

## **pH EFFECT ON SURFACTANT PROPERTIES AND SUPRAMOLECULAR STRUCTURE OF HUMIC SUBSTANCES OBTAINED FROM SEWAGE SLUDGE COMPOSTING**

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### **ABSTRACT**

This work evaluates the surfactant properties of humic acids (HA) obtained from sewage sludge composts and the production of value-added products from the residue that is typically a disposal problem. To obtain the HA, aerobically digested sewage sludge was composted with either wooden shavings (HACOMP1) or tezontle (HACOMP2) as a bulking agent. HACOMP1 and HACOMP2 samples were evaluated for their effect on surface tension and compared with a commercial vermicompost sample (HALCOMP). The surface tension values for a concentration of 5000 mg/L, showed a decrease from 72 mN/m to 49 and 51 mN/m for HACOMP1 and HACOMP2 respectively, while the commercial vermicompost diminished only to 65 mN/m. The changes in surface tension could be related to the presence of functional groups, particularly COOH and a predominance of either aliphatic or aromatic chains. This fact was confirmed by FTIR analysis, COOH quantification, and the  $E_4/E_6$  ratio. These results indicate that lower surface tension is due to the predominance of aliphatic chains, plus lower content of COOH groups and a higher  $E_4/E_6$  ratio (short size molecule). Also, samples exhibit pH dependence, having a lower surface tension at pH values from 3 to 4. According to size exclusion chromatography (SEC) tests, this effect could be related to changes in the supramolecular structure of the humic acids, in such way that at this pH value there is an arrangement of molecules that decrease surface tension. Humic acids obtained from sewage sludge compost affect surface tension in a way similar to other humic acids obtained from soils and compost obtained from other organic compounds. Thus, humic acids can be used as surfactants, with the added advantage that their use also disposes of the hazardous waste that is the source of these compounds.

Palabras clave: compost, lodo residual, tensión superficial, cromatografía de exclusión por tamaño, pH, ácido húmico

## RESUMEN

Este trabajo evalúa las propiedades surfactantes de ácidos húmicos (AH) obtenidos de compost realizados con lodos de plantas de tratamiento de agua, con el fin de obtener un producto de valor agregado a partir de un residuo que usualmente representa un problema de disposición. Para obtener los AH, el lodo biológico estabilizado de manera aeróbica fue descompuesto utilizando viruta de madera (HACOMP1) o tezontle (HACOMP2) como material abultante. Se evaluó el efecto de las muestras de ácidos húmicos obtenidos de los compost HACOMP1 y HACOMP2 sobre la tensión superficial y se comparó con muestras obtenidas de un vermicompost comercial (HALCOMP), encontrando que usando una concentración de 5000 mg/L se tiene una disminución desde valores de 72 mN/m hasta 49 y 51 mN/m para HACOMP1 y HACOMP2 respectivamente, en tanto que para el vermicompost comercial la tensión superficial disminuye solamente hasta 65 mN/m. Los cambios observados en la tensión superficial pudieran estar relacionados con la presencia de grupos funcionales, particularmente el contenido de COOH así como la predominancia de cadenas alifáticas o aromáticas. Este hecho fue confirmado por análisis FTIR, cuantificación de grupos COOH y cálculo de la relación  $E_4/E_6$ ; los resultados obtenidos indican que la mayor disminución de la tensión superficial se debe a la predominancia de cadenas alifáticas en los AH, así como a un bajo contenido de grupos COOH y a una relación  $E_4/E_6$  alta (moléculas de tamaño pequeño). Asimismo, la tensión superficial mostró una dependencia del pH, obteniéndose una mayor disminución a pH entre 3 y 4. De acuerdo con los resultados de la cromatografía de exclusión molecular este efecto podría estar relacionado con cambios en la estructura supramolecular de los ácidos húmicos, de manera que a estos valores de pH hay un arreglo de las moléculas que disminuye la tensión superficial. De manera general el trabajo muestra que los ácidos húmicos obtenidos de la descomposición de lodos residuales de plantas de tratamiento afectan la tensión superficial de manera similar a los ácidos húmicos obtenidos del suelo o de otros compuestos orgánicos, pudiendo ser usados como surfactantes, con la ventaja de que son obtenidos a partir de un residuo contaminante y peligroso.

## INTRODUCTION

Oxidation of organic matter from plants and animals, followed by a polymerization process, leads to the formation of humic substances (Stevenson 1994, Schulten and Schnitzer 1997). Humic substances are defined as heterogeneous, dark-colored refractory compounds, which are produced by the action of microorganisms (MacCarthy 2001, Sutton and Sposito 2005). These substances are classified into three groups according to their solubility: humic acids (HA), which are insoluble at pH 2; fulvic acids (HF), which are soluble at all pH values; and humins (HU), which are insoluble in acidic and alkaline conditions (Stevenson 1994, Wandruszka 2000, Chilom *et al.* 2009).

Most reports relating to humic substances have focused on the physicochemical characterization of humic acids extracted from soil. However, some studies of humic characterization have used compost obtained from organic waste. These studies have reported data for pH, organic matter and nitrogen

content, cation exchange capacity (CEC), elemental analysis of C, H, N, S, as well as infrared spectra and nuclear magnetic resonance (NMR) analysis (Reville *et al.* 2002, Zbytniewski and Buszewski 2005a, 2005b, Campitelli *et al.* 2006, González *et al.* 2006). Using the last two techniques it has been established that humic acids contain aromatic, carboxylic and phenolic functional groups (Swift 1989, Yates *et al.* 1999, Sánchez *et al.* 2003, Simpson *et al.* 2002). Chemical properties of humic acids are important, particularly the presence of acidic functional groups, because they define their complexation, folding, and supramolecular properties.

Because of their chemical structure, HA have characteristics that promote their accumulation at the air-water interface, which causes a decrease in the surface tension (ST) of water (Wershaw 1993, Wandruszka 1998, Tombácz 1999, Quadri *et al.* 2008). Also, previous studies have shown that ST is significantly affected by changes in environmental conditions. For instance, Yates *et al.* (1999) reported that for solutions of humic acids obtained from

rivers and soil, surface tension decreases as pH is lowered from 9 to 4. Moreover, surface tension also showed an increase when pH values drop from 3 to 2. Recently, Adani *et al.* (2010) confirmed ST reduction when pH drops to 3. This behavior may be related to acidic group neutralization, a fact that generates intramolecular electrostatic interactions that determine their physical shape. At high pH and low ionic strength, acid groups are fully ionized, and there is a strong repulsion between charged groups causing the molecule to expand (Tombácz 1999). This phenomenon is also related to the buffer capacity of humic acids that has been related to the physisorption of protons and hydroxyl ions, which gives them a buffer capacity between pH 5.5 and 8.0 (Pertusatti 2007). In addition, there are several studies showing that humic acids can form micelle-like structures that act as solubilizing agents for hydrophobic compounds (Guetzloff and Rice 1994, Terashima *et al.* 2004, Sierra *et al.* 2005) in a way similar to that of synthetic surfactants.

On the other hand, size exclusion chromatography (SEC) has been used to gain insight to HA structure at the molecular level under different conditions (Piccolo *et al.* 1996, Piccolo 2001, Maia *et al.* 2008). For example, Piccolo *et al.* (1996) reported that pH significantly affects the conformation and size of humic acids. SEC was also used to evaluate changes in the elution volume of sodium and ammonium humates obtained by composting (Maia *et al.* 2008). According to Pellegrino *et al.* (2005) HA can be used to aid bioremediation techniques, since they are natural surfactants that reduce the sorption of organic contaminants, showing removal of pollutants similar to that of the synthetic surfactants. Due to the fact that the surfactant properties can be affected by the degree of aromaticity of the molecule, the  $E_4/E_6$  ratio has been proposed as a measure of the degree of condensation of the aromatic carbon network in humic acids. Thus, while a high  $E_4/E_6$  ratio reflects a low degree of aromatic condensation, and a large proportion of aliphatic structure, a low  $E_4/E_6$  ratio reflects a high degree of aromatic condensation (Gieguzynska *et al.* 1998, Fong *et al.* 2006).

This work evaluates the surfactant properties of humic acids obtained from sewage sludge composts, resulting in the production of a value-added product from a residue that usually represents a disposal problem. The composting process was carried out by mixing aerobically digested sludge and grass, and using either wooden shavings or tezontle as a bulking agent. HA were characterized in terms of their chemical properties and structure, and compared with

samples of soil and HA obtained from other organic wastes. An interpretation of the effect of HA on the surface tension of the solution was also made. In addition, the surfactant effects of these materials were evaluated under different pH conditions in order to correlate their supramolecular structure with their surfactant properties.

## MATERIALS AND METHODS

The humic acids used in this work were obtained from: 1) Compost produced from mixing 30% municipal sewage sludge, 60% grass, and 10% wooden shavings (HACOMP1); 2) Compost employing 30% municipal sewage sludge, 60% grass, and 10% of tezontle, a porous volcanic material (HACOMP2); and 3) a commercial product named Vermilik, consisting of vermicompost humic acid (HALCOMP) produced from manure by Biotecnología Agrícola SA de CV that contains 28% organic matter. Bulking agents were used in order to evaluate their effect on the surfactant properties of the humic acids obtained in the compost process.

### Composting of sewage sludge

Sewage sludge was obtained from an activated sludge wastewater treatment plant located at the City of San Miguel de Allende, in central Mexico. Samples were collected after they had received an aerobic digestion treatment and thickening in a filter band. The 1 m<sup>3</sup> compost piles were produced by mixing the sludge with the grass and the bulking agent as indicated above. Subsequent temperature measurements confirmed that in both cases thermophilic temperatures were obtained from the 3<sup>rd</sup> to the 21<sup>st</sup> day. For HACOMP1 temperatures ranged between 50 and 65 °C, and for HACOMP2 between 40 and 55 °C. The residual organic matter was 19% for HACOMP1 and 21% for HACOMP2.

### Humic acids isolation

Humic acids were extracted by placing 10 g samples of the humic acid containing material, with 100 ml of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> 0.1 M in sealed bottles, and stirred during 24 h. The extracts were centrifuged for 20 min at 10 000 rpm, and the supernatant was carefully removed and passed through a 0.45 µm cellulose syringe filter. The filtered solution was acidified to pH 2 using 5 M HCl and maintained at 4 °C for 24 h. Then, it was centrifuged for 20 min at 10 000 rpm. In this step a precipitate containing the HA fraction was separated, which was washed twice with 0.1 M

HCl and twice with deionized water. The HA were further purified by stirring with a 0.06 M HCl solution for 12 h, and then centrifuged and washed with deionized water. The HA obtained was dried at room temperature and stored for further analyses.

#### Fourier-transformed infrared analysis (FT-IR)

The chemical composition of the humic acids was investigated using the FT-IR technique, with a FT-IR Perkin Elmer 100 series spectrophotometer operating in transmission mode using potassium bromide pellets (200 mg KBr) containing 1 mg of the relevant freeze-dried humic acid.

#### Acid-base titration

Total acidity and carboxylic group quantification of the HA were determined by means of titrations with barium hydroxide and calcium acetate respectively, as previously reported by Perdue (1985). The content of phenolic groups was calculated as the difference between total acidity and the amount of carboxyl groups. All experiments were run in triplicate and the acid-base content of the HA was reported as the average of three independent titrations.

#### UV-Vis analysis

HA samples (3 mg) were dissolved in 10 mL of 0.05 M NaHCO<sub>3</sub> solution, and UV-Vis absorption spectra were recorded in the 200-800 nm window using a Hach D/R 100 spectrophotometer. The E<sub>4</sub>/E<sub>6</sub> ratios were calculated as the ratio of absorbance of the sample at 465 and at 665 nm (Chen *et al.* 1977).

#### Surface tension (ST) and critical micelle concentration (CMC) measurement values for HA in solution

In order to determine the effect of humic acids on water surface tension, solutions containing HA were prepared by mixing concentrations between 10 and 6000 mg/L of dry powder and 0.1 M NaOH. The solution pH was adjusted to 11.8 with 0.1 M HCl, and stirred for 4 h. Afterward samples were filtered using a 0.45 µm membrane and left to stand overnight before measurements, at 4°C. All ST measurements were carried out at 25 ± 0.2 °C and the reported data are the average of three measurements. In order to evaluate the effect of pH on surface tension, solutions were prepared containing 100 mg/L of HA dissolved in 0.1 M NaOH; pH values were adjusted between 7 and 2 with 0.1 M HCl. All surface tension measurements were made using the Du-Noy ring methodology in a laboratory tensiometer (Cole Palmer, USA). After each measurement, the platinum

ring was washed and cleaned with acetone (J.T.Baker, Mexico). In addition, the ring was exposed to a flame in order to avoid the presence of any organic material on the surface.

#### Size exclusion chromatography analysis of humic acids

Changes in molecular size and shape of the HA under study were analyzed using an HPLC apparatus (Agilent 1260 Infinity series) equipped with a DAD detector (wavelength range 254-600 nm), using a standard size exclusion column (Polymer Standard Service, 8 x 300 mm). The injection volume was 100 µL and the mobile phase consisted on 0.001 M NaOH at pH 10.3 and a flow rate 0.8 mL/min. Chromatography samples were prepared as follows: 2.5 mg of HA were dissolved in 25 mL of 0.1 M NaOH; and pH values were modified using a 0.1 M HCl solution in the of 7-2 units range.

## RESULTS AND DISCUSSION

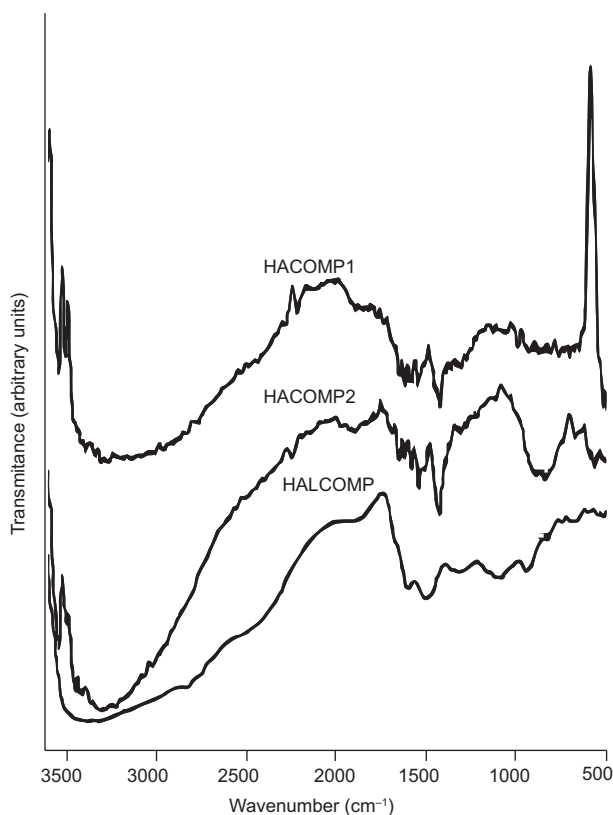
#### FT-IR spectroscopy

FT-IR spectra of the different HA samples used in this study (**Fig. 1**) show similarities with typical soil HA peaks (Stevenson 1994, Senesi *et al.* 1996, Francioso *et al.* 2002). In general, FTIR spectra of the sewage sludge compost HACOMP1 and HACOMP2 reveal similar, intense peaks at 1430-1460 cm<sup>-1</sup>, which are assignable to aliphatic structures. The absorption bands at 1720-1734 cm<sup>-1</sup>, 1600-1625 cm<sup>-1</sup>, and 1510-1516 cm<sup>-1</sup> were more pronounced for HALCOMP, indicating a higher content of C=O, COOH, and aromatic C=C groups. A broad absorption band at 3200-3400 cm<sup>-1</sup> (O-H vibration of carboxylic and alcoholic groups or N-H groups), a 1250-1280 cm<sup>-1</sup> peak (C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers), and a 800-1150 cm<sup>-1</sup> signal (C-O stretching of polysaccharide or polysaccharide-like substances) were also observed. These results showed that HA obtained from vermicompost contains aromatic groups, while HA from the sewage sludge compost has predominantly aliphatic structures.

#### Chemical and spectroscopic characteristics of the different origin-HA

Total (R-COOH+R-OH), carboxyl (R-COOH), and OH (R-OH) acidic group contents were determined and reported in **Table I**. For R-COOH acidity, the values range between 1.59 (for HACOMP1) and 2.96 meq/g (for HALCOMP). The HALCOMP2





**Fig. 1.** FT-IR of humic acids. HACOMP1, compost produced of municipal sewage sludge, grass and wooden shavings; HACOMP2, compost of municipal sewage sludge, grass and tezontle; HALCOMP, commercial vermicompost.

sample showed an intermediate content value of 2.12 meq/g. Sánchez *et al.* (2003) have characterized many HA from composts obtained from poultry manure made from sewage sludge, and reported R-COOH contents in the range of 2.60-5.67 meq/g. The carboxylic acidity of HA sewage compost samples (HACOMP1 and HACOMP2) and vermicompost (HALCOMP) are within those reported previously. Also, higher values of R-COOH were measured for HALCOMP, an observation that is consistent with FTIR analysis that showed a higher content of carboxylic groups.

The  $E_4/E_6$  ratio has been proposed as a measure of the degree of condensation of the aromatic carbon network in humic acids. In this way, while a high  $E_4/E_6$  ratio reflects a low degree of aromatic condensation and a large proportion of aliphatic structure, a low  $E_4/E_6$  ratio reflects a high degree of aromatic condensation (Gieguzynska *et al.* 1998, Fong *et al.* 2006). HACOMP2 and HACOMP1 samples did not show significant differences between them. Both were characterized by a high  $E_4/E_6$  ratio (7.2 and 7 respectively), which corresponds to a high content of aliphatic chains. The HALCOMP commercial sample had the lowest  $E_4/E_6$  ratio (5.7, **Table I**), which indicates more condensation of aromatic groups than that of the HA composts. These results are consistent with the FTIR analysis, whereby HACOMP2 and HACOMP1 displayed relatively higher absorption intensity at 1460  $\text{cm}^{-1}$  (Aliphatic C-H) compared to that observed for HALCOMP, which displays a high absorption intensity at 1610  $\text{cm}^{-1}$  (aromatic C=C and H-bonded C=O).

#### Surface tension (ST) as a function of humic acid concentration

The ST values determined as a function of the concentration of compost and commercial HA are very different. As can be seen from the data presented in **figure 2**, there is a decrease in ST when the concentration of humic acids in the solution is increased. This trend is maintained up to a particular concentration, after which ST remains relatively constant for higher HA concentrations. This point is known as the critical micelle concentration for surfactants. Some authors have identified a pseudo-CMC for humic acids, since the conformation of HA pseudo-micelles is similar to that of real micelles (Wandruszka 2000). In this work, the term pseudo-micelles or micelles will be used interchangeably. At a lower dosage, HACOMP1 is the humic acid that decreases the ST value the most, followed by HACOMP2. Their surface tension values were 49 and 51 mN/m respectively. This suggests that the bulking agent does not have a significant effect on the surfactant properties of humic acids

**TABLE I.** ACIDIC FUNCTIONAL GROUPS AND  $E_4/E_6$  RELATION OF HUMIC ACIDS AND SURFACE TENSION OBTAINED IN THE CRITICAL MICELLE CONCENTRATION OF HUMIC ACIDS.

Humic acid	$E_4/E_6$	Total acidity (meq/g)	COOH (meq/g)	OH (meq/g)	*CMC (mg/L)	**Surface tension (mN/m)
HACOMP1	7.00	13.11	1.59	11.52	2000	51
HACOMP2	7.20	10.11	2.12	7.99	3000	53
HALCOMP	5.70	12.30	2.96	9.34	4800	65

\*CMC = Critical micelle concentration

\*\* Surface tension at CMC

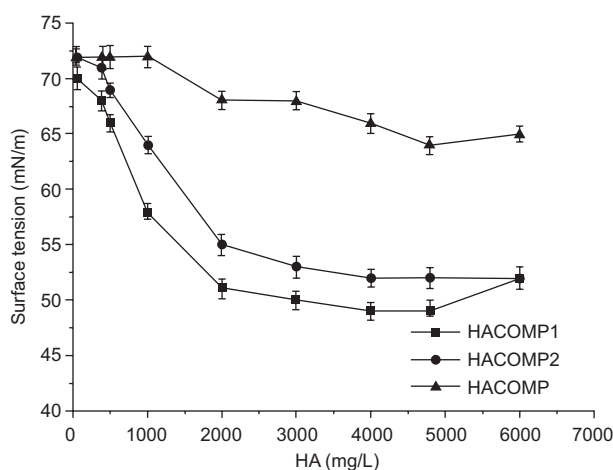


Fig. 2. HA surface tension as a function of HA concentration.

obtained from sewage sludge compost, so that any of the studied materials can be used. On the other hand, the vermicompost humic acid (HALCOMP) showed minimal ST reduction, with an average value of 65 mN/m at higher concentrations. Based on these results and the values obtained for carboxylic acidity (**Table I**), surface tension values are lower in the samples that contain a large number of COOH groups (HACOMP1 and HALCOMP). Also, the  $E_4/E_6$  ratio and FTIR analysis show that the last samples obtained from sewage sludge compost have a large proportion of aliphatic structures, so changes in surface tension could be related to the predominance of aliphatic structures in the humic acid.

Plotting two lines on the experimental surface tension points, one for the zone of continuous ST decrease and one for the zone where ST is almost constant, gives an intersection that corresponds to the CMC value. The computed critical micelle concentration value (**Table I**) indicates concentrations of 2000 mg/L for HACOMP1, 3000 mg/L for HACOMP2, and 4800 mg/L for HALCOMP. Thus, humic acids obtained from sewage sludge composts have a lower CMC than the commercial vermicompost HA. Consistent with these results Quadri *et al.* (2008) reported CMC values for HA of different samples obtained from compost of lignocellulosic wastes that oscillated between 471 to 4040 mg/L. Another interesting point is the value of surface tension at the CMC. The obtained values of 51, 53, and 65 mN/m for HACOMP1, HACOMP2, and HALCOMP, respectively, are similar to those obtained by Quadri *et al.* (2008) who reported values between 40.8 and 50.4 mN/m for the different humic acids obtained from lignocellulosic waste compost, and 36.1 mN/m for Aldrich humic acid.

These results indicate that humic acids obtained from sewage sludge compost can be used as a surfactant, because they decrease surface tension. Also, those humic acids have properties similar to humic acids obtained from soil and other organic waste compost.

### Surface tension (ST) for humic acids as a function of pH

**Figure 3** shows the ST profiles as a function of pH for the HA samples, indicating a decrease in surface tension when pH is lowered. For HALCOMP, when pH is lowered from 7 to 4, its ST decreases from 69 to 65.5 mN/m. The other two HA showed similar behavior at pH 3, and minimal surface tensions values were determined for HACOMP1 (60 mN/m) and HACOMP2 (61.5 mN/m). This behavior of the surface tension for the samples obtained from sewage sludge compost is similar to that reported previously by Yates *et al.* (1999) for humic acids of different soil samples. The decrease in surface tension when the pH is changed indicates the neutralization of the acid sites, creating amphiphilic species that migrate to the air-water interface (Yates *et al.* 1999). This phenomenon is consistent with the functional group density distribution and molecule size, which allowed extensive H-bonding with the aqueous solvent throughout the experimented pH range (Engelbrektsson and Wandruszka 1998). In this work, it can be observed that around pH = 4, HA are especially effective in forming amphiphilic molecules. In all cases, the ST increased again at low pH, where continued neutralization produced more hydrophobic molecules. It is important to note that for all humic acid solutions, a precipitation phenomenon was observed (at pH between 2 and 3).

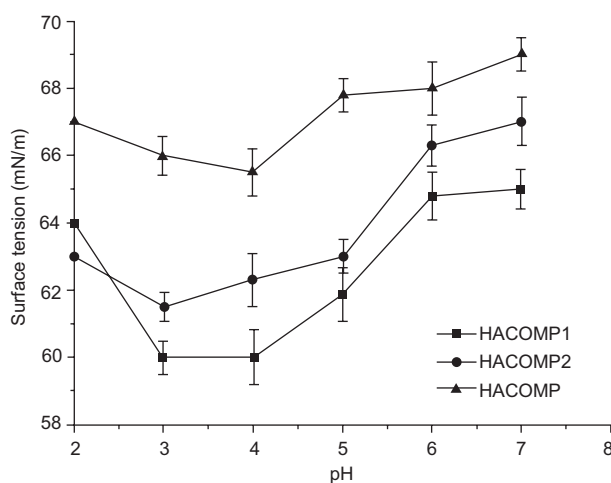


Fig. 3. Surface tension of HAs as a function of pH values. For all HAs, precipitation was observed at pH's between 2 and 3.

This could be due to an increase in  $H^+$  concentration that causes protonation of the HA carboxylic groups, which eventually lead to precipitation.

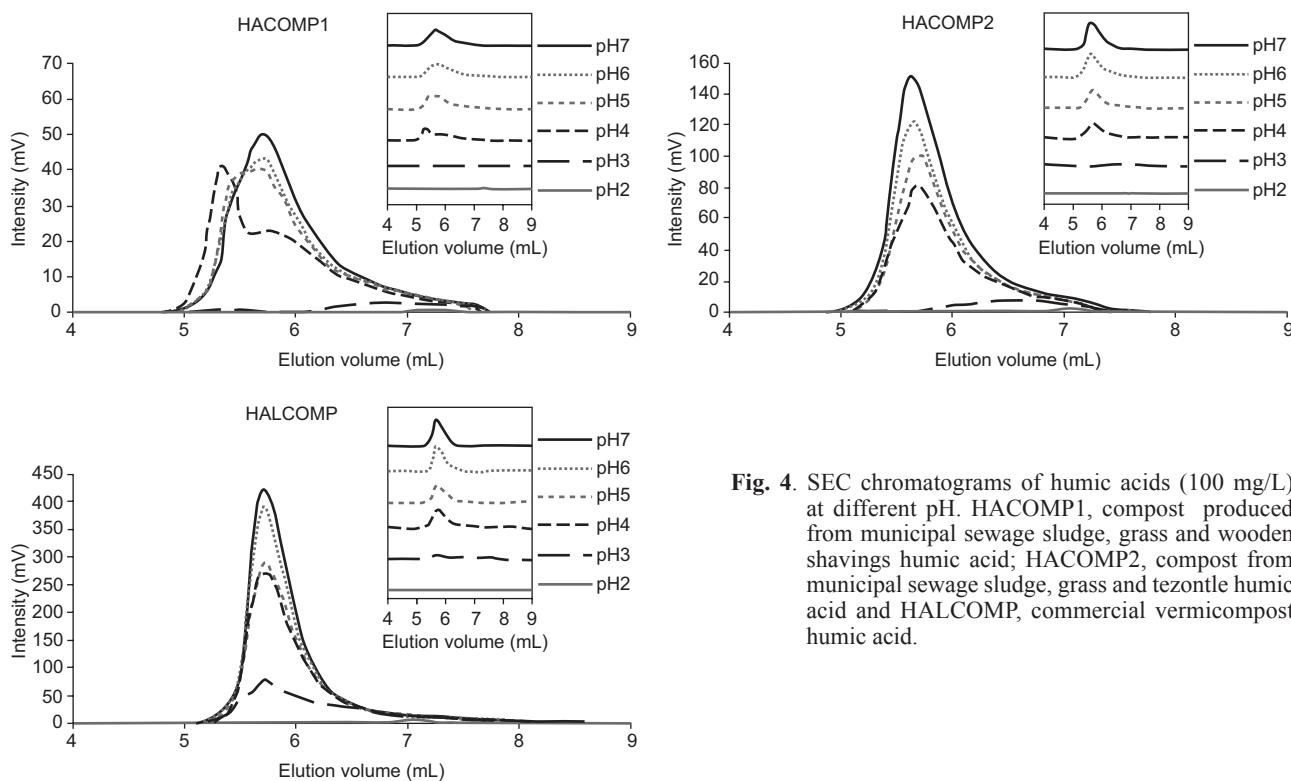
As can be seen, the lowest surface tensions were obtained in composts containing more aliphatic groups and fewer carboxylic groups, facilitating their neutralization and leading to rearrangement of hydrophobic and hydrophilic groups for micellar formation of the molecule. These results indicate that the tested composts have a strong amphiphilic character compared with commercial vermicompost products and have the same behavior as soil humic acids when there are changes in the pH of the solution.

### Supramolecular structure of HA as a function of pH

In order to correlate functional group content, acidity, and surface tension to the structure of the humic acids, SEC analyses were done at different pH. As shown in **figure 4**, there is one absorbance peak for each HA located near 5.8 mL of elution volume. As pH decreases, all the surveyed HA samples showed a decrease in the height of these peaks and slightly lower values of elution volume were observed. This phenomenon has been described previously as a change in supramolecular structure of soil humic acids (Piccolo *et al.* 1996). These changes in

the intensity of peaks are related to changes in the supramolecular structure of HA originating from the progressive neutralization of acid groups caused by a decrease in pH. It is important to point out that in all tested samples the peaks disappear at pH 2, suggesting that under acid conditions HA precipitates. These results show that changes in surface tension in the samples of humic acids obtained from sewage sludge compost are related to their supramolecular structure, as can be seen in previous work with samples of humic acids obtained from soils.

Considering the results obtained in this study for the tested samples (HACOMP1, HACOMP2, HALCOMP), it can be seen that all samples produced a decrease in water surface tension. As mentioned before, neutralization of carboxyl groups enhances the amphiphilic character of the molecules, and the lowest surface tension was obtained in all cases between pH 3 and 4. Also, surface tension was reduced more in humic acids obtained from sewage sludge compost samples (HACOMP1 and HACOMP2) that contain more aliphatic chains than aromatic groups. At the same time, samples with fewer carboxyl groups (HACOMP1 and HACOMP2) produced a greater effect on the decrease of surface tension. Thus, for the samples used in this study, ST decreases more for molecules containing predominantly aliphatic groups



**Fig. 4.** SEC chromatograms of humic acids (100 mg/L) at different pH. HACOMP1, compost produced from municipal sewage sludge, grass and wooden shavings humic acid; HACOMP2, compost from municipal sewage sludge, grass and tezontle humic acid and HALCOMP, commercial vermicompost humic acid.

and low concentrations of carboxyl groups. Also, the drop in pH resulted in the neutralization of humic acid COO<sup>-</sup> groups, which produced a reduction of intramolecular electrostatic interactions causing a contraction of the HA molecule. This fact can be observed in the changes and disappearance of the absorption peaks in the SEC analysis of the HACOMP1, HACOMP2 and HALCOMP samples. Taking into consideration the consistency of chemical and spectroscopic properties, as well as changes in ST and SEC analysis, it can be seen that changes in surface tension are determined by the presence of aliphatic/aromatic groups, COOH content in the HA molecule, and changes in the supramolecular structure of the humic acid.

### CONCLUSIONS

Humic acids obtained from sewage sludge composting can be used to modify surface tension of aqueous solutions in a way similar to HA obtained from soil or compost of other organic compounds. In this study, the use of wooden shavings (HACOMP1) or tezontle (HACOMP2) as a bulking agent in compost had similar results, because surface tension decreased from 72 mN/m to 49 and 51 mN/m, so the bulking agent had no significant effect. Changes in surface tension can be related to the presence of functional groups, particularly COOH. Properties of humic acids obtained from sewage sludge composting also depend on pH. In this work it was observed that, at pH values of 3-4, HA exhibits lower surface tension than the commercial one, which implies that both HACOMP1 and HACOMP2 have a lower content of COOH groups and a predominance of aliphatic chains, which is not the case for HALCOMP. The effect of pH on surface tension is related to changes in the supramolecular structure of the humic acids. These results suggest that humic acids obtained from sewage sludge compost can be used as a natural surfactant in a way similar to other humic acids obtained from other organic compounds, but they have the added advantage of using dangerous waste as a source of the humic acids.

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