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ORIGINAL PAPER

Characterization of humic materials extracted from hazelnut husk and hazelnut husk amended soils

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Abstract This study was carried out to determine effects of composted hazelnut husk (CHH) on some chemical properties of soil and soil humic acid (HA). Compost application increases organic matter (OM) content of the soil considerably, OM value of 3.18% became 3.89% in 3 years time interval. Before application of compost, the soil pH was found to be 5.37, while after compost application it became 5.61. FTIR characteristics of humic acid/humic acid-like materials extracted from the original hazelnut husk, composted hazelnut husk and composted hazelnut husk amended soil have been investigated. C and O content of humic acid-like/humic acid materials were in the range of 41.4–50.8% and 37.8–50.5%, respectively. The N content of the humic acid/humic acid-like materials are in the expected range for humic materials which is 2–6%.Comparison of FTIR spectra of hazelnut husk and composted hazelnut husk humic acid-like fractions shows that both exhibit similar but not identical series of IR bands indicating the presence of the same functional groups in both samples. The only difference in the spectra seemed to be a decrement in the peak intensities of composted sample compared to uncomposted one. The similar differentiation of the intensities of IR bands of compost applied soil sample has also been observed. The FTIR spectral results show that the characteristics of composted material tend to become similar to that of soil humic acids characteristics in time.

Keywords Compost · Humic acid-like · Humic acid · Hazelnut husk

Abbreviations

AS	Arid soil
CAS	Composted hazelnut husk applied soil
CHH	Composted hazelnut husk
HA	Humic acid
HAL	Humic acid-like
HH	Hazelnut husk
HS	Humid soil

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Introduction

Agricultural recycling of various organic waste materials such as sewage sludge, agricultural crop residues, wood processing wastes and food industrial refuses have become more popular practically and scientifically (Gerasimowicz and Byler 1985; Senesi et al. 1996; Gigliotti et al. 1999; Soler Rovira et al. 2003). One of the reasons for this is to achieve organic matter (OM) content of the soil as much as possible, since OM is one of the most important components of the soil that affects its fertility. The organic carbon (C) to nitrogen ratio (C/N) of the organic wastes is a useful parameter to predict the fate of organic N in soil.

In any case fresh or immature organic wastes have to be previously subjected to appropriate treatments such as composting before application to the soil (Ciavatta et al. 2001; Tiquia 2005). These treatments are aimed to increase maturity and stability in order to minimize or possibly eliminate adverse effects of the organic materials such as phytotoxicity. Therefore, composting of organic waste materials with the addition of N source could be recommended in order to decrease the C/N ratio of the organic material and to supply humified material for soil amendment (Senesi et al. 1996; Zinati et al. 2001; Soler Rovira et al. 2003). After application of organic wastes, the soil will have a great capability to transform those materials through biodegradation processes leading to humic-like substance synthesis (Deiana et al. 1990; Senesi et al. 1996; Zinati et al. 2001).

In previous studies (Calıskan et al. 1996; Ozenc and Calıskan 2001) it was suggested that hazelnut husk (HH) would be turned into compost and used as organic fertilizer. In addition, it improves the physical, chemical and biological properties of the soil (Ozenc and Calıskan 2001; Zeytin and Baran 2003; Bender Ozenc 2005).

Annually, a large quantity (about 500,000 tons) of in-shell hazelnuts are produced in Turkey, especially in Black Sea coasts. Most of the hazelnuts are exported, used as food and food additives, their shells are used as heating purposes in Turkey, but large quantities of husks are wasted. After drying, 1/5 of the 1 kg of hazelnut becomes husk and it has a great potential as an organic material for agricultural usage.

The core of the studies are related with organic wastes are based on their organic carbon and OM content. On the other hand, the studies on the humic substances of plant originated organic wastes, their analytical characteristics and their effects on the natural soil humic substances have recently started to take attention (Senesi et al. 1996; Ciavatta et al. 2001; Unsal and Sozudogru Ok 2001). Therefore, this study aims at characterizing the humic acid (HA) and humic acid-like (HAL) substances extracted from fresh HH, composted hazelnut husk (CHH), the composted hazelnut husk applied soil in comparison with HAs extracted from two different soils called humid and arid soils.

Materials and methods

Description of materials

In the study, HH is used as amendment organic material for soil was examined. HH is the cover of the nut shell which is originally green and then turns into yellowish-red and finally brown during the maturation of nut. In the harvesting, this husk is removed from the nut by machine.

Hazelnut husk was composted according to somewhat modified indore composting method under anaerobic conditions for about 18 months (Calıskan et al. 1996). The composting process was carried out using a mixture of HH, urea (46% N) and fine grained soil; in 1 m^3 of volume, a layer of the mixture was established with 57.5 kg husk, 1.15 kg urea and it is covered by 2.5 kg soil, producing 1–2 cm of thickness. The height of the whole mixture was about 25 cm. This layering process was repeated three times and the relative humidity was kept at 65% by adding water. A plastic cover covered the surface of the mass. The plastic covering was removed every 15 days of intervals to record temperature and moisture content. Besides, in every 3 months cover was opened and the mass was mixed thoroughly. Then, the decomposed materials were separated from the rest by sieving and then both were remixed. This process was repeated until the C/N ratio becomes less than 20/1 and the color becomes brownish-black.

The CHH was applied to the field each year in early spring as 75 kg da^{-1} per bed. Each bed includes 4–5 nut plants. The CHH application was carried out for 3 years. After a 3-year period, the surface soil samples (CAS) were taken and analyzed.

Before HA extraction, pH, electrical conductivity (Gabriels and Verdonck 1992), OM (DIN 1978), total organic C (Nelson and Sommers 1982) and texture of the soil (Bouyoucous 1951) were determined.

Humic acids and humic acid-like substances

Humic acids were extracted from soils while HALs were extracted from uncomposted and composted materials following the procedure suggested by Schnitzer (1982). The extracted HAs and HALs were analyzed for moisture, ash and total organic carbon contents (Nelson and Sommers 1982). Elemental analyses (C, H, N and S) were carried out using a LECO 932 analyzer. Fourier transform infrared (FTIR) spectra were recorded on KBr pellets (1 mg HA/HAL with 400 mg of IR-grade KBr) using a Nicolet 5 PC FTIR spectrophotometer equipped with Omnic software.

Results and discussion

Characteristics of materials

The main physical and chemical characteristics of HH, CHH and CAS are shown in Table 1. The pH of HH before composting is about neutral (7.09) but after composting process it becomes somewhat acidic (6.43) due to the formation of CO_2 during the composting process. The value is consistent with the literature value of pH 6.5–8.5 (Bewick 1980). Before application of compost, the soil pH was found to be 5.37 while after compost application it became 5.61. On the other hand, humid region soil has pH of 4.75 and the soil from arid region has pH of 7.30.

Regarding electrical conductivity drastic increase is observed on composting process of HH. Conductivity increases from 5.5×10^{-3} to 4.15 dS m^{-1}. This might be due to the formation of various organic, inorganic anions and cations. On the other hand, CAS has rather low EC (0.19 dS m^{-1}), which may be due to the various reasons such as leaching out of the salts and humification of the material. The humid and arid soil has similar EC being 0.33 and 0.37 dS m^{-1}, respectively.

Hazelnut husk does not contain $CaCO_3$, but CHH contains small amount of $CaCO_3$ (0.74%), which may be due to the carbonization during decomposition process (Bewick 1980).

Regarding OM content, compost application increases OM content of the soil considerably i.e. 3.18% became 3.89% in 3 years time interval and 75 kg da^{-1} compost. This introductory study has been carried with rather low amount of compost. The application of higher amount of compost may provide more increment in OM content of soil.

Depending on the composting process, C/N ratio of HH decreased from 32/1 to 12/1, a good value for the mineralization of organic materials (Table 1) (Bewick 1980). During composting (Senesi and Brunetti 1996) the organic C content decreases due to its release as CO_2 while N content increases and the C/N decreases in the system. The same trend was observed for the OM with values decreasing from 93.7% (in HH) to 65.7% (in CHH) (Bewick 1980).

Table 1 Selected properties of the materials under study

Materials	PH (1:3)	EC dS m^{-1} (1:3)	$CaCO_3$ (%)	OM (%)	TO C (%)	N (%)	C/N	Texture
HH	7.09	0.0055	–	93.7	40.4	1.26	32.0	–
CHH	6.43	4.15	0.74	65.7	28.4	2.44	12.0	–
CAS	5.61	0.19	–	3.89	2.26	0.37	5.00	CL[a]
HS	4.75	0.33	–	3.27	1.90	0.27	7.04	CL[a]
AS	7.30	0.37	1.33	1.60	0.93	0.16	5.81	SCL[b]

HH, Hazelnut husk; CHH, compost hazelnut husk; CAS, compost applied soil; HS, humid region soil; AS, arid region soil

[a] CL, Clay loam

[b] SCL, Silty clay loam

Humic acid and humic acid-like substances

The elemental compositions of HH-HAL and CHH-HAL are somewhat different from the values found in HA extracted from HS (Table 2). The high percentage of C content obtained for all materials except CHH-HAL (41.4%) indicates humification and condensation of aromatic rings.

Carbon content of HA of soil samples was found to be 48.7–51.7% and oxygen content found to be 37.8–40.3%. In literature (Stevenson 1994), carbon content of HAs of soils ranges from 50% to 60% and the oxygen content from 30% to 35%. The slight difference in carbon and oxygen content of samples may come from climatic conditions and management characteristics of the soil. Sulfur content was also analyzed but not detected.

During the composting process, C/N ratio of HH-HAL gets smaller i.e. 17.4 becomes 12.1. The CAS humic acid contains somewhat higher C/N ratio (13.8) then CHH (12.1). Changing in C and N content of the samples makes C/N ratio similar to that of native soil humic substances (Gerasimowicz and Byler 1985; Garcia et al. 1989). The nitrogen content of the HAs and HALs are in the expected range for HA which is 1–6% (Schnitzer and Khan 1972) (Table 2).

FTIR spectra of the samples were almost same but not identical according to the position of the main bands (Table 3). The variations in the spectra may come from slight differences in their composition. The bands could be assigned to the main groups as: OH stretching which appears around at 3560–3410 cm^{-1}, C–H band at around 2920–2850 cm^{-1}, amidic C=O and amide II band at 1550–1510 cm^{-1}. COOH at around 1200–1220 cm^{-1}, C=O at 1720 cm^{-1}, C=C stretching at 1640–1615 cm^{-1}, C–O of polysaccaride bands at 1040–1030 cm^{-1} (Table 3). The findings are in agreement with the results of Riberio et al. (2001).

Comparison of FTIR spectra of HH and CHH-HALs shows that both exhibit similar series of IR bands, indicating the presence of the same functional groups in both samples (Fig. 1a and b). The only difference in the spectra seemed to be a decrement in the peak intensities of composted sample (Fig. 1b) compared to uncomposted one (Fig. 1a). The similar differentiation in the intensities of IR bands of soil sample (HS-HA) and compost applied soil sample (CAS-HA) has also

Table 2 Elemental composition and atomic ratios of humic acid (HA)[a] and humic acid-like (HAL)[a] materials

Humic materials	C (%)	H (%)	N (%)	O (%)	Atomic C/N	Ratio C/H
HH-HAL	49.1	5.2	3.3	42.4	17.4	0.79
CHH-HAL	41.4	4.1	4.0	50.5	12.1	0.84
CAS-HA	50.8	5.0	4.3	39.9	13.8	0.85
HS-HA	51.7	5.5	5.0	37.8	12.1	0.78
AS-HA	48.7	5.7	5.3	40.3	10.7	0.71

HH, Hazelnut husk; CHH, compost hazelnut husk; CAS, compost applied soil; HS, humid region soil; AS, arid region soil
[a]Ash-free basis

Table 3 Band assignment of the IR Bands of humic acids and humic-like materials

Band (cm^{-1})	Proposed assignment	Sample
3560–3410	O–H stretching	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA
2920–2850	Aliphatic C–H	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA
1720	C=O (ketone and/or carboxylic acid)	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA
1640–1615	C=C	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA
1550–1510	Amidic C=O, amide II band	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA
1220–1200	COOH (C–O and O–H of COOH)	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA
1040–1030	C–O stretching of polysaccharide	HH-HAL, CHH-HAL, CAS-HA, HS-HA, AS-HA

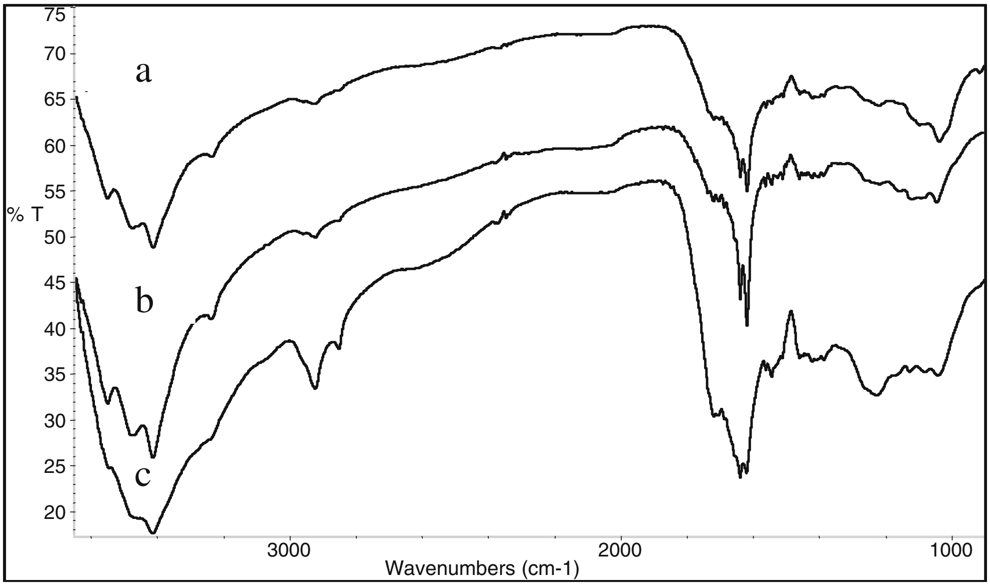

Fig. 1 FTIR spectra of (**a**) HH-HAL (**b**) CHH-HAL (**c**) CAS-HAL (HAL, humic acid like material; HH, hazelnut husk; CHH, compost hazelnut husk; CAS, compost applied soil)

been observed (Fig. 2). Eventhough, the spectrum of CAS-HA is more similar to the spectra of AS-HA and HS-HA than those of HH and CHH-HALs (Figs. 1 and 2), the influence of HH and CHH is still present in the OH region (3550–3410 cm^{-1}) and, especially, in C–H region (2920–2850 cm^{-1}) and carbohydrate band at around 1030 cm^{-1}. All the experimental results show that the characteristics of composted material tend to become similar to that of soil HAs characteristics in time as stated by Senesi and Brunetti (1996) and Sanchez-Monedero et al. (2002).

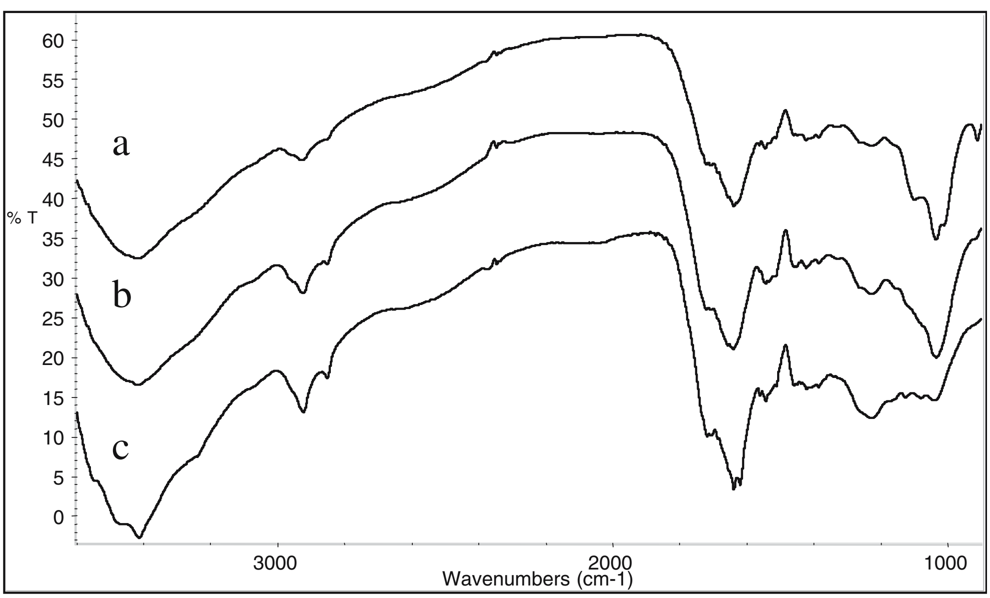

Fig. 2 FTIR spectra of substances (**a**) AS-HA (**b**) HS-HA (**c**) CAS-HA (HA, humic acid; AS, arid region soil; HS, humic acid region soil; CAS, compost applied soil)

Conclusions

The results of the study have shown that the application of the CHH to the soil increases OM content and soil pH considerably. Compost application was found to have minor effect on the nature of the HA and HAL substances of the soil. Since the original plant residues are the principal natural starters of native soil humic substances, the plant material transforms to the original OM of the soil with time as a result of humification.

After amendment addition, the observed changes in compost applied soil become less and less apparent in HA fraction and at the end approaches to the properties of the native soil HAs. The FTIR spectrum of CAS is more similar to those of humic and arid region soils but still shows the influence of HH and CHH properties.

The application of hazelnut compost to the soil has beneficial effect on the building up of soil OM. This introductory study has been carried with rather low amount of compost. The application of higher amount of compost may provide more increment in OM content of soil.

After all results obtained it can be proposed that the application of hazelnut compost to the same region soil provides economical advantages for hazelnut growers, besides soil fertility.

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