

# EPR AND DRIFT CHARACTERIZATION OF HUMIC FRACTIONS FROM SAWDUST-PAPER MILL SLUDGE COMPOST

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## INTRODUCTION

Composting is a bioxidative and exothermic controlled process for treatment and stabilization of organic materials. This treatment is an environmentally clean and economic way to recycle industrial wastes. During composting, mineralization process leads to production of water, CO<sub>2</sub> and NH<sub>3</sub>, and the humification produces stabilized organic matter which can be used as soil fertilizer. Humic Substances (HS) are the major components of compost and have important role in improving the physical-chemical properties and fertility of soils.

In this work, the spectroscopic characteristics of pyrophosphate-extracted humic fractions (humic acid, fulvic acid and humin) extracted at different composting stages were studied by using diffuse reflectance infrared Fourier-transform (DRIFT) and Electronic Paramagnetic Resonance (EPR) analyzes.

## MATERIALS AND METHODS

Sawdust and paper mill sludge (1:1 v/v mix) was composted in a 13-ton reactor (Tibagi Sistemas Ambientais Ltda., PR, Brazil), under temperature and aeration control. Samples were taken at 0, 2, 8, 15, 22 and 29 days of composting. The last 2 samples were not under forced aeration during the maturation process.

The compost samples were shaken overnight in a 0.5 M NaOH and 0.1 M Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub> solution under atmosphere enriched with N<sub>2</sub>. The humic acid (HA) fraction were precipitated from alkaline extracts by lowering the pH to 1 with HCl and purified by three cycles of dissolution in 0.1 M NaOH followed by reprecipitation in HCl. The HAs were further treated with a 0.25% HCl-HF solution for 48 h, and dialyzed against distilled water until Cl<sup>-</sup> free. The fulvic acid (FA), the material left in solution after the first precipitation of HAs at pH 1, was purified by eluting through an Amberlite XAD-8 resin with a 1 M NaOH solution, and, after adjusting the pH to 5, dialyzed and freeze-dried. The humin (HU), the solid fraction which remained in compost after the HA extraction, was extracted as for the HA after having treated the residual compost twice with a 10% HF solution for 24 h, dialyzed and freeze-dried. All humic fractions were characterized for their ash content (less than 1.9% w/w).

The DRIFT spectra of FA, HA and HU were obtained, after finely grinding with KBr, in a Perkin Elmer Spectrometer with a DRIFT accessory. The operating conditions were: 400 to 4000 cm<sup>-1</sup> range, 2 cm<sup>-1</sup> resolution, and 16 scans for each sample.

EPR spectra (~300 K and 77 K) of powdered FA, HU and HA samples were registered in a Bruker ESP 300E spectrophotometer, operating at a frequency of 9.7 GHz (X-band), with a 100 kHz modulation frequency, 2.024 G modulation amplitude and ~20 mW microwave power. Simulations of spectra were made using Win-EPR and SimFonia Bruker computer programs. Organic free radical (OFR) were quantified by using the intensity square line width approximation. The areas of the EPR peaks were calibrated with the EPR signal of a "strong pitch" reference (Bruker). The same reference pattern was used to obtain accurate g-values (g = 2.0028) of the samples.



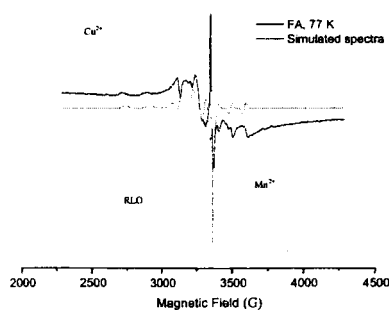
## RESULTS AND DISCUSSION

The infrared spectra of HA, FA and HU showed typical bands of HS, at 3300, 2950, 2850, 1660, 1590, 1260 and 1220 cm<sup>-1</sup>. These results revealed that compost was rather rich in hydroxyls, and carboxylate groups, and aromatic, aliphatic and carbohydrates moieties in all samples. The aliphatic component was predominant in the HA and HU fractions.

All EPR spectra showed a free radical line at g = 2.00 region, characteristic of semiquinone radicals, with average value of g = 2.0037 for HA, g = 2.0044 for FA and g = 2.0034 for HU (Table 1). The g values of FA fractions were larger and HU fraction lower than the g-value of the HA fraction. A higher g value is expected for species rich in oxygenated groups, as the FA fraction. FA usually shows width lines broader than that of HA isolated from the same source. This was confirmed by our results. The concentration of organic free radical of all fractions varied during the composting time, especially in the HU fraction which showed a strong variation from the beginning to the end of the process. The width of the resonance line was almost constant within each fraction.

The EPR spectra in magnetic field of 5000 G, RT and 77 K, of FA and HA samples presented lines of high-spin for complexed Fe<sup>3+</sup> ions in distorted octahedral and/or tetrahedral structures, in rhombic symmetry coordination (asymmetric line in g = 4.3). For the HU fraction, however, this signal was very weak indicating a lower concentration of iron. The spectra at 77 K showed signals around g = 6.0, usually attributed to high-spin Fe<sup>3+</sup> ions in strong axially symmetric crystal fields. This suggests that iron was bound to four nitrogen atoms in a planar configuration, probably from iron porphyrin structures. The 77 K spectra also exhibited a complex absorption pattern around g = 2 region, showing a hyperfine interaction quadruplet at g = 2.25 and A = 175 G. This may correspond to an inner-sphere copper complex having the ligands arranged in a square planar (distorted octahedral) coordination around the central Cu<sup>2+</sup> ion. A six lines pattern indicated the presence of manganese complexes. The EPR parameters (A = 88 G and g = 2.005) appeared consistent with outer-sphere complexes in which the Mn<sup>2+</sup> ions may be bound to six oxygen atoms of negatively charged carboxylate and phenolate groups in a distorted octahedral environment.

EPR experimental spectrum of a FA sample (77 K) and a simulated spectrum (Cu, Mn and RLO signals)



DRIFT spectra of the humic fractions of humic acid (HA), fulvic acid (FA) and humin (HU) - expansion from 2000 to 400 cm<sup>-1</sup>.

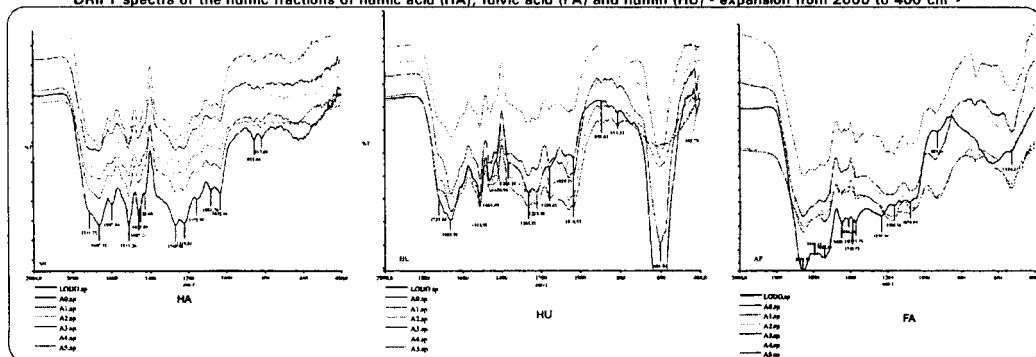


TABLE 1 - EPR PARAMETERS OF HUMIC FRACTIONS DURING COMPOSTING TIME.

Sample /days <sup>1</sup>	HA			FA			HU		
	g-factor	Lw *	OFR **	g-factor	Lw *	OFR **	g-factor	Lw *	OFR **
0	2.0037	5.8	1.91	2.0044	7.1	1.83	2.0033	4.1	21.2
2	2.0037	5.2	2.54	2.0044	6.9	1.59	2.0034	4.2	16.8
8	2.0037	5.2	2.11	2.0044	7.0	2.46	2.0035	4.3	10.5
15	2.0038	5.2	2.14	2.0045	6.9	2.44	2.0034	4.3	18.0
22	2.0037	5.3	3.00	2.0044	6.9	1.88	2.0033	4.2	19.4
29	2.0038	5.6	2.01	2.0045	6.7	1.85	2.0034	4.3	10.7
Lodo	2.0039	6.3	2.72	2.0046	8.0	4.41	2.0038	5.0	6.15

<sup>1</sup> composting days, \* Lw = line width in Gauss, \*\* OFR = organic free radical (spin g<sup>-1</sup> × e16)

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