Analytical Attributes of Humic Acids Derived from Tropical-based Resources

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ABSTRACT

Humic acids (HA) are widely researched and exploited compounds due to their exceptional chemical and physical properties. However, information on tropical-based HA is still lacking. This attempted to characterize HA derived from tropical peat and POME using chemical and physical methods. Elemental analysis of the HA showed that C ranged between 48.94 and 57.87%, H between 4.90 and 8.26%, N between 1.93 and 8.05%, and O between 30.96 and 40.85%. The functional group analysis indicated that peat-derived HA were more reactive than those derived from POME. Optical density and spectral examinations revealed that the HA had varying degrees of aromaticity. Generally, data obtained from the HAs studied (particularly from peat) agreed closely with those reported elsewhere.

Keywords: humic acids, peat, POME

INTRODUCTION

Organic matter content strongly affects soil fertility by increasing the availability of plant nutrients, improving the soil structure and water-holding capacity, and acting as an accumulation phase for toxic heavy metals in the soil environment (Stevenson and Fitch 1981; Stevenson 1985). To this end, the recycling of organic materials via their application to the soil can be an important and promising practice for agricultural activities. Humic substances are bulk constituents of organic matter, and have been shown to possess exploitable properties that fit agricultural, environmental, industrial and medical applications (Schnitzer 1986). By definition, humic acid is the fraction that is soluble in a dilute base, but is precipitated upon acidification.

Analytical data on HA isolated from diverse sources, particularly soils, peat, marine and lake sediments, and natural waters, have been steadily accumulating. However, information on HA derived from tropical resources is still limited and thus merits further exploration. It is well established that HA originating from different sources are different, and vary as a function of multiple factors such as climate, vegetation and nature of the substrate.
The present investigation was aimed at characterizing HA derived from tropical peat and palm oil mill effluent (POME), both of which are common sources of organic matter added to Malaysian soils. A better understanding of the chemical and physical properties of HA is imperative to comprehend the transformations the acids will undergo over time within the soil environment.

MATERIALS AND METHODS

Organic Materials

Peat was sampled between 0.5 and 2.0 m depth from the surface of a peat deposit in Dengkil, Selangor, Malaysia. Meanwhile, POME samples were sourced from a Guthrie palm oil mill in Rantau, Negri Sembilan. Two categories of POME, namely a decomposing POME and a clarified POME, were used in the study. The decomposing POME was generated from a 3-month (approx.) ponding process while the clarified POME emanated from a post-pressing process within the settling tank. Peat and both POME were then oven-dried at 60°C for 3 d, finely ground to pass through a 1.0-mm sieve, and extracted for HA.

Extraction of HA

Fifteen grams of peat/POME were weighed into a 250-ml polypropylene flask, 150 ml of 0.2 M NaOH solution was added, and the system was shaken intermittently for 24 h at room temperature. The resulting dark coloured supernatant was separated from the residual peat/POME by centrifugation at 10,000 rpm for 15 min, then acidified to pH 1 with 3 M H\textsubscript{2}SO\textsubscript{4} and allowed to stand at room temperature for 24 h to facilitate coagulation of HA (Schnitzer 1982).

The coagulated HA was purified by reprecipitation and redissolution using H\textsubscript{2}SO\textsubscript{4} and NaOH, respectively. After the final precipitation, the HA was placed in cellulose tubes and dialysed against distilled water for 7 d with diurnal water change. The mixture was then centrifuged. Residues of HA were subsequently shaken for 48 h with excess HCl-HF mixture (0.5%, v/v) to desorb the HA completely of silicate impurities. The acid mixture was removed by centrifuging (10,000 rpm for 30 min) and decanting the supernatant. The residual HA was thoroughly washed with distilled water until free of chloride (as shown by tests with silver nitrate) and finally dried at ambient temperature (< 40°C). Yield of HA were expressed as percentage derived on a weight per weight basis.

Characterisation Techniques

Purified HA were subjected to elemental and functional group analyses, optical density determination and spectroscopic examination. The ash contents of HA were obtained by igniting the acids at 700°C for 4 h. Carbon, H and N were estimated by dry combustion using a CHN analyser (VARIO-EL), and O was calculated by difference. Carboxyl groups were measured by the Ca(OAc)\textsubscript{2} method (Schnitzer and Gupta 1965) and phenolic hydroxyl groups by the colorimetric method using Folin-Ciocalteu's phenol reagent (Tsutsuki and Kuwatsuka 1978). Total acidity was ascribed to the sum of carboxyl and phenolic hydroxyl groups. Quinonoid C-O groups were determined by ferrous reduction in alkaline TEA solution using bulk electrolysis (Glebko et al. 1970). The E\textsubscript{465}/E\textsubscript{665} ratio was determined by dissolving 2 mg of HA in 10 ml of 0.005 N NaHCO\textsubscript{3} solution and measuring its optical density at 465 and 665 nm. Fourier transform infra-red analysis of HA was carried out by mixing 0.5 mg of HA with 400 mg infra-red grade KBr, and pressing into a pellet (Tan 1982). Spectra were recorded on a Perkin Elmer 1650 FTIR spectrophotometer for wavenumbers ranging from 4000 to 400 cm\textsuperscript{-1}.

RESULTS AND DISCUSSION

The chemical and physical attributes of HAs studied are given in Table 1. Peat yielded 16.73% (w/w) HA while the decomposing and clarified POME registered 1.82 and 3.47 HA, respectively. Higher yield of peat-derived HA, as compared to both POME, could be attributed to its higher organic matter content. Yield of HA derived from peat obtained is comparable to those reported by Husni et al. (1996) and Norhayati (1989).

Loss on Ignition

Percentage loss on ignition relates, indirectly, to the purity of HA. Higher loss on ignition means lower ash content, thus higher purity of the HA. Results indicated that ash contents of the acids were exceptionally low, which was possibly due to the exhaustive purification steps employed.
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TABLE 1
Chemical attributes of humic substances derived from POME and peat

<table>
<thead>
<tr>
<th>Humic acid</th>
<th>POME(^{a})</th>
<th>POME(^{b})</th>
<th>Peat</th>
</tr>
</thead>
<tbody>
<tr>
<td>% yield</td>
<td>3.47</td>
<td>1.82</td>
<td>16.73</td>
</tr>
<tr>
<td>% LOI</td>
<td>97.50</td>
<td>99.50</td>
<td>96.00</td>
</tr>
</tbody>
</table>

Elemental make-up:
<table>
<thead>
<tr>
<th>%</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat</td>
<td>57.87</td>
<td>8.26</td>
<td>2.91</td>
<td>30.96</td>
</tr>
<tr>
<td>POME(^{a})</td>
<td>48.94</td>
<td>5.76</td>
<td>8.05</td>
<td>37.25</td>
</tr>
<tr>
<td>POME(^{b})</td>
<td>52.32</td>
<td>4.90</td>
<td>1.93</td>
<td>49.85</td>
</tr>
</tbody>
</table>

O:H | Peat | 3.75 | 6.47 | 8.34 |
|     | POME\(^{a}\) | 19.80 | 6.08 | 27.11 |
|     | POME\(^{b}\) | 7.01 | 8.50 | 10.68 |

Functional groups:
<table>
<thead>
<tr>
<th>meq. g(^{-1})</th>
<th>Quinonoid</th>
<th>Carboxylic</th>
<th>Phenolic</th>
<th>Total acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C = O</td>
<td>POME(^{a})</td>
<td>2.52</td>
<td>2.92</td>
<td>3.34</td>
</tr>
<tr>
<td></td>
<td>POME(^{b})</td>
<td>2.85</td>
<td>2.08</td>
<td>4.06</td>
</tr>
<tr>
<td></td>
<td>Peat</td>
<td>3.27</td>
<td>5.56</td>
<td>6.69</td>
</tr>
</tbody>
</table>

Optical density:
<table>
<thead>
<tr>
<th>E(_4):E(_6) ratio</th>
<th>Peat</th>
<th>POME(^{a})</th>
<th>POME(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.22</td>
<td>6.09</td>
<td>7.67</td>
</tr>
</tbody>
</table>

\(^{a}\)clarified, \(^{b}\)decomposed

\(z = x + y\)

Elemental Analysis

Elemental composition of peat-derived HA conform to those reported elsewhere (Visser 1987, Garcia \textit{et al.} 1991, Husni \textit{et al.} 1996). Acids derived from POME showed higher values of H and N but lower value of O compared to peat-derived HA. Nevertheless the C level of peat-derived HA was intermediate between the HA derived from POME.

Data on atomic ratios showed higher values in peat-derived HA than those of POME-derived HA. Higher O:H value indicates poor aromatization and/or poor condensation, while narrower C:H ratio reflects the occurrence of smaller number of saturated groups (Kononova 1966). The C:N ratio of HA submitted to the order of peat>clarified POME>decomposing POME. Lower C:N value infers that mineralization was more intense (Norhayati 1989).

Functional Group Analysis

The reactivity of HA is greatly influenced by the nature and amount of oxygen-containing functional groups present. According to Schnitzer (1982), the acidity of HA is primarily due to the occurrence of ionizable hydrogens in aromatic and aliphatic carboxylic and phenolic OH groups, and is largely responsible for the exchange capacities of HA, which may have chelating effects that influence plant nutrition.

Comparatively, total acidity, carboxylic and quinonoid contents were higher in peat-derived HA, while POME-derived HA recorded higher phenolic OH content. However, disparity in functional group values between both POME-derived HA was narrow. Carboxylic and phenolic OH values obtained for peat-derived HA are higher than those reported by Husni \textit{et al.} (1996) for tropical peat and Norhayati and Verloo (1984) for tropical soil. Meanwhile, HA from POME appear to be similar in carboxylic and phenolic OH contents to HA derived from a commercial humate (Enersol Micronutrient), as reported by Lobartini \textit{et al.} (1992). Peat-derived HA contained approximately 1.5-fold higher amounts of carboxylic than phenolic OH, thus suggesting that the pH-dependent charge in peat is regulated by carboxyls. In POME-derived HA, phenolic OH dominated over carboxylic OH.

Optical Density

The E\(_4\):E\(_6\) values were highest in peat-derived HA, followed by decomposing POME-derived HA and clarified POME-derived HA. Wider ratios reflect a low degree of aromatic condensation and infer the presence of relatively large proportions of aliphatic structures (Kononova 1966). HA derived from clarified POME indicated greater aromatic condensation (narrower E\(_4\):E\(_6\)) than HA derived from decomposing POME. Incidentally, the C:N ratio of clarified POME-derived HA was also higher than that from decomposing POME-derived HA. Thus, reduced aromaticity of HA from the decomposing POME could be attributed to intense mineralization, as indicated by the lower C:N ratio.
Fig. 1. FTIR spectra of HA derived from a) clarified POME and 
b) decomposed POME.

Fig. 2. FTIR spectra of HA derived from peat.

PERTANIA J. TROP. AGRIC. SCI. VOL. 21 NO. 1, 1998
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Spectral Characteristics

Fourier transform infra-red (FTIR) spectra of the HA are shown in Figure 1, 2. Interpretation of the FTIR spectra are based on Schnitzer and Khan (1972). The HA displayed main absorption bands in the regions of 3400 cm⁻¹ (hydrogen-bonded OH), 2900-2850 cm⁻¹ (aliphatic C-H stretch), 1730-1715 cm⁻¹ (C=O of C₂H, C=O of ketonic carbonyl), 1650-1630 cm⁻¹ (C=O stretch of quinones, COO, hydrogen-bonded C=O), 1550-1520 cm⁻¹ (C=C of aromatic rings), 1460-1450 cm⁻¹ (CH₃ and 1420-1400 cm⁻¹ (CH₂, COO). Absorption bands in the 1290-1200 and 1160-1130 cm⁻¹ regions were assigned to symmetrical bonding of aliphatic CH₉, OH or C-O stretch of various groups. Meanwhile, absorbances in the 930-660 cm⁻¹ range included symmetrical and unsymmetrical C-H bonding, structural and out of plane vibrations of C-H in aromatic rings.

The 3400 cm⁻¹ assignment is supportive of Stevenson’s suggestion (1982) that HA engage in pronounced hydrogen bonding. The 2900-2850 cm⁻¹ assignment, usually superimposed in the shoulder of the broad O-H stretching band, confirmed the presence of large concentrations of aliphatics. The stronger band at 1650 cm⁻¹ infers higher concentration of COOH groups. Weak bands at 1550-1520 and 1460-1450 cm⁻¹ observed in HA under study are in agreement with those reported by Husni et al. (1996) and Garcia et al. (1991). They deduced that HA extracted using alkali extractant exhibited more pronounced aromaticity compared to that using pyrophosphate. The weak band obtained at 1290-1200 cm⁻¹ can be attributed to OH, from COOH deformation.

CONCLUSION

Comparatively, peat yielded higher HA than POME. Elemental composition of peat-derived HA compared closely with data reported by Husni et al. (1996). The HA derived from POME, however, varied in elemental composition. Clarified POME-derived HA registered higher C and H but lower N and O contents than decomposing POME-derived HA. Contents of C, H and O of peat-derived HA and that of decomposing POME-derived HA were similar. Quinonoid C=O and carboxylic groups, and total acidity were recorded marginally higher in peat-derived HA, compared to POME-derived HA, whilst the reverse was found for phenolic OH. This suggests that the reactivities of the HA are comparable. Optical measurements revealed aromatic characteristics for the HA, which were confirmed by the FTIR spectra. The Degree of aromaticity varied only marginally among the HA.

REFERENCES


(Accepted: March 1998)
(Received: November 1998)