Original Article

Extraction and characterization of humic acid from coal for the application as dispersant of ceramic powders

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ABSTRACT

Subbituminous coal was employed as raw material for the extraction of humic acid (HA) to be applied as ceramic dispersant. The extraction process is described in detail, showing it is a relatively simple procedure, which makes the production attractive and feasible on a laboratory scale. The HA was characterized via elemental analysis, infrared spectroscopy (FTIR), thermal behavior (TGA/DTA), zeta potential, turbidity and microstructure by scanning electron microscopy (SEM). Carboxylic and phenolic groups were identified and consequently the structure and surface properties were related to the polyelectrolyte nature of HA. The absence of complex-forming metals was confirmed by FTIR and TGA. The alkalization increased the negative surface charges as verified by the higher zeta potential. SEM analysis showed an extended pattern of molecules; therefore the HA can perform with maximum steric effect at pH 11. HA is a good dispersant for the ceramic industry according to the results of the rheological investigation in an alumina suspension. The decrease of the suspension viscosity using HA was significant and the values are compatible to those necessary to ceramic processing. The data of the characterization of HA correlated well with the parameters achieved in the rheological tests.

1. Introduction

Natural humification is a gradual process that naturally takes thousands of years, giving rise to humic substances (HS). These HS can be obtained from carbonaceous substances by extraction methods based on their solubility, which allows their separation into humic acid (HA), fulvic acid (FA) and humin (Hu). HA is a dark fraction usually extracted in alkaline solution and insoluble in acid medium [1,2].

Initially Schulten and Schnitzer [3] proposed a structure for HA formed by alkyl benzene moieties attached through covalent bonds (Fig. 1). Later, Piccolo [4] proposed that it is a self-assembled superstructure with relatively small heterogeneous molecules held together primarily by hydrophobic
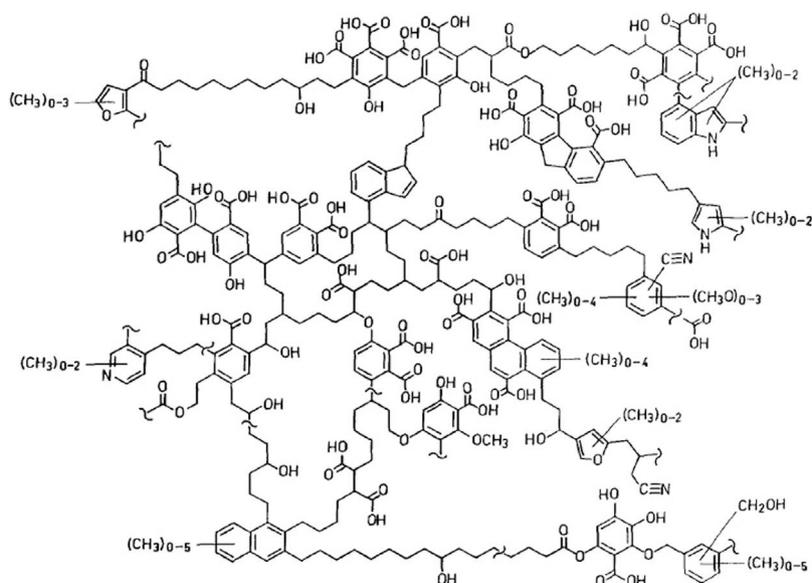
Fig. 1 – Superstructure proposed for humic acids.

dispersive forces and hydrogen bonds. These forces determine the conformational structure in the HA molecule. Given its superstructure, HA is a complex mixture in which there can be small, large, and polydisperse molecules [5]. Many authors ponder that HS have no precise and well-defined structure and properties, which depends on the source that generated them and the specific extraction conditions [6–8].

HA is the major component of natural organic matter in soil, water and sediments, so that HA can be obtained from any source of organic matter, among them peat and coal at different maturation degrees. The reserves of Candiota coal, Brazil's main coalmine, are approximately of one billion tons. The mining conditions are excellent, ensuring low cost of production (US$ 8–10/ton). However, due to the characteristics of this coal, such as high ash content and impurities, its use is restricted to the generation of energy. On the other hand, high availability and low price per ton are motivators for the expansion of its use in carbon chemistry. The use of low-rank coal for the synthesis of humic substances is the current focus of various industrial and academic research groups, in order to achieve a higher added-value product [6,9].

Researches involving coal for HA extraction basically aims to use this macromolecule as a soil fertilizer. However, HA has interesting surface properties, such as the presence of oxygenated functional groups, and an ability to interact with metals and metal oxides under different conditions [10–14]. Humic molecules have great potential to be used as a dispersant in ceramic suspensions, acting similarly to the polyacrylic acids commonly used with alumina [2,12,14].

The HA structure requires a complete characterization in order to properly evaluate its reactivity from a specific raw material, although the average properties of HA from different sources are comparable. In the same way, there is a necessity to study the mechanism of action when HA is in suspension with oxides particles [1,9]. Special attention should be given to the ceramic area since there is a shortage of researches on the application of HA in the ceramic industry.

Some studies have shown that the presence of organic matter and, hence, humic acids, has a strong influence on the deflocculation of clays [15]. However, the authors do not know specific studies on the extraction of HA and application as a ceramic dispersant.

Hidber et al. [16] have specified there is no ideal dispersant for all wet ceramic process. For a specific process, a dispersant might be effective in a limited pH region; another process might need a dispersant for a wide pH range. Therefore, the investigation of the HA as a dispersant in the present work, might contribute to the selection of a better dispersant for a specific process.

In this work, HA was extracted from subbituminous coal and characterized according to the usual tests, i.e., elemental analysis, infrared spectroscopy (FTIR), thermal behavior, zeta potential, turbidity and microstructure by scanning electron microscopy. The HA surface properties were evaluated based on its action as a polyelectrolyte. The potential use of HA as dispersant for the ceramic industry was studied by rheological tests using alumina suspensions. The rheological behavior for slip casting process was evaluated.

2. Experimental

The raw material used in the extraction of humic acid (HA) was the subbituminous coal from Candiota mine (southern of Brazil), with mean diameter of 0.032 mm determined by laser granulometry (Cilas 1180). The proximate analysis of coal revealed 53.36% of ash content, 24.28% of volatile matter and 5% of total moisture. The ultimate analysis on dry ash free basis showed carbon content (68.61%), hydrogen (6.5%), nitrogen (1.18%), sulfur (2.57%), and oxygen (21.14%) as the difference.

The HA was extracted in a proportion 1:10 (coal:extractor) using a NaOH $0.5 \, mol \, L^{-1}$ solution, followed by stirring for 3 h. The suspension was allowed to stand for 12 h and then cen-

Elemental composition (Wt.%, d.a.f.[a])					Atomic ratio[b]	
C	H	N	S	O	H/C	O/C
68.79	5.29	1.10	1.18	23.64	0.92	0.26

[a] d.a.f., dry and ash free basis.
[b] H/C, (%H/1.00)/(%C/12.01); O/C, (%O/16.00)/(%C/12.01).

trifuged. The dark supernatant, which contained the HA, was acidified with concentrated HCl under constant stirring until the pH 2 was reached. The mixture was stirred for 30 min and allowed to stand for 12 h. The precipitated humic acids were separated from the soluble fulvic acids by centrifugation (HA is insoluble in acidic medium). For the removal of inorganic contaminants, purification was carried out by adding 0.2 L of 5% HCl/HF solution 1:1 (v/v) to the HA. The mixture was stirred for 2 h and centrifuged. The purified HA was washed twice with deionized water and dried at 60 °C.

The HA elemental composition was determined by Elementar Vario Macro analyzer, and oxygen was calculated as the difference after correcting the C, H, N and S for an ash-free basis. FTIR analysis on Shimadzu IRAffinity-1 spectrophotometer (spectral range of 4000–400 cm^{-1}). Thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out on thermobalance Mettler Toledo TG/SDTA 851e, using synthetic air at 10 °C min^{-1} from room temperature up to 800 °C. The surficial properties were analyzed by zeta potential (Nano Z, Malvern, UK), Turbidity (TB-1000, MS Tecnopon Instrumentation, BR) and scanning electron microscopy (JSM 6060, Jeol, USA). SEM was performed at 10 kV after drying the acid (pH 3.5) or alkaline (pH 11) suspensions in stove at 50 °C and metalizing the HA particles with gold. In zeta potential, superficial charges were monitored with the pH variation of a 0.01 g L^{-1} HA solution. The pH was adjusted with NaOH or HCl solution and the ionic strength was kept with KNO$_3$ 10^{-3} M. The turbidity was performed with 0.02 L of an HA/NaOH (0.1 mol L^{-1}) solution in a concentration of 0.25 g L^{-1}. Since turbidity measures the presence of solids in a suspension, the experiment started with an alkaline solution (in which case the HA was dissolved), and then the suspension was acidified with HCl solution (1 mol L^{-1}). The rheological tests were performed in a viscometer Brookfield, RVDV-II+ (USA, Spindle SC4-18) to the deflocculation curve and in a Brookfield, HBDV-II+ (USA, Spindle CP-40, with cone-plate geometry) to the flow curves. Alumina suspensions (60 wt%) were tested in pH 11 with increasing HA addition and without HA. The HA was previously dissolved in a NaOH solution (0.005 M) in a concentration of 3 g L^{-1}.

3.   Results and discussion

The chemical composition of the HA extracted from a subbituminous coal shows a great amount of carbon and oxygen on HA structure (Table 1).

The atomic ratios H/C and O/C values are close to those found for HA of low rank coal, and may be an indicative of a higher aromatic character HA [10,17,18]. The amount of oxygen can be related to the presence of functional groups on humic acid surface, and the same can be said about the presence of hydrogen (Table 1). These groups are primarily carboxylic and phenolic ones and their respective bands in the FTIR spectrum are shown (Fig. 2).

The FTIR spectrum shows the presence of aliphatic (bands 2900–2860 cm^{-1}, 1460 cm^{-1}) and aromatic components (1600 cm^{-1}). The oxygen-containing groups are represented by the ~3600 cm^{-1}, 2600 cm^{-1}, 1715 cm^{-1}, 1200 cm^{-1} bands, on which the last two bands are attributed to C=O stretching, and to CO stretching and OH deformation on the COOH group, respectively. Specific details of these parameters can be found elsewhere [17].

HA is a practically pure product during the extraction process as it is separated from other fractions of organic substances and from the ashes initially present in the coal composition. A little quantity of inorganic constituents on HA is expected, and was found to be 5% according to the thermogravimetric data (Fig. 3). Humic acid may significantly differ regarding its inorganic constituents, depending on the differences in extraction and purification process. In general, HA ashes consist mainly in components of Si and Al; smaller amounts of alkaline/alkaline earth elements, Fe and Ti, as well as trace amounts of heavy metals [9]. The purification step with HCl/HF solution seemed to be efficient to remove the inorganics, as can be seen by the small band at 1100 cm^{-1} (due to the Si–O stretch) and the low resolution of bands below 760 cm^{-1} (due to mineral components) in FTIR spectrum (Fig. 2). This is an important feature to the utilization of HA since higher amounts of impurities could be prejudicial to the stabilization of a ceramic suspension.

The TGA curve showed three distinct steps of HA decomposition (Fig. 3): (1) moisture evaporation up to ~100 °C (5% weight loss); (2) breakdown of the carbohydrates and loss of carboxyl, methyl, methylene and alcohols groups as well as the loss of unsaturation between 100 and 300 °C (5% weight loss); (3) oxidation of the carbon chain and polycondensation of the aromatic structures between 300 and 650 °C (85% weight loss). DTA curve shows that two-exothermic events denotes 85% of weight loss. The first, with maximum temperature at ~350 °C, represents the decomposition of single bonds in the aliphatic chain, whereas the second corresponds to the thermal-oxidation of aromatic rings and loss of phenolic groups, since the last undergo degradation at temperatures above 400 °C. These aromatic moieties are derived from the lignin present in the higher plants that gave rise to coal and were formed during the extraction process of humic acid. The low decomposition temperature of HA assures a minimum interference in firing/sintering of ceramic pieces.

According to the TGA and FTIR data, there is no evidence of HA-metal ions complexation on the structure. The TGA data showed complete degradation of HA at 600 °C leaving a small amount of inorganics on the composition (Fig. 2). The presence of complexes could rise the final decomposition temperature. Similarly, FTIR spectrum showed the absence of vibration bands of carboxylate ion at 1370 cm^{-1} (Fig. 3). Since the great affinity of the humic molecules with metal ions is known, the absence of complexes is an important feature for the HA regarding to its polyelectrolyte action, and means that its charges are available to act in solution.
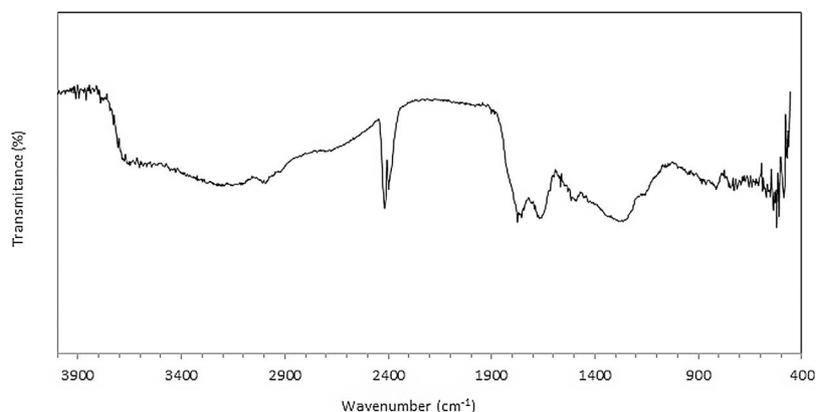
Fig. 2 – Infrared spectra of the extracted HA.
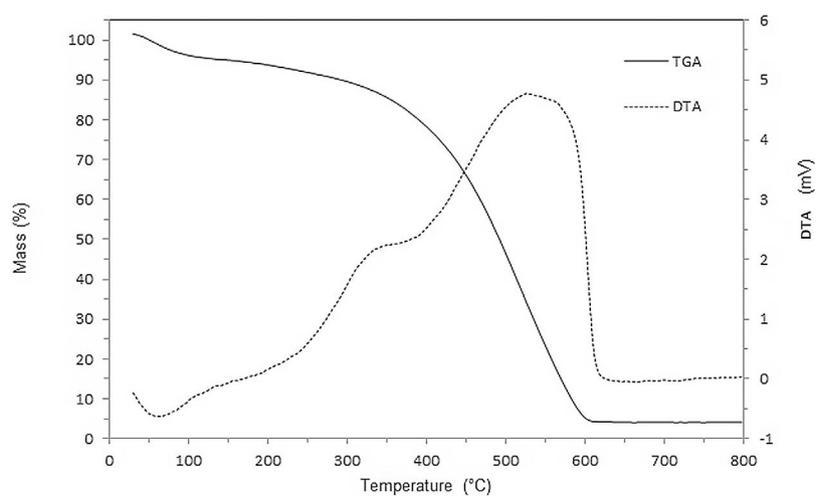
Fig. 3 – Thermogravimetric and differential thermal analysis of humic molecule.
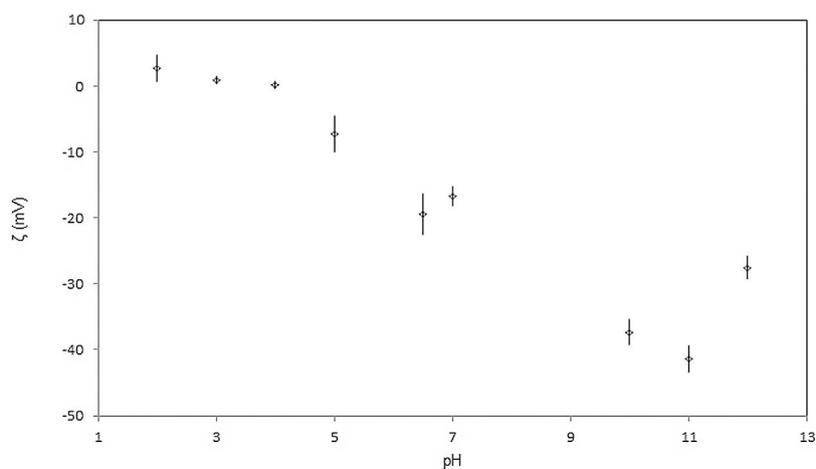
Fig. 4 – Zeta potential of the HA (0.01 g L^{-1}).

The HA molecules in alkaline medium presented higher zeta potential value (-42 mV) at pH 11 (Fig. 4). In ceramic suspensions, this is a good value to cause interparticle repulsion and slip stabilization. The negative sign is concerning to the formation of negative charges on the HA surface due to the presence of functional groups, and these have the ability to
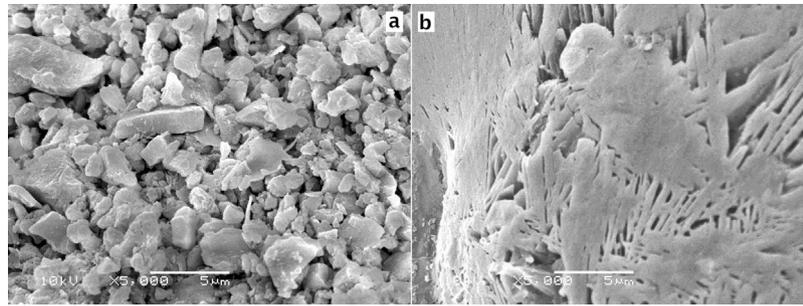
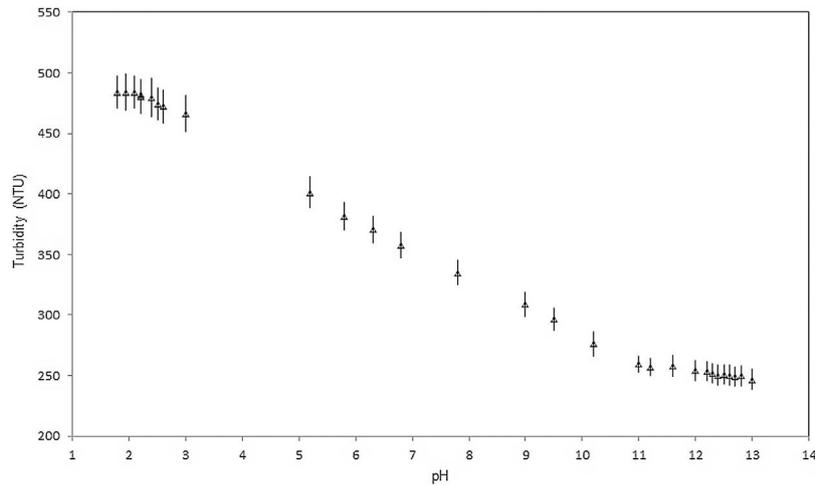Fig. 5 – HA microstructure at acidic (a) and alkaline medium (b).

Fig. 6 – Turbidity curve of the HA in aqueous solution (0.25 g L^{-1}).

change signal according to the pH of the solution [2]. This provides to HA its buffering power that directly affects the quality of the slip casting, which depends on the interaction among the dispersant molecules and the oxide particles in aqueous suspensions.

In acidic medium, the hydrogen is bound to the functional groups on the surface of the HA. The addition of NaOH in the solution cause the H$^+$ ions that were attached to the humic molecule bind to the OH$^-$ ions, resulting in an extensive deprotonation. Thus, zeta potential becomes more negative as the pH is increased (Fig. 4).

The hydrophobic character of HA in acidic medium due to protonation causes the chains to agglomerate like micelles, in order to reduce the free energy of the system, as postulated before [18]. The coiled configuration completely expels the water around the molecules and as a result the HA becomes insoluble and precipitates as showed on SEM analysis (Fig. 5a). On the other hand, the high density of negative surface charges that arise with increasing pH results in repulsion among molecules making them fully elongated and soluble (Fig. 5b). This elongated configuration is expected to be the best condition for ceramic suspension stability.

Turbidity measurements showed in Fig. 6 are in good agreement with the data obtained by zeta potential and SEM analysis. Turbidity occurs due to the presence of suspended materials, which affect the optical properties of the solution. The lowest turbidity values were measured at alkaline medium (Fig. 6), due to the solubilization of humic molecules. Increased turbidity value occurred with acidification of the solution until it reaches a critical value in which turbidity was maximum. This was attributed to the HA molecule agglomeration due to the reduction of surface charges. The highest turbidity values were found at pH ~3, where zeta potential showed to be the isoelectric point (IEP) of the humic molecules (Fig. 4).

According to the HA amphiphilic model, as pH decreases, the neutralization of negative charges occurs. At a critical point, aggregation is high enough to precipitation starts and then the surface tension is partially restored. Because of the increased hydrophobic nature of the HA in acidic region the interfacial adsorption and aggregation of the micelle type are favored [18]. This may explain the behavior of the HA surface properties in terms of zeta potential and turbidity.

The HA characteristics exhibited by means of zeta potential, turbidity and SEM analysis plays an important role in its applicability as dispersant in ceramic suspensions. The large amount of surface charges and the extended configuration, which occurs in very alkaline pH range (between pH 10 and 11), is in accordance of the results of Vermeer et al. [10]. They postulated that: "At high pH and low salt concentration the humic acid molecules are adsorbed relatively flat on the surface, but some parts of the molecule that are not in the direct vicinity of the surface protrude relatively far into the solution due to lateral repulsion effects". This fact, together with the
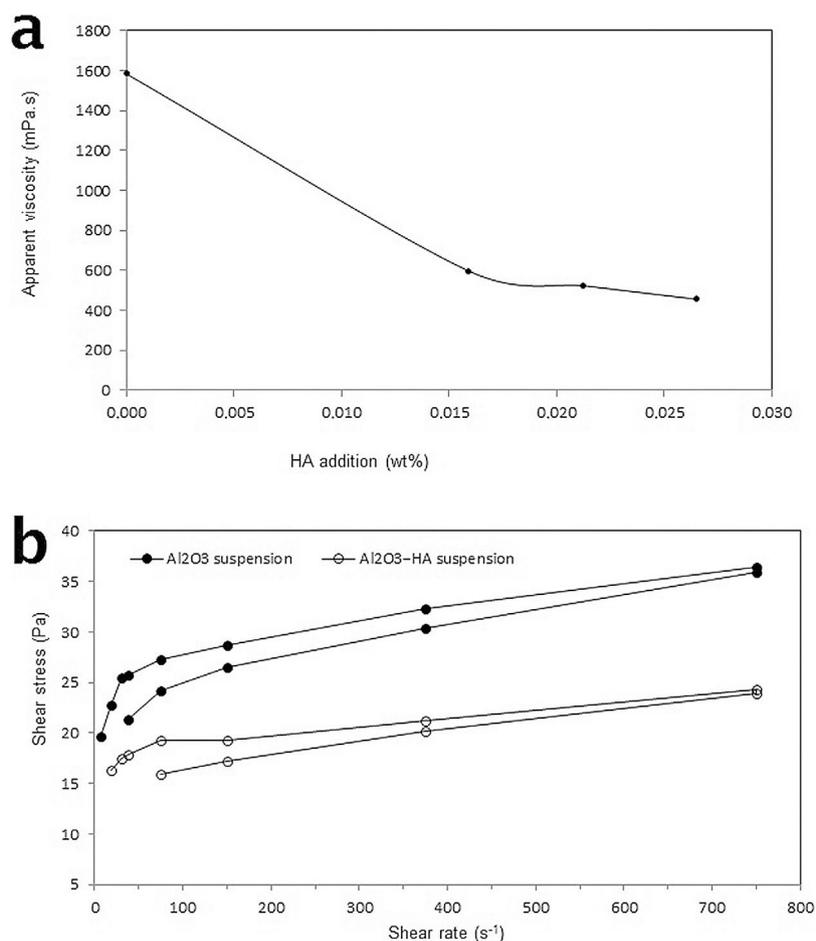
Fig. 7 – Rheology of an alumina suspension at pH 11 deflocculated with HA. Deflocculation curve at shear rate 13.2 s^{-1} (a) and flow curves (b).

high negative charge density at alkaline pH, is responsible for the electrosteric mechanism of the HA polyelectrolyte.

Fig. 7 shows that HA can act well for the dispersion of alumina suspensions, achieving a significant reduction in the suspension viscosity. In concentrated suspensions the particles are very close and tend to agglomerate. The HA can avoid agglomeration by increasing repulsive forces and by physical hindrance. As a consequence of that, the viscosity obtained with the HA is lower than that of the pure alumina suspension (Fig. 7a). The low viscosities achieved using HA at low shear rate (~500 mPa s at 13.2 s^{-1}) are good results for ceramic industry. As it is known, high content of solids and low fluidity are necessary, especially to the slip casting process [19]. Furthermore, the best rheological conditions using HA are shown in the flow curves (Fig. 7b). The suspension deflocculated with 0.016% HA exhibited typical characteristics of pseudoplastic behavior and slight thixotropy, which are required to the utilization of industrial ceramic suspensions [20]. Besides of that, the HA suspension reached good fluidity at lower shear rate, as a consequence of the decrease in both viscosity and thixotropy.

The yield of HA extraction from Candiota coal was 1.2% based on the initial organic matter. This value represents in practice and in the tested conditions that for each one kilo-

gram of coal will be extracted HA enough to act as dispersant in approximately 30 L of alumina suspensions. This fact is very attractive especially considering the low price of this coal per ton and its great availability. In addition, it provides data not yet published in this line of research.

4. Conclusions

The surface properties and polyelectrolyte nature make the HA an excellent candidate for the dispersion of ceramic suspensions. The characteristic of HA that makes it interesting as a dispersant is the existence of negative surface charges due to the oxygenated functional groups and the availability of such charges in solution. The results found (TGA/FTIR) also show the absence of metallic complexes in the humic molecule.

The results shown that the alkaline range (pH 10–11) is ideal for HA utilization as dispersant due to a higher zeta potential and a lower turbidity. The extended configuration of the molecule reinforces its performance by both electrostatic and steric mechanisms. Rheological findings correlated well with the higher efficiency of HA at this pH, which also confirmed the extended configuration of the HA molecule and its rela-

tion to improve the repulsive forces in suspension, promoting powder dispersion.

Tests of the use of HA as dispersant in alumina suspension showed the ability of the HA to reduce the viscosity, reaching the necessary values for industrial use. Likewise, the deflocculated suspensions showed a typical rheological behavior of pseudoplastic fluids, which is also required for the ceramic casting process by slip casting. Through the proposed characterization tests it was possible to estimate the best parameters for the deflocculation of the alumina slip. In other words, characterization data of HA surface properties correlated well with its ability to promote repulsion between particles as well as the stabilization of the suspension in a near-ideal rheological condition.

HA can be extracted practically in any laboratory with basic infrastructure, employing simple and low cost process shown herein. HA with physical and chemical characteristics similar to those of other commercial polyelectrolytes may reduce our dependence on the traditional dispersants. By using a local organic material with high availability and low cost, such as coal or peat, HA can be obtained in the form of powder or in solution. These can be used as dispersant for suspensions of ceramic oxides, among other applications.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

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