



ADVANCES IN NATURAL ORGANIC MATTER  
AND HUMIC SUBSTANCES RESEARCH  
2008-2010

XV Meeting of the  
International Humic Substances Society  
Puerto de la Cruz, Tenerife, Canary Islands, 27 June - 2 July 2010

Proceedings  
Vol 3



J.A. González-Pérez, F.J. González-Vila, G. Almendros Eds





## **pH Effect in Aquatic Fulvic Acid From Brazilian River**

Sérgio da Costa Saab<sup>a\*</sup>, Eduarda Regina Carvalho<sup>b</sup>, Rubens Bernardes Filho<sup>b</sup>, Márcia Regina de Moura Aouada<sup>b</sup>, Ladislau Martin-Neto<sup>b</sup>, Luiz Henrique C. Mattoso<sup>b</sup>

<sup>a</sup> Departamento de Física, UEPG, Av. Carlos Cavalcanti 4748, CEP 84030-999, Ponta Grossa PR Brazil; <sup>b</sup> Embrapa Instrumentação Agropecuária Rua XV de novembro 1452, CEP 13560-970, São Carlos, SP, Brazil  
E-mail: [scsaab@uepg.br](mailto:scsaab@uepg.br)

### **1. Introduction**

Presence of humic substances (HS) in a water supply is undesirable for several reasons, for instance: it produces esthetical problems as color in the water; stabilizes dispersed and colloidal particles during coagulation processes; leads to formation of biodegradable organic compounds during ozonation and thereby enhances regrowth of microorganisms within the water-distribution systems [1].

Atomic Force Microscopy (AFM) technique can image surfaces with atomic resolution by scanning a sharp tip across the surface at forces smaller than the forces between atoms [2]. AFM is a technique which has been employed to study the morphologies of humic and fulvic acid [3–5]. It is a powerful tool to characterize small colloids, as well as colloid agglomeration, adsorption onto surfaces, or modification in morphologies affected by changes in the physical-chemical properties.

The objective of this work was to get AFM images of aquatic acid fulvic (AFA) Brazilian river, and zeta potential with pH change to verify the structural and morphologic change of the AFA.

### **2. Materials and Methods**

The aquatic HS were isolated from a sample collected from a tributary stream of River Itapanhaú within of the State Park called "Serra do Mar". This is an environmental protection area located in the seaboard, 7<sup>th</sup> UGRHI of 11<sup>th</sup> group of UGRHI from São Paulo State, Brazil.

The extraction of fulvic acids from the river samples was made following the methodology suggested by International Humic Substances Society (IHSS) [6]. The imaging of AFM of AFA samples was carried out at two pH values 3.0 and 9.0. These were used to identify structural changes of FA when the pH varies. Images were obtained using the AFM microscope Didimension V, Veeco. Tapping mode was used and Silicon SPM.

For the study of zeta potential in function of the pH, AFA samples in a suspension of 100mg sample in 1L distilled water milliQ were used. The suspension was sonificated for 30 min in a 60W bath ultrasound in 20 mL parts. pH was adjusted with the addition of 0.1M HCl or NaOH at 20 °C and after 24 h the pH was readjusted. The equipment used was Malvern Instruments, Zeta sizer nano ZS model Zen 3600.

### 3. Results and Discussion

Figure 1a (up) shows de AFA AFM images at pH 3.0 and in figure 1a (down) the height and diameter of AFA particles on the mica sheet measured from the two straight lines indicated in figure 1a (up). Agglomerates in the shape of pyramids can with diameter around 150–300 nm and 10–55 nm high are observed.

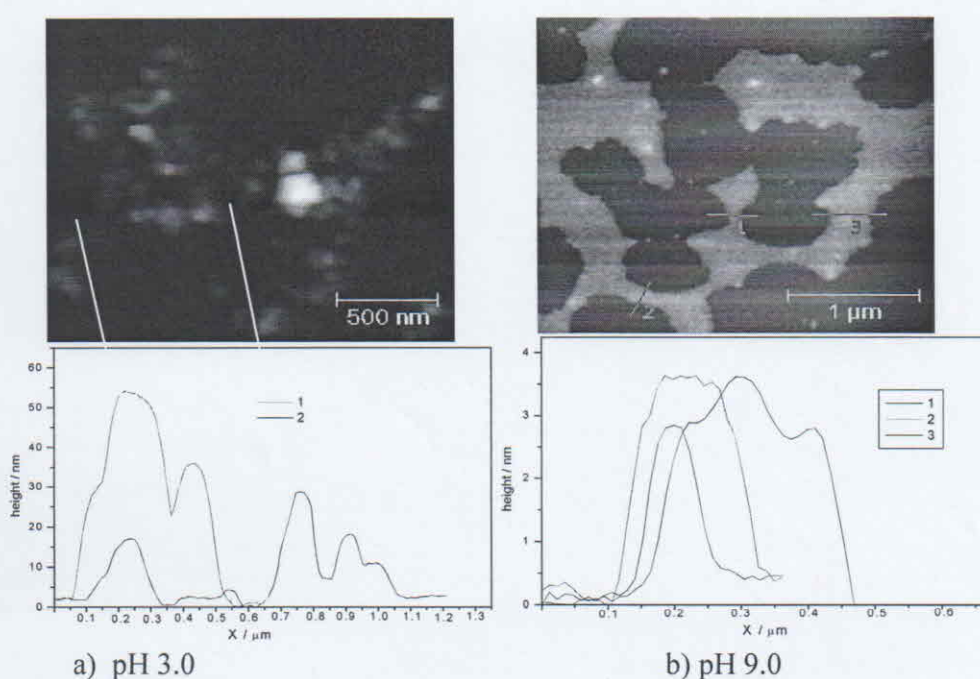


Figure 1: AFA AFM image at pH a) 3.0 and b) 9.0. Figure 1b (up) shows the AFA AFM images at pH 9.0. Figure 1b image indicates a more open distribution of AFA on the mica sheet when compared with figure 1a image at pH 3.0. Dimensions can be observed in figure 1b (below) where the AFA height on the mica at pH 9.0 was between 2.5–4.0 nm and diameter between 100–300 nm. With pH increase, AFA particles expand and repel one another electrostatically. Strengths become weaker, due to H bonding, van der Waals interactions and interactions of  $\pi$  electrons from adjacent molecules, with dissociation of carboxylic and phenolic groups, generating negative charges [7] as shown in figure 2 (zeta potential)

Figure 2 shows the zeta potential variation with the pH of the river AFA sample. Zeta potential becomes more negative with the increase in pH. There is a sharp increase in the negative charge from pH 7.0, this fact coincides with the beginning of phenolic acid groups ionization, with a gradual increase of these groups from pH 7.0. Thus, the contribution of



phenolic acids for the formation of AFA negative charges in solution is more important than the carboxylic groups.

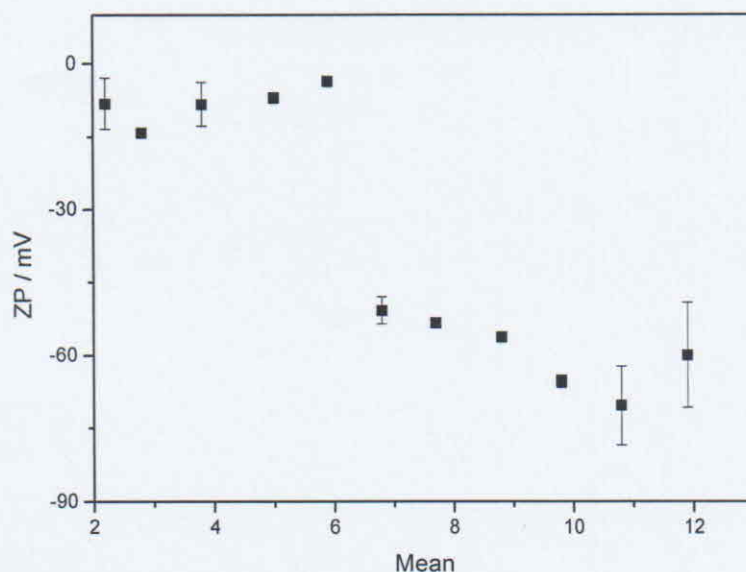


Figure 2: Zeta potential variation with the AFA sample pH

#### 4. Conclusions

This work showed that through atomic force microscopy techniques, structural change in fulvic acid of a Brazilian river was identified when the solution pH varied. Results suggest that in acid pH weak electrostatic interactions and hydrogen bonding are responsible for aggregates formation while in alkaline pH electrostatic interactions are strong due to increase in the phenolic groups ionization and low hydrogen interaction forming more open structures.

#### References

1. E. R. Carvalho; L. Martin-Neto; D.M.B.P. Milori; J. C. Rocha; A. H. Rosa, *J. Braz. Chem. Soc.*, 15 (2004) 421.
2. F. L. Leite; P. S. P. Herrmann; J. Adhesion, *Sci. Technol.*, 19 (2005) 365.
3. K. Namjesnik-Dejanovic and P. A. Maurice, *Colloids and Surf. A: Physicochem. Eng. Aspects*, 120 (1997) 77.
4. M. Plaschke; J. Rothe; T. Schäfer; M. A. Denecke; K. S. Dardenne; K. Pompe; H. Heise, *Colloids Surf. A: Physicochem. Eng. Aspects*, 197 (2002) 245.
5. J. M. Gorham; J. D. Wnuk; M. Shin; H. Fairbrother, *Environ. Sci. Technol.*, 41 (2007) 1238.
6. R. S. Swift; in Sparks (Ed), *Methods of Soil Analysis Part 5*, Soil Sci.Soc.Am., Madison, 1996, p.1018.
7. R. A Alvarez-Puebla. and J .J. Garrido, *Chemosphere*, 59 (2005) 659.