



Sepiolite and sepiolite-bound humic acid interactions in alkaline media and the mechanism of the formation of sepiolite-humic acid complexes



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ABSTRACT

The surface-controlled reactions and interfaces of clays and/or clay minerals are strongly determined by the adsorption of dissolved humic substances which have surface active characters. Consequently, this may lead to an improved understanding of organo-clay complexes for remediation purposes of polluted areas. The interactions between sepiolite and sepiolite-bound humic acid (HA), and its influence on the mechanism of the formation of sepiolite-humic acid complexes were examined by characterizing the structure of sepiolite through UV/Vis spectroscopy, field emission scanning electron microscopy (SEM + FEG), specific surface area, pore size and volume, and Fourier transform infrared spectroscopy (FTIR). The UV-vis spectral results of the raw sepiolite showed that there is no correlation between UV₂₅₄ and the amount of humic substance released from sepiolite is dependent on increasing extraction time. The low values of humification index of the sepiolite confirmed the presence of HA with higher, and similar molecular weight, particle size, humification degree and aromaticity. Hence, it can be concluded that HA groups are presumably associated with the large quantity of silanol groups located on the sepiolite external surface preferentially through H-bonds and/or surface complexation interactions between the functional groups in HA and dissolved metal cations (Mⁿ⁺). This finding is in good agreement with results from FTIR and SEM-FEG investigations. EDAX analysis of the HA-extracted sepiolite illustrated a strong decrease in Mg²⁺, Ca²⁺ and K⁺ content indicating that electrically charged sites on HA may form metal complexes of high stability through chelation.

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1. Introduction

Humic materials are the most widely-spread natural complexing ligands occurring in nature. One of the main functions of dissolved humic materials in the environment is to remove toxic metals, anthropogenic organic chemicals, hydrophobic (including PAHs) and other pollutants from water (Peña-Méndez et al., 2005; Shin et al., 1999; Radian and Mishael, 2012). The higher solubility and mobility of the pollutants in the presence of dissolved humic materials due to their ability to reduce surface tension of water, result in their binding to dissolved humic materials. This can not only affect their transport and aqueous concentration but it can also influence their chemical degradation, photolysis, volatilization, toxicity, and bioavailability (Chiou et al., 1986; Spitzzy and Leenheer, 1991; Rav-Acha and Rebhun, 1992; Kordel et al., 1997; Frimmel, 1998; Laor et al., 1998; Frimmel and Christman, 1988; Frimmel et al., 2002). It has also been known that dissolved humic substances, such as humic acid (HA, insoluble at acidic pH) and fulvic acid (FA, water soluble at acidic to alkaline pH), are complex and heterogeneous mixtures of polydispersed materials, negatively charged due to

the presence various chemically reactive functional groups, including carboxylic (—COOH) and phenolic —OH groups on aromatic and aliphatic chain, with pH-dependent properties (Gu et al., 1994; Vermeer et al., 1998; Vermeer and Koopal, 1998; Chen et al., 2007). FA has a higher amount of carboxylic and phenolic groups (higher molar mass), contains more carbon, and is less soluble compared to HA, which consists of a more aromatic structure (Stevenson, 1994). The major reason for the importance of FA and HA in soil/clay chemistry, sediment biogeochemistry and environmental reactivity is the presence and position of the functional groups (particularly carboxyl and phenolic hydroxyl groups), which make FA and HA effective in cation exchange and complexation reactions (Tan, 1986; Simpson et al., 2006).

Among the inorganic substances that constitute the soils, clays and metal oxide minerals are the most abundant, and their surface-controlled reactions and interfaces are strongly determined by the adsorption of dissolved humic substances which have surface active characters. As a consequence, this characteristic could improve the understanding of organo-clay complexes for the purpose of contaminated soil remediation. Some of the dominant factors influencing the nature of complexation between dissolved humic substances and clays are (i) the nature of the clay mineral (surface chemistry, specific surface area, pores), (ii) environmental conditions such as pH, ionic strength,

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composition of cations, anions, etc., and (iii) the nature the dissolved humic substances that are often interdependent (Theng, 2012). Researchers have extensively investigated the influence of the change in solution conditions (e.g. nature of exchangeable cations, medium pH and ionic strength, molecular weight of humic substances) on dissolved humic substances (FA/HA) adsorption on clay mineral surfaces (Mortland, 1970; Greenland, 1971; Baham and Sposito, 1994; Schlautman and Morgan, 1994; Arnarson and Keil, 2000; Satterberg et al., 2003; Feng et al., 2005). It is apparent that while the process of selective adsorption of dissolved humic substances onto clay surfaces is generally accepted, there is considerable variation due to the heterogeneities and complexity of humic substances in their composition and conformation that are reported to be preferentially sorbed (Nayak et al., 1990; Murphy et al., 1994; Collins et al., 1995; Vermeer and Koopal, 1998; Vermeer et al., 1998; Namjesnik-Dejanovic et al., 2000; Khalaf et al., 2003; Wang and Xing, 2005; Feng et al., 2006; Chilom and Rice, 2009). Furthermore, adsorption of FA/HA on minerals is dependent on clay-polyvalent ion like Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , and on the surface properties of the mineral (Varadachari et al., 1991; Varadachari et al., 1994; Varadachari et al., 1995; Kretschmar et al., 1997; Tombácz et al., 1998; Furukawa, 2000; Specht et al., 2000; Chorover and Amistadi, 2001; Książopolska, 2001; Balcke et al., 2002; Kaiser and Guggenberger, 2003; Feng et al., 2005; Majzik and Tombácz, 2007; Martinez et al., 2010; Książopolska and Pazus, 2011; Zhang et al., 2012; Ding et al., 2013). As a result, the differences in type of clay minerals would lead to different combinations of adsorption mechanisms (Evans and Russell, 1959; Werhaw, 1986; Theng and Tate, 1989; Wershaw and Pinckney, 1980; Zhou et al., 1994; Ohashi and Nakazawa, 1996; Wattel-Koekkoek et al., 2001; Wattel-Koekkoek, 2002; Saada et al., 2003; Tombácz et al., 2004; Majzik and Tombácz, 2007; Sposito, 2008). Most of these studies have focused on the interaction between dissolved humic substances and the crystalline clay minerals such as kaolinite (typical two-sheet phyllosilicates), vermiculite (the expanding three-sheet phyllosilicates), smectite (strongly expanding three-sheet phyllosilicates), chlorites (four-sheet silicates). These are bound to the soils but also to the layer-fibrous structure clay minerals such as the palygorskite and sepiolite including dissolved humic substances. However very little work has been published regarding their relevance to many aspects of surface and environmental chemistry. An attempt was made by Benli (2014) to present the effects of humic acid release from sepiolite on its interfacial and rheological properties of alkaline dispersions. The results observed that highly alkaline pH caused an increase in the total amounts of HA and free ions in relation to the formation/precipitation of both hydrophobic HA aggregate and HA-Mg^{2+} complexes which have a spherical shape in the size range of $18\text{--}63 \pm 8$ nm at pH 11.5. Based on these findings, alkaline environment also results in significant changes in the surface properties of sepiolite from the anisotropic to the higher hydrophobic level like natural hydrophobic minerals, e.g. talc. In an early technical note (Singer and Huang, 1989) it was shown that the effect of pH and heat activation on the adsorption behavior of humic acid was obtained from a typical Cryoboralf on the sepiolite used from Vallecas and the palygorskite from Florida. Humate adsorption on both palygorskite and sepiolite at pH 6.5 was found to increase with increased initial humate concentration, and decrease with preheating the clay samples and then considerably dispersing in the humate solutions. Golden et al. (1985) also investigated the instability of palygorskite and sepiolite taken from the same region under slightly alkaline conditions (0–8 mmol NaOH) to determine the transformation of palygorskite and sepiolite to smectite under laboratory conditions. In a similar manner, the study about the behavior and stability of the Vallecas sepiolite in aqueous solutions of neutral and weak alkaline (0.04 N NaOH) conditions at room temperature have been conducted by Martinez-Ramirez et al. (1996) Collectively, these two studies indicate that palygorskite treatment for 24 days in these media yielded a smectite, and that after 24–28 days in similar conditions, the sepiolite is destroyed gradually, e.g. produced small surface structural changes. Currently, there is no published research on the structural and functional characterization

of sepiolite-complexed dissolved organic matter and the corresponding interaction mechanisms of humic substances with sepiolite surfaces in order to better understand the adsorption and colloidal-rheological environmental applications of sepiolite.

The clay minerals palygorskite and sepiolite occur in many arid and semi-arid soils (Kadir et al., 2002). They are both fibrous in form, a characteristic dictated by their chain-type (linear) structure and are predominantly silico-magnesian containing varying amounts of Al^{3+} , K^+ , Ca^{2+} , Fe^{2+} , Fe^{3+} ions. They contain hydroxyls, zeolitic and bound water. Sepiolite and organo sepiolite have a significant potential as alternative adsorbents. This is due to their inherent strong sorption and complexation ability (mainly due to their high surface area, to their structural channels running parallel to the fibre length, and to their pores) toward various environmental pollutants of concern. This coupled with their environmental compatibility and cost effectiveness makes them ideal alternative adsorption materials for a wide range of industrial and pharmaceutical wastewater treatment applications.

The purpose of the present study is to develop an understanding of the interactions between sepiolite and humic acid bound to sepiolite, and their impact on the mechanism of sepiolite-humic acid complexes formation with a view to optimize the adsorption capability of the system. Two different approaches have been used to study the sepiolite-complexed organic matter. One involves the gradual removal by extraction of the humus substances from the sepiolite and replacing it by humic acid and the other is to understand the relations between surface complexation, and their nature in the sepiolite-organic matter system.

2. Materials and methods

2.1. Materials

Sepiolite used in the experiments is natural, non-swelling fibrous clay from Sivrihisar-Kurtseyh occurring at the upper Sakarya Section of Central Anatolian Neogene Basins southeast of Eskisehir, Turkey.

Inorganic chemicals such as HCl and NaOH used for adjusting pH and zeta potential measurements were obtained from Fisher Scientific, and all solutions were prepared using de-ionized water with a conductivity of 0.067 $\mu\text{S}/\text{cm}$.

2.2. Methods

Raw sepiolite was comminuted by two stage crushing in laboratory jaw and roll crusher to prepare samples <2 mm as a starting material, and it was then dry ground in a vibrating ball mill for short grinding time at 25 min to avoid the structural deformation (Vučelić et al., 2002; Kojdecki et al., 2005). Particle size distribution of ground samples was analyzed by a technique based on laser light scattering using MALVERN Mastersizer 2000.

The density of both sepiolite samples was measured using a Quantachrome Ultracycrometer 1000, and bulk density was measured with Haver bulk density tester according to EN 1097-3 standard (1998). The BET surface area, pore volume and average pore diameter of sepiolites before and after extraction experiments were determined using the Quantachrome instrument using nitrogen gas adsorption at -196 °C. Before each measurement all samples were outgassed for 10 h by heating 50 °C (Sarıkaya, 1981) under vacuum.

Chemical analysis of the sepiolite was determined with an X-ray fluorescence (XRF) spectrometer (Rigaku ZSX Primus II XRF). X-ray powder diffraction patterns (XRD) of the tested sepiolite samples were measured by Panalytical X Pert Pro MPD. Total organic carbon (TOC) measurement of the original sepiolite samples was carried out at Istanbul Technical University EMCOL Labs in Turkey. A JEOL JSM-7100F field emission scanning electron microscope (SEM-FEG) equipped with a Link System energy dispersive X-ray (EDX) microanalyser was used to observe the textural features of natural and humic acid extracted sepiolite. Fourier transform infrared spectra (FTIR) were recorded on the Agilent Cary 640 FTIR high

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