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Advantages and Limitations of Using FTIR Spectroscopy for Assessing the Maturity of Sewage Sludge and Olive Oil Waste Co-composts

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Additional information is available at the end of the chapter

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Abstract

Composts prepared using different solid and liquid organic wastes from various sources can be used as growing media when these materials present adequate proprieties for plant development. The stability and maturity are among the main characteristics of composts. The purpose of this study is to recommend specific bands of the IR spectrum recorded on different composts to enable qualitative and rapid monitoring of the stages of biodegradation during composting. At the beginning of humification, the significant decrease in the intensity of the band located at 1735 cm^{-1} shows that lignin is affected at the first stage of the composting process. At the end of the humification, the band located toward $3450\text{--}3420\text{ cm}^{-1}$ at the beginning of the process undergoes a systematic shift ($\Delta\nu$ of the order of 10 cm^{-1}) toward lower wave numbers. The band located at $1660\text{--}1650\text{ cm}^{-1}$ on the Fourier transform infrared spectroscopy (FTIR) spectra before composting shifts systematically toward 1640 cm^{-1} at the end of humification. This phenomenon can be used as index of compost maturity. Measuring the band at 1035 cm^{-1} as an internal standard, it is possible to quantify the degradation rate of organic matter.

Keywords: FTIR, composting, humic substance, maturity, humification, shift bands

1. Introduction

Olive oil production in Morocco amounts to approximately 60,000 tons year⁻¹. Olive mills produce large amounts of solid waste, around 70,000 tons year⁻¹, which serves for combustion, and olive mill wastewater reaching about 640,000 tons year⁻¹. However, the liquid is sent directly into the sewer systems, stored in evaporation lagoons, or illegally spread on the land [1]. In addition, the purification system used in the treatment of wastewater generates considerable quantities of sludge, estimated in 2010 at 40,000 tons year⁻¹, and the forecasts are for 300,000 tons year⁻¹ in 2025 [2]. The problems raised by the elimination of this sludge are generally underestimated or poorly taken into account when wastewater plants are designed. The possibilities of sludge evacuation are limited and are subjected to various technical, economic, legal, and environmental constraints.

The by-products of wastewater treatment and of olive oil wastes can become environmental pollutants owing to their high organic loads and the presence of molecules such as phenolics [3]. Some of the sugars and polyols can be used as sources of carbon and energy for the growth of microorganisms. The high levels of phenol monomers and polymers lead to chemical oxygen demand (COD) and biological oxygen demand (BOD) about 200–400 times higher than those of typical municipal sewage. However, these organic wastes are known to contain fertilizing elements, encouraging their recycling in agriculture. The need to preserve natural resources and especially nonrenewable sources implies organic waste recycling [4]. Sustainable reuse of waste in agriculture as compost or substitute peat is advantageous because of its environmental and economic benefits. However, the direct use, especially of sewage sludge, in agriculture is limited by the presence of pathogens, including parasites, viruses, bacteria, and fungi, as well as organic pollutants (phthalates, HAPs, PCBs, etc.) and trace metals (Cr, Cd, Hg, Zn, Cu, Pb, etc). To overcome these risks, treatment is necessary to reduce and eliminate adverse effects and to maximize the effectiveness of the materials once applied to the soil. The composting of organic waste seems to be one of the best ways to reduce potentially dangerous harmful residues especially olive residues when combined with organic waste such as animal manure.

For several years, our own research area focused mainly on the recycling of olive mill waste (pomace, liquid effluent) and the sludge generated by the treatment of wastewater from sewage treatment plants. Both these types of organic waste are major sources of phosphorus and organic nitrogen [2, 5, 6, 7], and their recycling involves a composting process, which produces humic substances (HSs) that can be used to improve soil quality. During this last decade, works in our laboratory focused on the humification process occurring in (i) the detoxification of liquid effluent from oil mills in order to change its phenolic composition [7]; (ii) the co-composting of solid olive mill waste, straw, and household waste with the liquid effluents from oil mills [5, 8]; and (iii) the composting of moistened municipal waste and co-composting of sewage sludge with green waste (straw, fresh green plants, palm waste, household waste) [2, 9].

Various techniques and spectroscopic methods have been used for the analysis and characterization of HS in our work. The studies were conducted on humic substances (HSs) and their essential fractions (fulvic and humic acids). Our research is consistent with literature data and

allows the atomic composition of HS to be determined. Despite their heterogeneity, similarities in composition are observed between the different humic fractions in particular segments of the isolated molecules, obtained by destructive techniques. The major differences and some characteristic functions of HS can be detected by nondestructive spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR) and ^{13}C -NMR [2, 5]. The relative proportions of functional groups and their degree of branching affect the characteristics of humic and fulvic (HA and FA) fractions directly. As shown by El Fels et al. [10], the differences in the atomic and molecular composition (molecular fragments obtained after Pyr-GC-MS) could be interpreted by determining a humification rate. However, these techniques combined with the physicochemical parameters cannot predict the chemical/biological reactivity.

The extreme variability in the molecular features of HSs relates back to precursor compounds and the environmental conditions under which HS formed such as origin of starting material and processing [11]. Despite that the interest of HS and their structural characterization have been published for many different substrates [12, 13], their molecular structure is still under discussion. The reason is that HS have been shown to contain a wide variety of associated molecular components such as polysaccharides, polypeptides, lignins, hemicellulose, esters, phenols, ethers, carbonyls, quinines, lipids, peroxides, various combinations of benzene, acetal, ketal, and lactol, and furan ringed and aliphatic compounds [11]. Some studies suggest the predominance of aromatic units in HSs, whereas others have shown that many humic extracts contain largely aliphatic structures. Many factors, such as the origin of humic material, the extraction technique, and the purification methods are responsible for the discrepancies found [14]. The hypothesis of by Schnitzer and Khan [12] is that humic acids (HAs) can be assumed to be highly cross-linked aromatic polymers of high molecular weight with covalent carbon-carbon, ether, and ester linkages connecting the substituted aromatic moieties. Other studies support HSs as groups of similar particles associated by weak covalent and noncovalent bonds to "homogeneous" aggregates, which in unfractionated HSs form large mixed aggregates [15, 16]. Therefore, purification is needed to eliminate the weakly bound long alkyl chains from the raw humic material. It removes the extractable monomers or fragments that interfere with the analysis of the main macromolecular structure of the HSs. Purification permits the isolation of the more homogeneous structures and provides better representative information about the real changes of humic macromolecular structure when using various chemical and spectroscopic techniques (elemental analysis, Fourier transform infrared analysis, and ^{13}C -NMR spectroscopy). Gonzalez-Vila et al. [17] suggest that a systematic study of the organic material in composts should include the characterization of both the colloidal organic fraction (which conforms to the operationally defined compost HSs) and the "extractibles" (lipids and water-soluble products).

The extraction and structural determination of a pure fraction of HS is not as yet feasible owing to their complexity and heterogeneity. Only the evolution of HS during their successive transformations made it possible to identify a series of groups and functions present. FTIR and NMR analyses of humic structure sequences indicated that during co-composting process, the HS results from the biodegradation of cellulose, lignin, and hemicellulose and consist of molecules generally containing functional groups such as O-H, C-O, C-O-C, and O-CH₃. These

groups give rise to characteristic bands in the IR spectrum, which have been the subject of various assignments.

Analysis of FTIR spectra in the case of chemical/biochemical reactions generating specific end products is done by following the appearance/disappearance of characteristic bands of some functional groups in the products formed, or by following the band shifts in the case of reactions that involve structural changes. In contrast, during incomplete transformations as in composts, the FTIR spectra recorded at different stages of humification contain both characteristic bands of the products formed and these of the starting reagents which are not completely consumed. Studies conducted by Wershaw et al. [18] on peat soil, agricultural soil, and lake sediment found that many of the chemical structural features of the original plant material were incorporated into the humic acid structure, including lignin, carbohydrate, and long-chain aliphatic structural groups. It is necessary to know the nature, composition, and the starting raw material structure to distinguish the bands of the HS formed.

This review examines the FTIR results obtained from our earlier works on the different composting processes to characterize and quantify the HSs. An appreciation of the analytical methodology depends on an understanding of aspects of the chemistry of HS. The FTIR spectrum of a given co-compost is the result of the contribution of different components of the raw material that constitutes it, such as cellulose, hemicellulose, and lignin. In order to highlight the contribution of each component to the spectrum, we performed FTIR spectrum analysis, taking into account the bands of the starting raw material that may be incorporated and not degraded at the end of the process. This procedure allows the identification of FTIR spectrum bands that can reliably track the evolution of the degradation of organic matter in a given compost.

2. Using FTIR as rapid tool to analyze organic composts

Fourier transform infrared spectroscopy (FTIR) is currently one of the most important analytical techniques available to analyze various substrates. One of the greatest advantages of this technique is that virtually any sample in any state may be analyzed. For example, liquids, solutions, pastes, powders, films, fibres, gases, and surfaces can all be examined with a judicious choice of sampling technique. FTIR has facilitated many different IR sampling techniques, including attenuated total reflection (ATR) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy [19].

FTIR spectroscopy is used to study different composts without any previous chemical treatment likely to cause inappropriate reactions. This technique is widely used to characterize the evolution of organic substrates, mainly when these HSs are extracted from the soil and from composted waste, such as sewage sludge and olive oil mill waste [6, 20, 21]; HA was extracted from sewage sludge and bottom sediments [22, 23, 24]. In addition to identifying the functional groups by their characteristic frequencies, it is possible to follow the HS composition by comparing the relative intensities of certain absorption bands [22, 23, 25, 26]. The disappearance or the appearance of new bands in the FTIR spectrum provides information about

the matter evolution and its interaction with heavy metals when they are present in sewage sludge [24, 27]. However, as reported by Haberhauer et al. [28], Ellerbrock et al. [29], and Kaiser and Ellerbrock [30], in the case of HS, HA, and FA extracted from composts, even after purification, there often remains a relatively large portion of organic compounds such as cellulose, lignin, hemicellulose [15], or mineral (silicates or clays) presenting bands that overlap with those of HS compounds, i.e., in the 1200–1000-cm⁻¹ region [28, 30]. Also, the indexing of FTIR spectra of entire compost remains complicated considering the overlap of mineral phase bands with those of recalcitrant organic matter and those of HSs formed during the humification process. In this case, it is difficult to accurately attribute the FTIR spectrum absorption bands in the 3500–3280-cm⁻¹ and 1200–1000-cm⁻¹ regions. Observed wave numbers and intensities of bands at these regions of spectrum vary from one bibliographic reference to another, and various attributions have been put forward:

- The broad and intense asymmetric bands appearing at 3450–3280 cm⁻¹ were attributed to the elongation of vibrations of OH linked by hydrogen bonding and NH groups of HA extracted from a soil or sewage sludge [24, 31, 32, 33].
- On the IR spectrum of HA extracted from composts of sludge, a band in the region 1200–1000 cm⁻¹ has been attributed to aromatic ethers and to Si-O by [24], and to C-O stretching vibration of C-carbohydrates, aromatic ethers, and polysaccharides by [27, 34, 35, 36].

Smikovic et al. [37] attribute the band at 1035 cm⁻¹ in the IR spectrum to mineral compounds. Although different wastes can be distinguished by their fingerprint region (1500–900 cm⁻¹), this region also reveals fresh and undecomposed materials [38]. In our research, the infrared spectra (FTIR) recorded on different composts and their HA and FA fractions show the changes occurring toward the end of the humification. Small differences in band positions that we found on the FTIR spectra of several samples from different composts require careful examination of the FTIR spectra in order to relate the spectral changes to structural changes in HS during their humification and to provide a more accurate attribution of the vibration wave numbers corresponding to the groups in HS and determine the noncharacteristic bands, which give limited information.

3. Methodology

3.1. Composting trials

Different composting trials were conducted in a heap on a purpose-built platform as follows:

- Activated sludge from Marrakech treatment plant (50%) mixed with (50%) of palm waste for 180 days [2].
- Olive mill water (15%) mixed with pomace (75%) and (10%) of municipal solid waste for 150 days [8].
- Activated sludge taken from the wastewater aerobic treatment plant of Khouribga (Morocco) (66%) mixed with (34%) of fresh plant matter for 130 days [39]

- Lagooning sludge from Marrakech treatment plant (90%) with straw (10%) for 180 days [11].
- Olive mill water (25%) mixed with pomace (70%) and straw (5%) [5].

The mixtures were prepared so as to optimize the co-composting parameters, i.e., 60% humidity and a C/N ratio of about 30. To provide aerobic conditions, the mixtures were mechanically turned each week. The sampling was carried out at different stages during composting. These were at the initial mixing stage, intermediate stage, and final co-composting stage.

3.2. Humic substance extraction

The humic substance (HS) from each composting sample was extracted. The samples were treated three times with 40 mL of distilled water so as to extract the water-soluble non-HSs (sugars, proteins, etc.). Then the HSs were extracted with 40 mL of NaOH (0.1 M). This was repeated several times until the extract obtained was colorless. The supernatant obtained was centrifuged at 4000g for 15 min. After filtration, the supernatants were pooled to determine the level of total soluble carbon.

The HA were separated from the total HSs by acidification with H_2SO_4 to reach a pH of 1. At this pH, the HA form a precipitate, while the FA remain in solution. After being left to settle for 24 h at 4°C, centrifugation at 4000g for 20 min left the FA in solution while the HA were recovered in the pellet. The content of each fraction was determined by the KMnO_4 oxidation method.

3.3. Lipid removal

Free lipids were removed before extraction of HSs using a 2:1 chloroform–methanol mixture as mentioned by Amir et al. [16]. Lipid extraction was carried out three times at 4°C using 15 g fresh samples with 120 mL solvent mixture. These pretreated samples were then subjected to evaporation to remove remaining solvent, and they were then washed three times with water to remove other nonhumic water-soluble molecules, such as sugars and proteins, which might interfere with the analysis of the HSs. Humic substance assay was performed as mentioned above.

3.4. FTIR of extracted humic acid

Potassium bromide pellets of each freeze-drying of the various complete samples and each of the extracted fractions were prepared by pressing under vacuum a mixture of 250 mg of dried KBr and 1 mg of sample (composts, humic acid, and separated fractions). The spectra were obtained using an FTIR Perkin Elmer 1600 [6, 7, 8, 9, 11] and the Bruker Vertex 70 FTIR [2] spectrometers (128 scans at a resolution of 2 cm^{-1} were carried out). Infrared spectral analyses were carried out over a $4000\text{--}400\text{ cm}^{-1}$ range. The instrument was carefully calibrated using water vapour. The uncertainty in band frequencies is estimated to $\pm 1\text{ cm}^{-1}$.

4. Spectroscopic characterization of composts

The spectral data obtained from the analysis of FTIR of FA, HA, and HSs extracted from several composts at different stages of humification [20, 22, 23, 39] are presented in (Tables 1 and 2). In the absence of an internal reference, it is difficult to relate the evolution of band intensities to the appearance/disappearance of new product. The general pattern of bands on the compost spectra shows no dramatic intensity changes. However, the wave numbers measured on the FTIR spectra of whole compost [2] and extracted HS [39] compared to frequencies of bands during composting show modifications (Figure 1). Different mechanisms and structures have been proposed ranging from basic conceptual structures [13], to more detailed structures on the basis of degradation products using pyrolysis and NMR as shown by [2, 22, 23]. However, it is difficult to obtain structural information on HS from the composting process by using FTIR spectra without the input data obtained by other techniques. The variation of the band intensities provides information on the evolution of the humification process [9], but the intensity ratios of the bands cannot give quantitative information on the degradation rate. In addition, these intensity ratios vary from one bibliographic reference to another [8, 40]. However, with regard to the structural complexity of the HS, only their functionality should be used, which involves the characterization of the functional groups present in the HS [41].

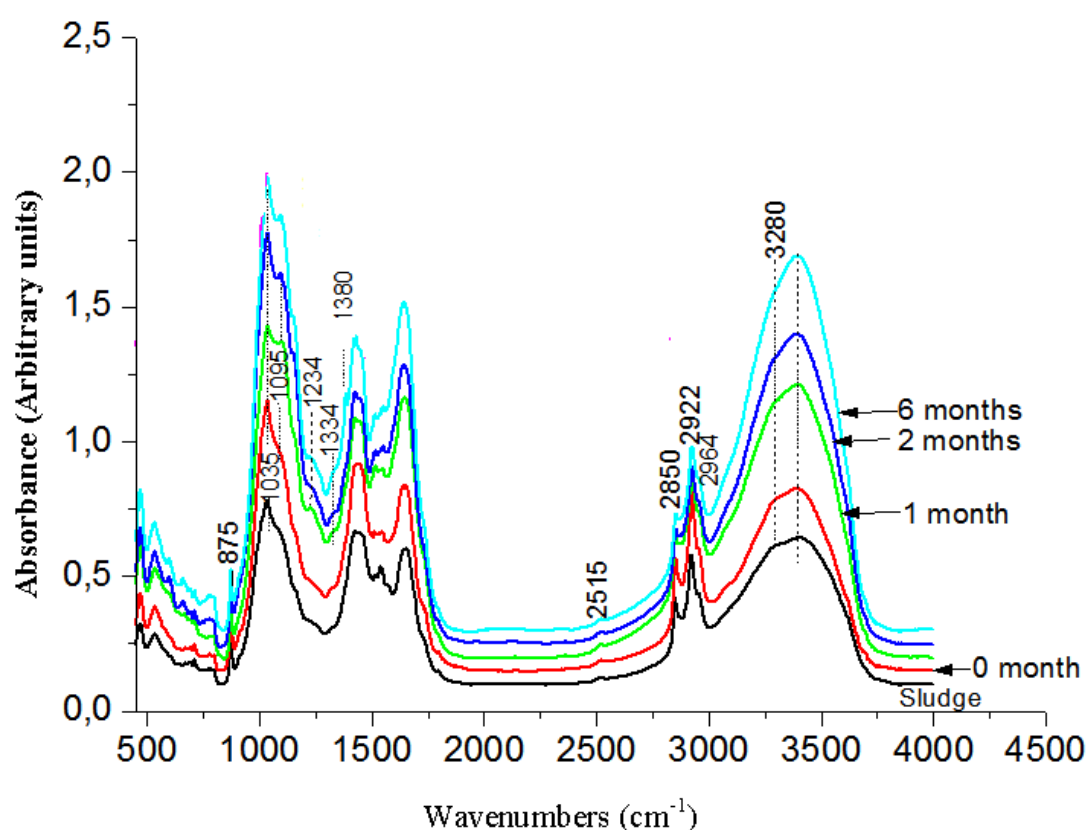


Figure 1. FTIR characteristic of whole composts versus time of composting of sludge with lignocellulosic waste [2].

Fulvic acid				Humic substance				
RM	60 d	135 d	$\Delta\nu$ (cm ⁻¹)	RM	15 d	60 d	135 d	$\Delta\nu$ (cm ⁻¹)
3412	3405		18	3426	3426	3423	3400	26
		3394						
2931	2934	2936		2927	2926	2925	2927	
				2853	2856	2856	2854	
1652	1644	1637	15	1651	1652	1651	1651	0
1561	1561	1561		1540	1533	1533	1533	
				1420	1430	1428	1428	
1408	1408	1405						
1385	1384	1386		1386	1386	–	1386	
1239	1221	1221	17	1226	1244	1244	1244	18
1143	1143	1143						
1124	1121	1121						
1072	1074	1080						
1037	1035	1037	0	1035	1032	1040	1036	1
				874	874	875	874	
620	622	624						

$\Delta\nu = (\nu_{\text{RM}} - \nu_{\text{Final phase}})$; RM = raw material; d = day.

Table 1. FTIR characteristic of extracted humic substance and fulvic acid at versus times of composting of sludge/green waste [6, 39].

Fulvic acid*				Humic acid**					Lyophilized samples***				
RM	90 d	180 d	$\Delta\nu$ (cm ⁻¹)	RM	15 d	60 d	135 d	$\Delta\nu$ (cm ⁻¹)	RM	E1	E2	E3	E4
3418	3400	3400	18	3420	3418	3418	3408	12	3430		3426	3405	
				3385			3385						3394
2920	2922	2911		2924	2922	2925	2925		2922	2928	2917	2928	2929
1656	1647	1640	16	1652	1643	1643	1642	10	1633	1634		1619	1622
1544	1550	1550		1543	1554	1544	1543						
1411	1400	1408	3						1377				
				1385		1386	1387	2	1385				
										1408	1408	1408	
									1260	1256	1261	1267	1258
				1235	1236	1236	1235						
1198	1198	1198											
1040	1038	1038	0	1033	1035	1033	1035	0	1038	1034	1040	1040	1034
625	617	617							544	536	597	619	591

$\Delta\nu = (\nu_{\text{RM}} - \nu_{\text{Final phase}})$; d = day; E = different treatment.

Table 2. FTIR characteristics of extracted humic substance and fulvic acid for different times of composting of sludge, green waste, and olive oil mill waste [11*, 9**, 20***].

Results of infrared analysis of co-composts of different types of organic matter at different stages, with or without an HS extraction process, showed that only five regions of the FTIR spectrum seem to provide information on the evolution and stability of the humification process. The band located at around 3430 cm^{-1} in the FTIR of composts at the initial stage shift during composting to stabilize at lower wave numbers (3402 cm^{-1}) at the end of the humification process. The increase in the relative intensity of this band during composting shows that the compost has a better water retention capacity, which is likely related to the increase of the cation exchange capacity that changes during composting. Water retention in the soil is correlated to the CEC that is linked to the hydration properties of organic matter and clays [42].

The $3000\text{--}2800\text{-cm}^{-1}$ region reflects the hydrophobic properties of the aliphatic organic matter. The bands in this region are better resolved than those in the spectra of composts. We noted a decrease of these bands during the first 8 weeks of humification consistent with the microbial oxidation of the carbon chains of aliphatic and peptidic compounds, which provides information on the maturity of the co-composting process. Moreover, peaks that characterize both methyl and methylene groups in lignin and in compost remain centered at 2855 cm^{-1} and around 2920 cm^{-1} , but the other characteristic peak of the methyl groups is located at 2958 cm^{-1} after the humification process (Figure 1). This frequency change reflects that the structure of the aliphatic groups generated after composting is different from that of the lignin and the cellulose characterized by C-H bands situated at wave numbers below 2930 cm^{-1} (Table 3).

Holocellulose	Cellulose		Hemicellulose				Lignin	
3425 ^a	3417 ^c	–	3200 ^e	3425 ^a	3436 ^b	–	3410 ^f	3410–3460 ^d
2928 ^a	2924 ^c	–		2928	2932	–	2933 ^f	2937 ^e
–	2916 ^c	–	2900 ^e			–		2917 ^d
					2850			2845 ^e
–	–	–	2800 ^e			–		
1736 ^a	–	–	–	–	–	–	1705 ^f	1717 ^d
1634 ^a	1634 ^c	–	1630 ^e	1646 ^a	1634	1606 ^d	–1605 ^f	1610 ^d
	–	–	–	–	–	–		
1537 ^a	–	–	–	–	–	–		1514 ^d
1463 ^a	1460	–	–	–	–	1460	1460 ^f	1462 ^d
	1433	1431 ^d	1430 ^e	1413 ^a	1421	–	1424 ^f	
1382 ^a	1378	1373 ^d	1367 ^e		1378			
		1338 ^d						
1320 ^a	–	1319 ^d	1315 ^e	1324 ^a	1324	–	1327 ^f	1328 ^d
								1276 ^d
1258 ^a				1242 ^a	1262	1251		
	1208	1203 ^d	1220 ^e	–	–	1212	1213 ^f	1220 ^d
1161 ^a	1161	–	1160 ^e	–	–			
1110 ^a	1114	–	1110	1130 ^a	1130	–	1113 ^f	
1064 ^a	1064	–	1055 ^e	–	1044	1049		1038 ^d

Holocellulose	Cellulose		Hemicellulose		Lignin
904 ^a			908		
–	897	–	878 ^e	873 ^a	854 ^d
–			621 ^a	590 ^f	

^a Xu et al. [53].

^b Xu et al. [45].

^c Liu et al. [54].

^d Boeriu et al. [44].

^e Méndez et al. [55].

^f Eyheraguibel [56].

Table 3. Usual wave numbers from FTIR spectra.

In the region 1750–1700 cm⁻¹, FTIR spectra (Figure 1) show a significant reduction in the intensity of the band located at 1735 cm⁻¹ at the beginning of composting. Lignin is known to contain carboxyl groups represented by carboxyl vibrations between 1750 and 1550 cm⁻¹ in the FTIR spectra, and a significant difference was found in the finger print region (1830–730 cm⁻¹) [43, 44]. The FTIR spectra of flax, hemp, and straw lignin show three peaks, whereas the peak at 1647 cm⁻¹ seems to be absent in AlcellTM lignin (Figure 2), the band at 1705 cm⁻¹ increases in oxidized lignin (flax-ox), in solvent-extracted hardwood lignin and in sulfur-free softwood lignin, but is absent in softwood lignosulfonates and Kraft lignin. From the analysis of the FTIR spectra of plant material, the 1750–1700-cm⁻¹ region is characteristic of lignin. In the case of the cellulose and holocellulose extracts, the presence of bands around 1700–1740 cm⁻¹, in the FTIR spectrum of the holocellulosic fraction and its absence in the spectra of cellulosic and hemicellulosic extracts (Table 3), was interpreted by the presence of a fraction of lignin which joins the holocellulose during extraction [45]. On the FTIR spectra of purchased cellulose and hemicellulose, no band was observed in at this region [46]. Our FTIR spectra (Figure 1) show a marked decrease in the band at 1735 cm⁻¹ at the beginning of composting. This decrease indicates that structural changes occur in the lignin at the beginning of humification. This is supported by the decrease in the intensity of the band around 1514 cm⁻¹, which characterizes the aromatic skeletal vibration in lignin [47].

In the region 1650–1600 cm⁻¹, FTIR spectra show an increase in the intensity of the band at 1647 cm⁻¹ during co-composting. This band, characteristic of $\nu_{C=O}$ of the ionized COO⁻ function, shifts toward 1640 cm⁻¹ at the end of humification. However, the band located at 1155 cm⁻¹ is attributed to the ν_{C-O} increase. The change in the intensity of bands observed around 1647 cm⁻¹ and 1155 cm⁻¹ indicates the presence of a carboxyl function which characterizes an ester form.

In the region 1000–1040 cm⁻¹, the band located at 1035 cm⁻¹ persists during the humification process and even after calcination at 650°C (Figure 3). It is due to the mineral phase provided by the sludge. The presence of similar bands in this region of the IR spectrum is common when the IR spectrum is recorded from soil that has undergone a specific extraction process [28, 29].

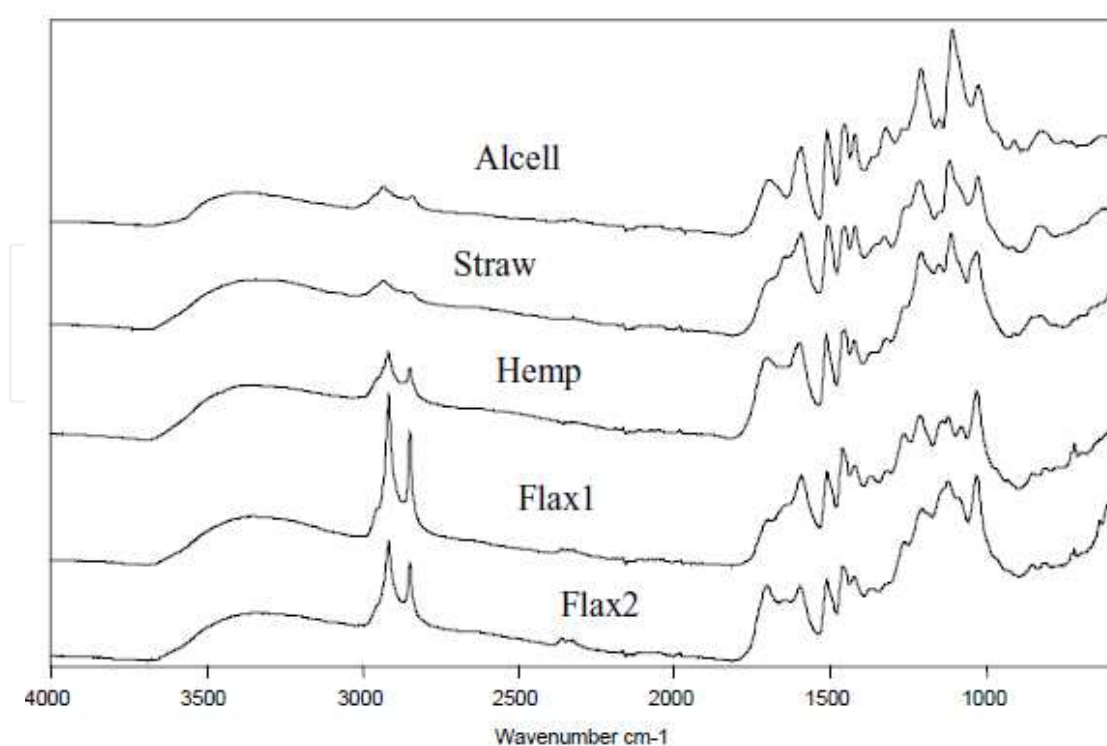


Figure 2. FTIR spectra of lignin from different substrates [52].

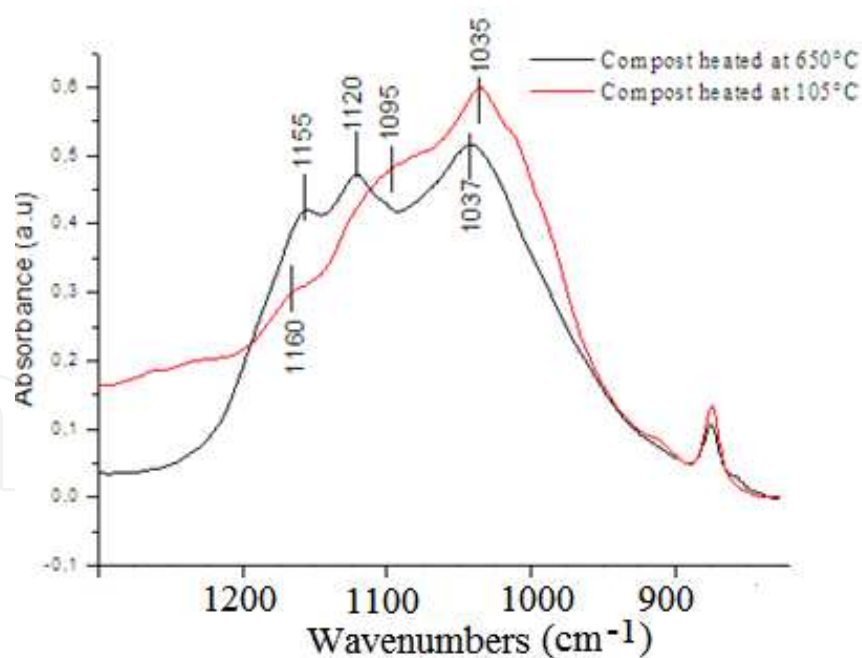


Figure 3. FTIR spectra before and after calcination of compost.

The remaining part of the recalcitrant organic matter such as lignin hemicellulose could contribute to the FTIR spectrum. As shown by Faix et al. [48], the lignin compounds are characterized by the frequencies of the guaiacyl unit (1269 cm^{-1} , G-ring and C=O stretch; 1140

cm⁻¹, CH in-plane deformation; 854 and 817 cm⁻¹). On the other hand, the hemicellulose fraction contains noticeable amounts of polysaccharides and can contribute to the FTIR spectrum by bands identified at 1413 and 1242 cm⁻¹, which designate the methyl C–H wagging vibrations and carbonyl absorbance in pectic polysaccharide substances [45]. Bands around 1161 and 897 cm⁻¹ were attributed to C–O–C stretching at the β-(1-4)-glycosidic linkages [49]. It seems that the assignment of bands appearing at wave numbers below 1600 cm⁻¹ remains difficult because this region contains vibrations characteristic of different compounds present in recalcitrant organic matter.

The comparison of the FTIR spectrum obtained from HA extracted from uncomposted sludge after lipid removal, lipid-free HA (LFHA), or without lipid removal (HA0) shows the same profiles with shift frequencies (Table 4). The bands located at 3414 and 1652 cm⁻¹ shift to 3404 and 1646 cm⁻¹, respectively, at the end of the humification process. However, the wave numbers from FTIR of HA0 are lower (3397 and 1644 cm⁻¹). Piccolo et al. [50] and Preston and Schnitzer [51] suggested that fatty acids occur in HSs partly as phenolic esters and partly adsorbed by weaker forces such as H-bonding and van der Waals forces. Lipids are present as an admixture, or held by noncovalent bonds to humic macromolecules. Our spectra show that the presence of the lipid fraction provokes band shifts toward lower frequencies. This type of shift is encountered in the case of hydrogen bonding interactions. Nevertheless, our spectral data show that even in the presence of the lipid fraction, the FTIR spectra provide information on changes that occur during composting on condition that the appropriate spectral regions are considered.

HA0	LFHA			Δν (cm ⁻¹)
	0 d	30 d	180 d	
	3414	3413	3404	7
3397				
2921	2930	2933	2930	
2854	2854	2855		
1644	1652	1647	1646	2
1544	1540	1511	1510	
1453	1456	1458	1458	
1414	1420	1420	1419	
	1387	1387	1387	0
1264	1264	1264	1263	
1231	1230	1229	1227	4
1120	1126	1126	1125	
1076	1076	1076	1076	
1032	1036	1036	1037	5

HA0	LFHA			$\Delta\nu$ (cm ⁻¹)
	0 d	30 d	180 d	
987	987	987	987	0
611	611			

$\Delta\nu = (\nu_{RM} - \nu_{Final\ phase})$; LFHA = lipid-free humic acid; HA 0 = without lipid removal; d = day.

Table 4. FTIR spectral characteristics versus composting time [11].

It appears from this study that FTIR spectroscopy can be used as a tool to monitor organic matter degradation and stability during composting. The comparison of the relative intensities of the aliphatic chain bands (region 3000–2800 cm⁻¹) reflects the evolution of the compost during the process of humification. The band at 1035 cm⁻¹ attributed to mineral compounds could be used as internal reference. FTIR spectra show that whatever the organic substrate used, humification is accompanied by the disappearance of the band at 1750–1700 cm⁻¹ whose intensity decreases at the beginning of composting. In parallel, we found that the bands located at 3420 and 1655 cm⁻¹ gradually shift to around 3400 and 1640 cm⁻¹, respectively, at the end of composting. This shift toward lower wave numbers can be used as an index of the stability of compost.

5. Conclusion

The detailed analysis of FTIR spectra recorded on different composts led to the identification of five important regions of the spectrum, which can reflect structural changes during composting. From the specific frequency bands, it is possible to follow qualitatively and rapidly the biodegradation steps during composting:

- At the first stage of humification, the significant decrease in the intensity of the band located at 1735 cm⁻¹, which is found only on the FTIR spectrum of lignin, shows that lignin is assigned to the first stage of the composting process.
- At the end of the humification process, the band located around 3450–3420 cm⁻¹ is shifted to lower wave numbers by around $\Delta\nu = 10$ cm⁻¹.
- The band located at 1660–1650 cm⁻¹, on the FTIR spectra before composting, is shifted to lower wave numbers by around a $\Delta\nu = 7$ –8 cm⁻¹ at the end of humification. These shifts can be used as a maturity index of the compost.
- The band at 1040–1035 cm⁻¹ is not affected by the process of humification and may be due to the mineral phase in the sludge.
- The 3000–2800-cm⁻¹ region reflects the hydrophobic properties of the aliphatic organic matter. The decrease of these bands during humification is consistent with the degradation of aliphatic carbon chains and peptidic compounds, which provides information on the

maturity of co-composting process. Using the band at 1035 cm^{-1} as an internal standard, it is possible to quantify the degradation rate of organic matter in the compost during the humification process, thereby making the FTIR technique quantitative as well as qualitative for assessment of compost maturity.

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