

Spectroscopic Evaluation of Charcoal Derived Humic-Like Acid

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1. INTRODUCTION

The aim of this work is to study the suitability of using different charcoals in order to produce humic-like acid. Fluorescence and UV-visible spectroscopy were applied to evaluate the humification degree by using different index: E_4/E_6 (2, 8), A_{254}/A_{465} (8) (UV-Vis spectroscopic); I_{400}/I_{360} (4) and I_{470}/I_{360} (4) (fluorescence spectroscopy in synchronous-scan mode); A_{440} (5) and A_4/A_1 (9) (fluorescence spectroscopic in emission scan).

2. MATERIALS AND METHODS

2.1. Organic Material

It has been used different types of charcoal from: sugar cane bagasse; orange bagasse; sugar cane straw; Elephant grass (*Pennisetum purpureum*) and *Eucalyptus grandis*. Humic acid was also extracted from humus samples from compost of leaves grass and commercial compost by earthworm.

2.2. Oxidation and extraction

Approximately 5.0 g of dry charcoal was mixed with 200 mL of 25% of nitric acid. The mixture was heated at 80°C in reflux condition for 4 h. After this time, the samples were kept at room temperature for 12 h (6). After oxidation, the samples were filtered using a 0.45 µm cellulose membrane. The filtrate separate was considered fulvic acid and the solid material was dissolved in 0.1M KOH (50 mL solution/g solid) and shaken for 12 h in sealed flask with N₂ atmosphere. Humics substances have been separated applying the method recommended by the International Humic Substances Society (IHSS). Total carbon concentration was determined by oxidation with sodium dichromate by photometric methods.

2.3. Spectrophotometric measurements

2.3.1. UV-visible spectroscopy

Humic acid of the charcoal from sugar cane bagasse (BC), charcoal from orange bagasse (BL), charcoal from straw of sugar cane (PC), charcoal from elephant grass (CE), charcoal from *E. grandis* (CV), compost of leaves grass (C) and commercial compost by earthworm (HM) were dissolved at 20 mg/L in de NaHCO_3 0.05 mol/L and pH was kept in 8.5. Ultraviolet and visible spectrophotometric measurements have been made between 190 and 900nm with a Cary-100 UV-VIS Varian^{inc} spectrophotometer using quartz cells (1×1 cm). E_4/E_6 (2, 8) and A_{254}/A_{436} (8) ratios were calculated by measured absorbances.

2.3.2. Fluorescence Spectroscopy

Each humic acid sample was also dissolved at 20 mg/L in NaHCO_3 0.05 mol/L and pH was kept in 8.5 (5). Fluorescence spectra has been collected using a fluorescence spectrophotometer from Photon Technology International® equipped with both excitation and emission monochromators. Emission scan were collected between 260-660nm with excitation wavelength of 240 nm and these spectra were divided into four regions. Than rations between the last quarter (A_4) (580-650nm) (9) and the first quarter (A_1) (350-420 nm) (9) were calculated. Emission scan spectra was also collected with excitation wavelength of 440 nm and the total area under the spectra (A_{440}) (5) was calculated. Synchronous spectra were recorded with excitation wavelength range 300-475 nm and a $\Delta\lambda$ of 55 nm. The fluorescence intensity in 360, 400 and 470 nm was determined and the ratios between these intensities were calculated I_{400}/I_{360} (4) and I_{470}/I_{360} (4).

3. RESULTS AND DISCUSSION

3.1. UV-visible spectroscopy analysis

The UV-Vis spectra of different samples have showed a high absorption in the 210-240 nm range and a decrease in absorption with the wavelength increase. It is a typical result for humic acid. Characterization of the samples by different index is showed in Table 1. It can be seen low ratio E_4/E_6 for samples C and HM and high value for samples BL, PC, BC, CE and CV. Ratio A_{254}/A_{436} shows greater value for HM, BL and C. The low values for E_4/E_6 or A_{254}/A_{436} ratio can be attributed to absorption by aromatic C=C functional groups as well as to the high degree of condensation of the aromatic rings.

3.2. Fluorescence spectroscopy analysis

Fluorescence spectra of humic-like acid obtained by acid oxidation exhibits a broad feature emission band with a maximum at ~510 nm. This band is consistent with data published by IHSS. In the other hand, samples C and HM showed a different behavior, as the intensity decreases by increasing the wavelength.

Table 1. Ratios of the measured UV-Vis absorbencies

	HM	CV	BL	C	PC	BC	CE
E_4/E_6	3.65	4.25	7.60	3.52	6.42	6.20	5.89
A_{254}/A_{436}	5.338	4.151	5.766	5.161	4.466	4.255	4.490

Fluorescence synchronous spectra are presented in Figure 1. Most of the samples (BL, CE, PC, BC and CV) show a similar behavior with a more intense peak at 350 nm and a shoulder between 410-470 nm, where the intensity decreases continuously. The sample HM showed a slightly difference with more intense peak at ~375 nm. Sample C showed a different behavior with an intense decrease of intensity until 330 nm.

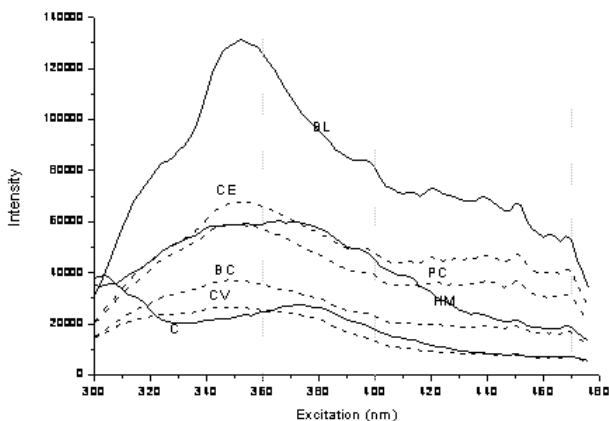


Figure 1. Fluorescence synchronous-scan excitation spectra ($\Delta\lambda = 55$ nm).

The index obtained with fluorescence spectroscopic (Table 2) reinforces the conflicting types of evaluation. Index I_{400}/I_{360} indicates that HM, CE and C as the most humificated. I_{470}/I_{360} indicates as being the samples CE, PC, BC. The index A_{440} indicates BL, CE and PC while the A_4/A_1 indicates BC, PC and BL, as the most humificated, respectively. Therefore, it seems that each group of a specific chemical species should be evaluated by a specific index.

Table 2. Ratios of the measured fluorescence spectroscopic parameters

Sample	Fluorescence Parameter			
	I_{400}/I_{360}	I_{470}/I_{360}	$A_{440} \cdot 10^6$	A_4/A_1
HM	0.77	0.31	1.75	0.08
CV	0.52	0.27	0.65	0.15
BL	0.64	0.42	4.59	0.16
C	0.71	0.29	0.70	0.15
PC	0.69	0.54	2.71	0.19
BC	0.65	0.47	1.48	0.19
CE	0.73	0.61	3.47	0.15

4. CONCLUSIONS

UV-Vis spectra show a typical humic acid behavior for all samples. The ratio E_4/E_5 for samples HM and C shows lower value indicating high degree humification. The same information was also taken from A_4/A_1 and I_{470}/I_{360} Fluorescence index. All these values are near of those given in some references.

Synchronous spectra of sample C showed a similar profile of compost materials (4). Also, the same spectra of sample HM showed a similar profile with those from compost of soil mill olive waste; commercial humic acid by Aldrich Chemicals; compost of a mixture of animal manures and non-composted animal manure (4). All others samples showed similar profiles of the soil humic substances from China and Czech Republic (4).

All index values and the profile of UV-Vis and Fluorescence obtained scan graphics are in accordance with reported references showing the suitability of using different charcoals as starting material to produce humic-like acid.

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