions within the supernatant were directly measured by an Atomic Absorption Spectrophotometer (Varian AA240FS, Agilent Technologies, CA, USA). After phase-separation of supernatant in centrifugation, alkaline modified Sep samples were washed several times with fresh bi-distilled water, re-centrifuged and decanted until their pH reached to the initial pH; finally, all modified samples were dried at 60 °C overnight. These samples were also used for HA loading studies. After 50 ppm of HA was added to the 5 mass% of Sep dispersion, HA loaded samples were shaken for 24 h under natural pH. For the mechanical activation of HA loaded samples, they were re-agitated for 2 min at 20,000 $\times g$  with an Arcelik brand mixer.

### 2.4. Contact angle measurements and surface free energy determinations

Water contact angles of Sep fibres were measured by a Sigma 701 tensiometer (KSV Instruments Ltd, Helsinki, Finland) with the capillary rise method (Benli et al., 2012). A Sep sample of 0.5 g (– 150  $\mu\text{m}$  particle size) was placed in a standard tube of 9 mm internal diameter; the bottom was replaced with a filter paper of 16,000 cm<sup>2</sup> mesh density, the tube was tapped approximately 50 times and finally it was compressed tightly with a metal rod until the bed height no longer changed. During the experiments, once the gauze was in contact with the surface of the wetting liquid, the mass of absorbed liquid was automatically recorded. The relation between the rate of capillary rise and penetration time in such a porous system is given by a modified Washburn equation (Parry et al., 2008):

$$m^2 = \cos \theta \frac{C_w \rho_L^2 \gamma_L t}{\eta_L} \quad (1.a)$$

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