



Research article

Surfactant properties of humic acids extracted from volcanic soils and their applicability in mineral flotation processes

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ABSTRACT

Surface Tension (ST) of water solutions of humic acids extracted from volcanic ash derived soils (soil humic acids, S-HA), were measured under controlled conditions of pH (13.0), temperature (25 °C) and ionic strength (NaOH 0.1M) to establish the Critical Micellar Concentration (CMC). All S-HA were characterized by elemental analysis, acid-base titration, Transmission Electronic Microscopy (TEM) micrographs, isoelectric point (IEP) and solid state ¹³C-NMR. After that, these humic acids were evaluated as potential biomaterials to be used in mineral flotation processes, where a series of experiments were conducted at different S-HA and molybdenite ratio (from 0.2 to 50 g ton⁻¹) establishing the IEP of all resultant materials. The use of solid state ¹³C-NMR enabled the following sequence of intensity distribution areas of S-HA to be established: O/N Alkyl > Alkyl C > Aromatic C > Carboxyl. The experimental values of ST and the calculated CMC (ranging from 0.8 to 3.3 g L⁻¹) revealed that for S-HA no relationship between the abundance groups and their behavior as surfactant materials was observed. In relation with IEP determined for all materials, the highest surface charge, which can be useful for flotation processes, was obtained with 0.2 g of S-HA per ton of molybdenite. Additionally, TEM studies confirm the formation of pseudoaggregates for all the S-HA considered. Finally, the S-HA could be considered as an alternative to chemical products and commercial humic acids materials in mineral flotation processes.

1. Introduction

Soils derived from volcanic materials located in Chile, represent about 69% of the arable area being those classified as Ultisols and Andisols the most significant. Ultisols has low organic matter content, with a transition of their inorganic fraction to more crystalline structures. By the other side, Andisols are modern soils of volcanic origin, with predominance of low crystallinity inorganic compounds and higher organic matter content than Ultisols.

The organic matter (OM) content of Chilean volcanic soils ranges from 4 to 35% in superficial horizon (Galindo et al., 1992). Considering this important amount of OM, soils properties such as active/free iron oxide ratio, isoelectric point (IEP), cation exchange capacity (CEC), and potassium-calcium cation exchange equilibrium have been related to

this important organic component mainly in Chilean Andisols and Ultisols (Escudey et al., 2004).

Humic substances (Natural Organic Matter) widely found in soils, between other environmental matrix was defined as a natural poly-electrolyte organic compounds with complex structures (Schnitzer and Khan, 1972; Stevenson, 1994). Since humic acids (HA) are soluble, they influence the migration of organic pollutants in the environment. The interaction mechanisms of HA with organic contaminants remain unclear, considering that most of these substances contain functional groups, e.g. carboxylic, phenolic, hydroxyl, carbonyl, amines, amides and aliphatic fragments. However, these interactions have been largely justified on the basis of HA detergency characteristics (von Wandruszka, 2000). Very early, Wershaw et al. noted that HA molecules were self-assembled compounds dispersed in the soil solution

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bearing micelle type supramolecular structures (Wershaw et al., 1977). Many authors (Guetzloff and Rice, 1994; Kerner et al., 2003; Quadri et al., 2008; Quagliotto et al., 2006) have tried to demonstrate that HA has the ability to form micelle-like structures, similar to those formed by synthetic surfactants. The ability to form such structures depends on the length and flexibility of the constituent chains, as well as, on the existence of internal hydrophobic and external hydrophilic groups, e.g. carboxylic, phenolic and hydroxyl.

Recently an interesting review (Salati et al., 2011) collects values of critical micellar concentration for HA extracted from different kind of sources, such as organic wastes, green wastes and composting, indicating the decrease of surface tension below a critical point and the subsequent aggregates (micelles) formation, wherein the difference of the values reflect both its origin and management (Quadri et al., 2008; Rosen and Kunjappu, 2012).

Various studies have suggested that HA are amphipathic species, which implies that their behavior on solution may involve the formation of pseudomicelles and aggregates that are similar to those formed by the synthetic surfactants (Guetzloff and Rice, 1994; Kelleher and Simpson, 2006; Quagliotto et al., 2006). A model proposed by Conte et al. (2005), suggests the formation of relatively small sub-units that are associated through the weak molecular interactions that form pseudo-micellar aggregates (Conte et al., 2005). It is believed that HA pseudo-micellar aggregates can be formed by intermolecular enrollment and association, depending on the structural characteristics and the poly-dispersion of the respective HA (von Wandruszka, 2000).

The HA surfactant properties through their poly-functionality might allow their use as foaming reagent during processes associated to the concentration of Sulphur minerals via froth flotation, as it has been proposed previously (Reyes-Bozo et al., 2011a) with HA provenient from biosolids and other synthetic products. Also, it has been reported the adsorption of HA onto Sulphur minerals such as chalcopyrite, molybdenite, and pyrite (Reyes-Bozo et al., 2015) and the impact on the floatability of these substances (Reyes-Bozo et al., 2011b, 2014). During the process of the froth flotation, the use of surfactant substances that are adsorbed in the air-water interphase allow the generation and the stabilization of foams, which permits the separation of the mineral particles from the undesired gangue.

Considering the aforementioned information, in this work the results of the surfactant properties from HA extracted from volcanic soils are presented, establishing through their solid state characterization by ^{13}C -NMR it is possible to determine the existence or non-existence of a dependency of the CMC measured through the Du Nouy's ring tensiometer. Finally, the evaluation of a potential applicability in Sulphur minerals concentration processes, by the determination of the molybdenite surface charge in presence of this kind of material is done.

2. Experimental

2.1. Samples

2.1.1. Soils

Soil samples from southern Chile were collected from 0 to 0.20 m depth of uncultivated pasture areas of Collipulli (CLL, Ultisol), and the Andisols Ralun (RAL), Nueva Braunau (NBr), Frutillar (FRU), Osorno (OSR), Vilcun (VIL) and Temuco (TeM). All samples were air dried and sifted through a 2-mm mesh sieve. A description and characterization of samples is presented in Table 1.

2.1.2. Humic acids purification

The solid sample was equilibrated with 1 mol L^{-1} HCl, obtaining a suspension whose pH ranges between 1.0 and 2.0 at room temperature. The volume was then adjusted with 0.1 mol L^{-1} HCl to get a 10 mL liquid/1 g dry sample ratio. The suspension was centrifuged to separate the sediment (R1) from the supernatant (FA-1). R1 was neutralized (pH = 7.0) with a 1 mol L^{-1} NaOH solution, and then a volume of

0.1 mol L^{-1} NaOH was added under N_2 atmosphere to give a 10:1 final extractant to soil ratio. The extraction was carried out under N_2 atmosphere with occasional stirring for a minimum of 4 h. The alkaline suspension was left overnight and then the supernatant was separated by centrifugation. Subsequently, the supernatant was acidified with 6 mol L^{-1} HCl under constant stirring to get pH 1.0 and then allowed to stand for 12–16 h. The precipitated HA fractions and FA (FA-2) supernatant were separated by centrifugation. The precipitated HA was re-dissolved in a minimum volume of 0.1 mol L^{-1} KOH under N_2 ; solid KCl was then added to attain a 0.3 mol L^{-1} K^+ concentration and then centrifuged to remove the suspended solid. The HA was re-precipitated by adding 6 mol L^{-1} HCl under constant stirring until a pH = 1.0 was reached. The suspension was allowed to stand another 12–16 h, and then centrifuged, discarding the supernatant. The HA precipitate was suspended into a 0.1 mol L^{-1} HCl and 0.3 mol L^{-1} HF mixture and stirred overnight at room temperature (if necessary, repeating the acid treatment (HCl/HF) until the ash content be less than 1%). After centrifugation, the precipitate was transferred to a dialysis tube (Visking, Co.) using distilled water until the dialysed water gave a negative test for chloride (AgNO_3). After freeze-drying, the HA was kept refrigerated (Watanabe and Kuwatsuka, 1991).

2.2. Acid base titration

The total acidity was determined by acid base titration adding a measured excess of a barium hydroxide ($\text{Ba}(\text{OH})_2$) solution under N_2 and back-titrating the unreacted $\text{Ba}(\text{OH})_2$ with standardized hydrochloric acid (HCl) solution (Wright and Schnitzer, 1959). The carboxylic acid was quantified utilizing an excess of a calcium acetate ($\text{Ca}(\text{CH}_3\text{COO})_2$) solution under N_2 . The released acetic acid is titrated with a standard sodium hydroxide (NaOH) solution. Total and carboxylic acidity enables the phenolic acidity to be worked out. All determinations were performed out by triplicate.

2.3. ^{13}C -NMR solid-state

Solid-state ^{13}C NMR spectroscopy was performed in order to establish the intensity distribution of functional groups (Lüdemann and Nimz, 1973). Bruker 400 MHz Avance III HD spectrometer equipped with a 4 mm triple resonance probe was used. The cross polarization magic angle spinning technique was applied at a spinning speed of 14 kHz and a contact time of 1 ms. A pulse delay of 500 ms was used which was proven to be long enough to avoid saturation. The ^{13}C chemical shifts were referenced to external tetramethylsilane (= 0 ppm) and adjusted with glycine (= 176.04 ppm) as an external standard. For quantification, the spectra were subdivided into different chemical shift regions according to: alkyl C (0–45 ppm), N-alkyl/methoxyl C (45–60 ppm), O-alkyl C (60–110 ppm), aromatic C (110–160 ppm), carboxyl/amide C (160–185 ppm) and carbonyl C (185–245 ppm), (Lüdemann and Nimz, 1973). The relative ^{13}C intensity distribution was determined by integrating the signal intensity in different chemical shift regions with an integration routine supplied with the instrument software. Corrections concerning the intensity distribution of spinning side bands were made (Knicker et al., 2005).

2.4. Surface tension (ST)

Solution ST was measured using a Du Nouy ring tensiometer, model DCAT 11EC Dataphysic. The ring was cleaned between each measurement by washing first with methanol and finally held in a flame until it glowed red. Stock solutions were prepared by placing an amount of solid humic acid in 25 mL of NaOH 0.1 mol L^{-1} . This preparation contains around 12 g humic acid per liter, where the pH was maintained at 13. Diluted solutions were prepared by mixing the stock solutions with the appropriate volume of NaOH solution. All measurements were made at 25 °C controlled by a thermostat bath equipped

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