Preliminary Design for Establishing Compost Maturity by Using the Spectral Characteristics of Five Organic Fertilizers

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Abstract

The maturity of compost is involved in the availability of nutrients to crops and improvement of soil properties after fertilization. The determination of composts maturity mostly required analyses in the laboratory previously and it must consume a lot of time and cost. This studies were conducted to use Fourier Transform Infrared (FTIR) spectroscopy and solid ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) spectroscopy to understand the mature characteristics of five type of common composts. The FTIR analysis showed that all composts contained aromatic groups. In addition, the surface of composts were enriched with the functional groups including hydroxyl group, carboxyl group, amino group etc. However, these functional groups changed along with maturity degree. It is preliminarily recognized that the aliphatic group located at 2,930 cm^{-1} and 2,850 cm^{-1} showed a decreasing peak, and amino acid at 1,385 cm^{-1} was disappearing gradually due to the decomposition by bacteria. There may be used to identify the maturity degree of composts. Productions of aromatic group at 1,650 cm^{-1}, carboxy (-COOH) and phenolic OH groups at 1,385 cm^{-1} may prove the full maturity of composts. ^{13}C NMR analysis showed that five type of matured composts are mainly consisted with aliphatic groups and aromatic groups. The surfaces of the composts contained C-O bounds (CO carbons-alcohols, ester, ethers, carbohydrates and other functional groups), COO^- (carboxyl and ester carbons) and C = O bond (aldehydes and ketones). The strength of different absorptive characteristics of FTIR and ^{13}C NMR may be a clue of the maturity of composts for future designing reference of detective instruments.

Introduction

Organic agriculture has paid more attention and the application of organic fertilizer was gradually increased recently [1]. Organic fertilizer is produced through composting of complex organic materials which are decomposed by microorganism and converted to simple and stable components as fertilizer [2,3]. Mature compost can serve nutrients quickly for plants after application due to its low C/N ratio [4]. Application of mature compost can provide large amount of elements (N, P, K etc.) and trace elements (Fe, Mn, B etc.) to crops, and even inhibit activities of pathogen in the soil [4,5]. Humic acid is the main component of the humus. Carboxylic and phenolic groups in humic acid containing OH bonds which are the sites for bonding with metals [6,7].

Traditional index for evaluation of compost maturity includes pH (Joyce et al., 2010)[8], electrical conductivity[4], C/N ratio[5,8], humic acid (HA) and fulvic acid (FA) ratio [3,5] and germination of vegetable seeds. Generally, several indices are combined to judge the maturity of compost [9]. However, these methods mostly require chemical and biological analyses in the laboratory, and these procedures must consume a lot of time and cost, and the disposal of chemicals will cause pollution of environment.

In the past there were many successful examples of studies with FTIR and ^{13}C NMR analyses [8]. These methods are also widely used in medicine, foods and engineering, etc. In agriculture they are also used for the examination of timber quality [10], germination characteristics of rice [11,12,13] and humic acid characteristics [14]. These methods are highly correlated positivity with traditional chemical or biological methods of analyses [5]. They are not only saving time and labor but also reducing use of chemicals that pollute environment in comparison with the traditional chemical analytical methods. In this research, Fourier Transform Infrared (FTIR) spectroscopy and ^{13}C Nuclear Magnetic Resonance (^{13}C .NMR) were used for understanding the characteristics of five composts. It may serve the clue to design the simple type spectral instrument for detecting the mature degree of composts in the future.

Materials And Methods

Producing and Sampling of Composts

Treatment of five types of compost by using commonly available materials were chicken manure, pig manure, cattle manure, lemon manure and soybean meal. Every kind of material was mixed with sawdust at the ratio of 3 to 1, respectively. The moisture were adjusted to 55–60% and the thermometer were inserted into the middle layer of the above-mentioned composts. They were turned over twice a week. Beginning at third week, the compost was turned over once a week. Water content was monitored with tensiometer and controlled at 60–65%. Properties of the compost were determined on samples (500 g) taken at 1, 2nd, 4th, 6th and 8th week. Sampled at 500 g each were randomly collected for FTIR analysis at 0, 3rd, 6th and 9th week. Each sample was heated in oven at 70–75 ^{o}C for 2–3 days and then ground as crushed powder for subsequent analysis.

Measurements of general properties for composts

Sample at 0.2 g was used to measure C with an element analyzer (Elementar vario EL III). N was measured following Kjeldahal method [15]. The C/N ratio was then calculated. The composts were saturated with water and stirred thoroughly for pH determination with grass electrodes [16]. Sample at 100 g was ashed in an oven at 600 ^{o}C about 24 hours for the measurement of organic matter. The weight loss was the organic matter content and expressed in percentage of the sample weight (Nelson and Sommer 1982). Sample at 0.2 g was decomposed by H_2SO_4 and then measured K (potassium), Ca (calcium), Mg (magnesium), Fe (iron), Mn (manganese), Cu (copper) and Zn (zinc) [17,18] by Inductiively coupled plasma spectrometer (ICP, JY Ultima2). Phosphor was extracted by Bray No. 1 method and measured with Molybdenum method [19].

Measurement of humic acid

Extraction and purification of humic acid from matured composts were based on the method recommended by the International Humic Substance Society (IHSS) [20,21], Procedures for extraction and purification of humic substance were briefly described as follows. Compost sample at 20 g was put in 300 ml of 0.1 M HCl (w/v = 1:10) and pH at 1–2 for the suspended fluid. The sample was subjected to oscillection by a back and forth scillator for 1 hour and then centrifuged for 10 min at 15, 400 g. After discarding the clear liquid, the sample in solid was added 200 ml (w/v = 1:10) 0.1 M NaOH, aerated with N_2 for 2 min to remove oxygen and closed tightly with a cap for more than 4 hrs oscillation. It was centrifuged for 20 min at 15,400 g. The upper clear liquid was collected and adjust to pH at 1.0 with 6 M HCl and settled for 12–16 hours. The upper clear and the sediment were separated first by siphoning and then by centrifuging at 1,000 g for 20 min. The sediment (humic acid) was then dissolved with mineral amount of 0.1 M KOH under N_2 aerated condition. KCl was added to adjust the solution to contain 0.3M of K^+. The suspended soild was removed after 10 min centrifugation under 15,400 g. The humic acid was then reprecipitated by acidification as previous step. After centrifugation the upper clear liquid was removed and the humic acid in precipitate was suspended in a solution of 0.1 M HCl with 0.3 M HF. The sample was oscillated over night at room temperature and then centrifuges again. This procedure was respected 3 times in order to reduce the ash content to 1% or less. The humic acid was rinsed with distilled water 3 times to remove residual acid and then suspended liquid is freeze dried before storing in a discator.

FTIR measurement on compost

The analysis was based on method of silverstein *et al*. (1981). Sample at 1 mg was grounded in an agate motor and added into 200 mg of KBr pre-dried at 110 ^oC and mixed well before put in a die, then rotated the die several times with 10,000–15,000 lb/m^2 preserved for 3 min under air-pressurization. The sample was now in KBr pellet. Fourier Transform Infrared spectrophotometer (FTIR) (Shimazu, Japan) was used to measure light transmissivity at wave number from 4,000 to 400 cm^{-1} [22].

^{13}C Nuclear Magnetic Resonance spectrophometer analysis

One gram of sample was put in a grass tube of 4 cm long with 10 mm inner diameter and subjected to solid Nuclear Magnetic Resonance spectrophotometer (MSL-200 NMR type, Germany) measurement under super conductive magnetic field. The spectral frequence of the instrument was 50.33 MHz with 1 ms retardation time (acquisition time, delay time) and 1s recycle time. The magic angle spinning rate was about 3.5 KHz. The spectra were separated into 0–50, 50–90, 90–110, 110–140, 140–160 and 160–190 ppm sections based on chemical shift in order to show single intensity of different types of carbon. Relative content of each carbon chemical structure was its areal integration by a computer program. The area of each section was calculated and expressed in its percentage [8,9,23,24].

Results And Discussion

Characterstics of five composts

Chicken manure compost showed its temperature raise to 65–75 ^oC after 3 days of composting. The compost is turned over twice in the first week. It is overturned once a week from the second week. Compost samples are collected at 0, 2nd, 4th, 6th and 8th week for property analysis. Table 1 showed that chicken manure compost had a pH at 7.8 before fermentation. The pH value gradually decrease with composting time. The pH reachs a neutral value at 7.1 after 6 weeks. The organic matter content starts from 92.5% and decreases to 64.0% at the 8th week while the humic acid increase with the composting time [25]. The C/N ratio decreases from 23.7 to 19.7, indicating it is fully decomposed and mature since the general compost has a C/N ratio below 20 [26]. Carbon content decreases from 58.1–43.3%, while nitrogen decreases from 2.45–2.2%. On the other hand, Increasing with composting time, P, K, Ca, Mg, Fe, Mn, Cu, Zn and Na all gradually increasing. Table 2 indicates cattle manure compost has a pH at 7.3 at 0 week and 7.1 at 8th week. Organic matter content drops from 91.3–55.2%, while humic acid increases from 1.91–3.25%. After 6 weeks the C/N decreases to below 20, indicating that the cattle manure compost had been decomposed and matured. The contents of P, K, Ca, Mg, Fe, Mn, Cu, Zn and Na all clearly increase with composting time. Table 3 indicates pig manure compost has pH at 7.2 at the 0 week but decreases from 88.8–6.11% while humic acid increases from 0.7–2.5%. Carbon content decreases from 61.2–48.6% while nitrogen increases from 23.3–2.45%. Contents of P, K, Ca, Mg, Fe, Mn, Cu, Zn and Na are all significantly increasing with composting time. C/N ratio decreased from 26.3 to 19.8. At 8th week the ratio drops below 20, indicating maturity of the pig manure compost. Table 4 shows that the pH value indicates weak acidic for soybean manure compost at 0 week but gradually decreases with composting time, reaching 6.2 at 8th week. The organic matter content drops from 90.2–67.0% at 8th week. Humic acid increases from 0.47–1.26%, carbon from 55.1–47.0% while nitrogen from 5.04–5.33%. The contents of P, K and Na were not stable along the composting time with up and down in values. There was an increasing trend for Ca, Mg. Fe, Mn, Cu and Zn. As soybean had high nitrogen content, its C/N ratio was below 20 with slightly decreased along composting time. It was below 10 at the 2nd week and reaching 9.1 at the 8th week. Thus the soybean manure compost is not recommended for field application in large quantity to avoid damaging crops. Table 5 showed pH value suggested week acid at the beginning of the lemon manure compost and had an increasing trend which was related to the decomposition of organic acid in the lemon peel. The organic matter decreased from 90.2–58.9% while humic acid increased from 1.3–4.9%, carbon decrease from 26.07–58.1% while nitrogen increased slightly from 2.62–2.94%. There was an increasing trend for P, K, Ca, Mg, Fe, Mn, Cu, Zn and Na with composting time. The C/N ratio started at 27.4 and drops to 19.8 at the 8th week. Thus the lemon manure compost is mature after 8 weeks.

Table 1
The chemical properties of chicken manure at different sampling stage

Sampling time	pH	OM[3] (%)	HA[4] (%)	C/N	C	N	P	K	Ca	Mg	Mn	Fe	Cu	Zn	Na
					(%)						(%)				
W0[2]	7.8^{a1}	92.5^{a}	1.8^{b}	23.7^{a}	58.1^{a}	2.45^{a}	0.89^{b}	3.08^{b}	4.15^{ab}	0.83^{c}	478^{b}	607^{c}	78^{b}	597^{b}	5257^{a}
W2	7.6^{a}	88.6^{a}	2.3^{ab}	23.0^{a}	55.4^{a}	2.40^{a}	0.78^{b}	2.82^{b}	3.26^{b}	0.90^{c}	387^{b}	628^{c}	86^{b}	695^{b}	5174^{a}
W4	7.6^{a}	79.3^{ab}	3.2^{ab}	21.6^{a}	50.5^{a}	2.34^{a}	1.42^{a}	4.12^{a}	4.14^{ab}	1.78^{b}	1008^{a}	2532^{b}	136^{a}	1318^{a}	7226^{a}
W6	7.3^{a}	68.8^{b}	4.1^{a}	20.6^{a}	47.6^{ab}	2.31^{a}	1.47^{a}	4.18^{a}	4.83^{a}	2.29^{a}	1197^{b}	3266^{a}	167^{a}	1550^{a}	7698^{a}
W8	7.1^{a}	64.0^{b}	4.9^{a}	19.7^{b}	43.3^{b}	2.20^{a}	1.87^{a}	4.25^{a}	5.64^{a}	2.94^{a}	1565^{a}	4565^{a}	129^{a}	1929^{a}	5856^{a}

[1]Different letters indicate significantly different results by LSD tests at $p < 0.05$.

[2]0, 2, 4, 6, 8 week after compost.

[3]organic matter.

[4]humic acid.

Table 2
The chemical properties of cattle manure at different sampling stage.

Sampling time	pH	OM[3] (%)	HA[4] (%)	C/N	C	N	P	K	Ca	Mg	Mn	Fe	Cu	Zn	Na
					(%)						(mg/kg)				
W0[2]	7.3^{a1}	91.3^{a}	0.9^{c}	34.3^{a}	65.6^{a}	1.91^{b}	0.35^{b}	0.21^{b}	0.91^{b}	0.17^{b}	78^{c}	135^{c}	127^{c}	193^{d}	480^{c}
W2	7.2^{a}	88.2^{a}	1.3^{c}	25.8^{a}	62.2^{a}	2.41^{ab}	0.28^{b}	0.38^{b}	1.40^{b}	1.88^{b}	127^{c}	267^{bc}	215^{b}	323^{c}	898^{b}
W4	7.3^{a}	76.5^{ab}	2.5^{b}	23.4^{ab}	57.9^{a}	2.48^{a}	0.72^{a}	0.58^{a}	2.45^{ab}	1.97^{b}	216^{b}	485^{b}	264^{ab}	536^{b}	1209^{a}
W6	7.1^{a}	65.9^{b}	4.5^{a}	18.0^{b}	57.1^{a}	3.17^{a}	0.86^{a}	0.45^{a}	2.88^{a}	2.41^{a}	250^{ab}	2243^{a}	298^{ab}	639^{b}	906^{b}
W8	7.1^{a}	55.2^{b}	5.0^{a}	17.3^{b}	56.2^{a}	3.25^{a}	0.88^{a}	0.60^{a}	3.32^{a}	2.61^{a}	362^{a}	2683^{a}	367^{a}	1029^{a}	1134^{a}

[1]Different letters indicate significantly different results by LSD tests at $p < 0.05$.

[2]0, 2, 4, 6, 8 week after compost.

[3]organic matter.

[4]humic acid.

Table 3
The chemical properties of pig manure at different sampling stage.

Sampling time	pH	OM[3]	HA[4]	C/N	C	N	P	K	Ca	Mg	Mn	Fe	Cu	Zn	Na
		(%)	(%)		(%)						(mg/kg)				
W0[2]	7.2^{a1}	88.8^{a}	0.7^{c}	26.3^{a}	61.2^{a}	2.33^{a}	0.32^{b}	0.16^{b}	10842^{b}	1604^{c}	113^{b}	217^{d}	152^{c}	434^{c}	596^{b}
W2	7.1^{a}	85.9^{a}	1.4^{b}	26.0^{a}	58.1^{a}	2.23^{a}	0.47^{ab}	0.32^{a}	16817^{b}	2751^{b}	202^{b}	423^{c}	261^{b}	743^{ab}	1111^{a}
W4	6.8^{a}	78.1^{a}	1.6^{b}	24.1^{a}	54.9^{a}	2.28^{a}	0.68^{a}	0.35^{a}	25773^{ab}	3374^{b}	261^{b}	428^{c}	282^{b}	998^{b}	1427^{a}
W6	7.0^{a}	72.6^{a}	2.1^{a}	21.9^{ab}	51.9^{ab}	2.37^{a}	0.86^{a}	0.39^{a}	25560^{ab}	4914^{ab}	308^{a}	1412^{b}	278^{b}	1048^{b}	1203^{a}
W8	7.0^{a}	61.1^{a}	2.5^{a}	19.8^{b}	48.6^{b}	2.45^{a}	0.79^{a}	0.32^{a}	38424^{a}	7361^{a}	406^{a}	4167^{a}	568^{a}	2067^{a}	1057^{a}

[1]Different letters indicate significantly different results by LSD tests at $p < 0.05$.

[2]0, 2, 4, 6, 8 week after compost.

[3]organic matter.

[4]humic acid.

Table 4
The chemical properties of soybean manure at different sampling stage.

Sampling time	pH	OM[3]	HA[4]	C/N	C	N	P	K	Ca	Mg	Mn	Fe	Cu	Zn	Na
		(%)	(%)		(%)						(mg/kg)				
W0[2]	6.8^{a1}	90.2^{a}	0.47^{b}	10.9^{a}	55.1^{a}	5.04^{a}	0.75^{b}	1.71^{a}	20399^{a}	6577^{a}	111^{a}	258^{c}	17^{a}	96^{a}	3679^{a}
W2	6.6^{a}	86.8^{a}	0.62^{b}	9.8^{a}	54.8^{a}	5.14^{a}	0.72^{b}	1.72^{a}	16324^{a}	6332^{a}	101^{a}	313^{c}	20^{a}	97^{a}	3513^{a}
W4	6.4^{a}	76.5^{ab}	1.11^{a}	9.8^{a}	54.1^{a}	5.18a	1.33^{a}	1.64^{a}	15876^{a}	6960^{a}	115^{a}	494^{bc}	18^{a}	106^{a}	3447^{a}
W6	6.2^{a}	75.1^{ab}	1.24^{a}	9.7^{a}	47.5^{a}	5.19^{a}	1.49^{a}	1.79^{a}	21447^{a}	9639^{a}	154^{a}	716^{b}	19^{a}	136^{a}	3507^{a}
W8	6.2^{a}	67.0^{c}	1.26^{a}	9.1^{a}	47.0^{a}	5.33^{a}	1.21^{a}	1.60^{a}	22625^{a}	11832^{a}	167^{a}	1989^{a}	24^{a}	134^{a}	3128^{a}

[1]Different letters indicate significantly different results by LSD tests at $p < 0.05$.

[2]0, 2, 4, 6, 8 week after compost.

[3]organic matter.

[4]humic acid.

Table 5
The chemical properties of lemon manure at different sampling stage.

	pH	OM[3] (%)	HA[4] (%)	C/N	C	N	P	K	Ca	Mg	Mn	Fe	Cu	Zn	Na
					——(%)——						——(mg/kg)——				
W0[2]	6.4^{a1}	90.2^{a}	1.3^{c}	27.4^{a}	71.7^{a}	2.62^{a}	0.23^{a}	1.98^{a}	16029^{c}	1022^{c}	9^{c}	177^{c}	5^{b}	11^{c}	380^{b}
W2	6.4^{a}	86.1^{a}	1.9^{c}	25.9^{a}	70.7^{a}	2.73^{a}	0.21^{a}	2.61^{a}	14115^{c}	2674^{b}	13^{c}	238^{b}	11^{a}	26^{c}	360^{b}
W4	6.3^{a}	76.5^{ab}	2.3^{ab}	27.1^{a}	62.6^{b}	2.29^{a}	0.32^{a}	2.07^{a}	18657^{c}	2288^{b}	22^{b}	301^{b}	12^{a}	35^{b}	301^{b}
W6	6.5^{a}	66.2^{b}	3.1^{b}	21.8^{ab}	63.2^{ab}	2.90^{a}	0.33^{a}	2.33^{a}	25027^{b}	4524^{c}	31^{b}	412^{b}	11^{a}	36^{b}	316^{b}
W8	6.7^{a}	58.9^{b}	4.9^{a}	19.8^{b}	58.1^{b}	2.94^{a}	0.32^{a}	2.33^{a}	51256^{a}	5746^{c}	63^{a}	988^{a}	16^{a}	63^{a}	534^{a}

[1]Different letters indicate significantly different results by LSD tests at $p < 0.05$.

[2]0, 2, 4, 6, 8 week after compost.

[3]organic matter.

[4]humic acid.

In general animal manure compost will decrease its pH value while soybean and lemon manure compost increase their pH values probably due to ammonia N is gradually decomposed by bacteria in the acidic compost of chicken, cattle and pig manures [26]. In the composts of plant manures the organic acid gradually decomposed by bacteria [27]. Thus animal composts and plant composts showed opposite trend in pH values with large amplitude. However all the five types of compost have pH values falling in the range of weak acid and weak alcohol, and so their application will not affect the soil pH too much to affect the effectiveness of nutrients. The contents of organic matter of all five composts described here showed gradual decrease with composting time because the organic matter was gradually decomposed by increasing bacteria amount, resulting in a decrease of organic matter [27]. Due to decomposition of organic matter by bacteria, the organic matter gradually converts to complicated humic acid resulting in an increase of humic acid for all the composts with composting time. The C/N ratio decreased gradually to below 20 at different composting time. Thus in the FTIR and NMR analyses, all samples were taken from the compost with 8 weeks of composting time (all samples with C/N ratio below 20).

FTIR analyses in five composts at different composting time

Through FTIR analysis, the kind and strength of functional groups from different sources of compost (Table 6 and Table 7). The absorption of all five composts with FTIR analysis showed similar characteristics to previous studies [26,28]. According to Shin *et al.* [29], the peak of aliphatic group area at 2,930 cm^{-1} and 2,850 cm^{-1} gradually decreased while amino acid at 1,385 cm^{-1} gradually disappeared due to decomposition by bacteria. These can be used to determine the maturity degree of the compost. The aromatic group at 1,650 cm^{-1} and carboxyl (COOH) and phenolic OH at 1,650 cm^{-1} and other functional groups can be used to verify the maturity of the compost. The construction and interpretation of the spectra of different composts can be evaluated from these change of peaks. This way may be served as a reference for design of special machine when maturity degree of compost was to determine. The functional groups such as carboxyl-COOH, phenolic-OH can bond with metallic ions and so reduce the toxicity of heavy metals from soils.

Table 6
Types of functional groups and their strength as determined by FTIR analysis on different composts.

Composts	strong	medium	weak
Chicken manure	OH group、C = C bonding、C-O or –OH(1160 cm^{-1})	COOH、 C = O	CH、CH_2、CH_3
Cattle manure	OH group、C = C bonding、C-O or -OH(1160 cm^{-1})	COOH、C = O	CH、CH_2、CH_3
Pig manure	OH group、C = C bonding	COOH、C = O、C-O	CH、CH_2、CH_3
Soybean manure	C = C bonding	OH group、COOH、C = O、C-O	CH、CH_2、CH_3
Lemon manure	C = C bonding	OH group、COOH、C = O、C-O	CH、CH_2、CH_3

Table 7
The absorption of FTIR spectroscopy of main wave number at different sampling stage.

Sample time	Absorption degree (%)			
Wave number(cm^{-1})	0 week	3th week	6th week	9th week
Chicken manure				
1450	22.35	19.32	18.15	17.16
1600	19.11	17.23	15.33	13.51
3050	12.33	12.02	11.21	10.27
Cattle manure				
1400	12.08	11.08	10.31	9.05
1650	17.56	16.33	16.12	14.05
3000	15.41	14.33	13.28	11.36
Pig manure				
1380	14.71	13.56	13.15	12.22
1580	20.35	18.78	18.25	16.06
2930	19.47	16.58	15.33	14.19
Soybean manure				
1350	12.89	11.65	11.33	10.56
1480	15.15	14.36	13.52	11.79
2900	9.88	9.05	9.01	8.85
Lemon manure				
1320	12.21	11.55	11.08	9.98
1460	14.25	13.21	12.33	11.95
2950	12.03	11.35	10.12	9.08

Table 8

The ^{13}C NMR spectroscopy of five different composts

	Chicken manure	Cattle manure	Pig manure	Soybean manure	Lemon manure
	%				
0-50 ppm	28.38	22.13	31.62	37.94	36.23
50-110 ppm	32.26	32.20	41.36	43.16	41.10
110-160 ppm[a]	16.51	10.49	17.71	18.40	17.43
160-190 ppm[b]	19.15	13.08	16.51	18.87	18.22
190-220ppm	3.69	2.81	3.72	5.73	5.55
aliphatic C[c]	60.65	54.33	72.97	81.10	77.33

a. Characteristic carbons in the range of chemical shift are assigned as aromatic C
b. Characteristic carbons in the range of chemical shift are assigned as carboxylic C

c. Expressed by the sum of the percentages of the characteristic carbons in the range of chemical shifts of 0-50, 50-110 ppm

For chicken manure the peak of absorption decreased slowly at wave number 1,450 cm^{-1} with composting time. The peak of absorption decreased from mature compost at 22.35% to completely mature one at 17.16%. This showed that the chicken manure decreased its amino acid content due to decomposition by bacteria as the compost becomes more mature. The rapid decrease of amino acid in the chicken manure is probably due to nitrogen decrease with its composting time [7]. At wave number 1,600 cm^{-1} the peak of absorption also decreased rapidly with maturity degree, showing that the aromatic group compounds are also gradually decomposed. At were member 3,050 cm^{-1}, its peak of absorption slowly decreased indicating that aliphatic group compounds decomposed more slowly with maturity. So the measurement of maturity of the chicken manure compost should be set at wave number 1,450 cm^{-1} (wave length about 7,000 nm) with its light absorption below 17%. Light absorption is below 13% at wave namber 1,600 cm^{-1} (wave length about 6,250 nm) or below 10% at wave length about 3,270 nm may be used as an reference in designing simple machines for maturity measurement of chicken manure. For cattle manure, the light of sorption at wave number 1,400 cm^{-1} decreased with composting time from 12.08% at non-mature to 9.05% at completely mature state. This showed that the amino acid was slowly decomposed as maturity degree of the cattle manure compost advances. Compared with the chicken manure compost, N content increased with its maturity, probably due to shrinking of the volume. At wave number 1,650 cm^{-1} its light absorption decreased from 17.65–14.05% while the aromatic group compounds were gradually decomposed by bacteria. At wave number 3,000 cm^{-1}, its light absorption slowly decreased from 15.41–11.36% indicating slower decomposition of the aliphatic group compounds in the cattle manure compost as its maturity increases. The maturity degree measurement of the cattle manure compost can be set at wave number 1,400 cm^{-1} (wave length about 2,140 nm) with light absorption below 9% at wave number 1,650 cm^{-1} (wave length about 6,060 nm with absorption below 14%, and wave number 2,930 cm^{-1} wave length about 3,330 nm) with absorption below 11% [30]. It showed the characteristic absorption peaks of cattle manure (at 3,312, 2,930, 1,050 and 895 cm^{-1}) decreased noticeably. For pig manure compost, the light absorption at wave number 1,380 cm^{-1} decreased with composting time from 14.71% at non-maturity to 12.22% at complete maturity. The amino acid decreases due to decomposition by bacteria. Its decreasing rate is similar to that of cattle manure compost but lower than that of chicken manure compost. The light absorption decreased from 20.35–16.06% at wave number 1580 cm^{-1}, Similar to that of cattle manure and chicken manure composts. Its aromatic group compounds decreased at rate simiilar to the cattle manure compost but slower than chicken manure compost. The light absorption at wave number 2,930 cm^{-1}. Decreased from 19.47–14.19%. Compared with chicken manure and cattle manure composts, the aliphatic group compounds decomposed faster. The maturity degree measurements should be set at wave number 1,380 cm^{-1} (wave length about 2,200 nm) with absorption below 12%, at wave number 1,580 cm^{-1} (wave length 6,300 nm) with absorption below 16% and at wave number 2,930 cm^{-1} (wave length about 3,400 nm) with absorption below 14%. For soybean manure compost, the light absorption at wave number 1,350 cm^{-1} decreased with composting time from 12.89–10.56%, indicating amino acid decomposed rather slowly with maturity of compost. The light absorption at wave number 1,480 cm^{-1} decreased from 15.15–11.79% indicating faster decomposition rate for aromatic group compounds than for amino acid. Its decreasing rate is similar to those of cattle and pig manure compost [31]. concluded that the yield, economic growth, and soil quality of experimental crops were similar under the application of soybean meal and cattle compost.

The absorption at wave number 2,900 cm^{-1} decreased from 9.88–8.85%, similar to that of chicken manure compost, indicating that the decomposition rate of the aliphatic group is similar to that of chicken manure compost but slower than those of cattle and pig manure composts [32]. It showed that the oxidation of composting particles in spectra at 2856 and 1568 cm^{-1}, which are attributed to the the oxidation of pig manure. The maturity measurement of the soybean manure compost can be set at wave number 1,350 cm^{-1} (wave length about 7,400 cm) with light absorption below 10%, at 1,480 cm^{-1} (wave length about 6,700 nm) with absorption below 12% or at 2,900cm^{-1} (wave length about 3,400 nm) with absorption below 8%, For lemon manure compost (Table 7) the light absorption at 1,320 cm^{-1} decreased with composting time from 12.21% at non-mature to 9.98% at complete mature state, indicating slow decomposition rate for amino acid during composting time of the lemon manure compost. The absorption at 1,460 decreased from 14.25–11.95% showing slow decomposition of amino acid (slower than the other four types of manure compost). The absorption at 2,950 cm^{-1} decreased from 12.03–9.08% showing slow decomposition of aliphatic group compounds (slower than the other 4 types of compost). This is due to high content of fiber in this lemon manure compost, rendering slower decomposition amino acid, aromatic group compounds or aliphatic group compounds is analyzed from FTIR (slower than other 4 types of compost).

Summarizing the FTIR on analyses conducted in different time for the five types of compost, we found that the change of compounds at different compost was different. In general, amino acid, aromatic group compounds and aliphatic group compounds showed more apparent changes.

For chicken manure compost, signifcant changes occur at wave umber 1,600 cm^{-1} (wave length about 6,250 nm) with light absorption below 13%. For cattle manure compost, it falls on wave number 1,650 cm^{-1} (wave length about 6,060 nm) with absorption below 14%. Pig manure compost falls at 1580 cm^{-1} (wave lenght about 6,330 nm) with absorption below 16% and at 2,930 cm^{-1} (3,410 nm)with aborption below 14%. Soybean manure compost falls at 1,480 cm^{-1} (6,750 nm) with absorption below 12%. Lemon manure compost falls at 1,460 cm^{-1} (6,840 nm) with absorption below 12%.

^{13}C NMR analyses on five types of compost

To understand the total functional group and their relative ratios in compost, ^{13}C solid NMR spectrophotometer was applied to analyze the component types and relative ratios of the compost [33]. Figure 1 showed solid ^{13}C NMR spectrophotometer analyses on compost of different sources. Based on previous studies chemical shift area may be divided into: 0–50 ppm of alkyl structure; 50–110 ppm of C-O bonding (CO carbon alcohols, ester, ethers carbohydrates); 110–160 ppm of aromatic carbon structures, 160–190 ppm of carboxyl and ester carbons, 190–220 ppm of C = O bond Aldehydes and ketones) [34,35], and resonance spetcral analyses are shown in Table 2 (Table 8). The results showed that all five types of compost are mainly composed of aliphatic group carbon and chromatic group carbon, C-O bond (CO carbons-alcohols, esters, ethers, carbohydrates), carboxyl and ester carbons and C

= O bond (aldehydes and ketones) and other functional groups are on the surface. The results from FTIR and ^{13}C NMR analyses showed that main functional groups are on the surface of the compost, providing a reference for further experiment.

Conclusion

Animal compost (chicken Manure, cattle Manure and pig Manure) has pH values changing from weak base to neutral with composting time. Plant compost (soybean manure and lemon manure) changing from weak acid to neutral as composting time increases. Except for chicken manure compost, all the other four types of compost showed a gradual increase in nitrogen content. FTIR analysis showed that chicken manure compost loses nitrogen due to decomposition of amino acid in large quantity. After 8 weeks, all five types of compost are deemed mature (as C/N ratio drops below 20). All five types of compost showed that some materials may gradually disappear. This may be detected with FTIR, and its light absorption may be used to determine the maturity degree of the compost. This may serve to offer optimal conditions for designing simple light wave machine for maturity determination of a compost in the future.

Declarations

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References

1. Liebig, M. A. & Doran J. W. Impact of organic production practices on soil quality indicators. J. Environ. Qual. 28, 1601–1609, (1999)
2. Hendrix, P. F., Coleman, D. C.& Crossley Jr, D. A. Using knowledge of soil nutrient cycling processes to design sustainable agriculture. J. sustain. agric. 2, 63–82. (1992)
3. He, X. T., Traina, S. J. & Logan T. J. Chemical properties of municipal solid waste compost. J. Environ. Qual. 21, 318–329, (1992)
4. Iwegbue, C. M. A., Egun, A. C., Emuh F. N. & Isirimah, N.O. Compost maturity evaluation and its significance to agriculture. Pak. J. Bio. Sci. 9, 2933–2944, (2006)
5. Provenzanoa, M. R., Malerba, A. D., Pezzolla, D. & Gigliotti, G. Chemical and spectroscopic characterization of organic matter during the anaerobic digestion and successive composting of pig slurry. Waste Manage. 34, 653–660, (2014)
6. Piccolo, A. & Stevenson, F. J. Infrared spectra of Cu^{+2}, Pb^{+2} and Ca^{+2} complexes of soil substances. Geoderma. 27, 195–208, (1981)
7. Liu, H. J., Chen, D. D., Zhang, R. F., Hang, X. N., Li, R. & Shen, Q. R. Amino acids hydrolyzed from animal carcasses are a good additive for the production of bio-organic fertilizer. Front. Microbiol. 7, 1–10, (2016)
8. Clemente, J. S., Gregorich, E. G., Simpson, A. J., Kumar, R., Murias, D. C. & Simpson, M. J. Comparison of nuclear magnetic resonance methods for the analysis of organic matter composition from soil density and particle fractions. Environ. Chem. 9, 97–107, (2010)
9. Verrillo, M., Cozzolino, V., Spaccini, R. & Piccolo, A. Humic substances from green compost increase bioactivity and antibacterial properties of essential oils in Basil leaves. Chem. Biol. Technol. Agric. 8, 1–14, (2021)
10. Chang T.C., Chang H.T., Wu C.L.& Chang S.T. Stabilizing Effects of Extractives on the Photooxidation of Cryptomeria Japonica Heartwood. Qtr. J. Ch. Forestry. 42, 227–238, (2009) (In Chinese)
11. Albrecht, R., Sebag, D. & Verrecchia, E. Organic matter decomposition: bridging the gap between Rock–Eval pyrolysis and chemical characterization (CPMAS ^{13}C NMR). *Biogeochemistry*. 122, 101–111, (2015)
12. Chalbot, M. C., Nikolich, G., Etyemezianb, B., Dubois, D.W., King, J., Shaferd, D., da Costae, G. G., Hinton, J. F. & Kavouras, I.G. Soil humic-like organic compounds in prescribed fire emissions using nuclear magnetic resonance spectroscopy. Environ. Pollut. 181, 167–171, (2013)
13. Zheng, S. Q., Zhang, J. M., Chi, F. Q., Zhou, B. K., Wei, D., Kuang, E.J., Jiang, Y., Mi, G. & Chen, Y. P. Response of the chemical structure of soil organic carbon to modes of maize straw return. Sci. Rep. 11: 6574, (2021)
14. Chang Chien, S. W., Huang C. C. & Wang, M. C. Analytical and spectroscopic characteristics of refuse compost-derived humic substances. Int. J. Appl. Sci. Eng. 1, 62–71, (2003)
15. Chang, S. S. Nowaday analytical method of plant in Taiwan. Nutrient diagnosis technology of crops. Bullitin of Taiwan Agricultural Research Institute. 13, 53–59, (1981) (In Chinese)
16. Cheng, L. L. Determining Lime Requirement for Adjusting Soil pH in Apple Orchards. New York Fruit Qtr. 3, 15–18, (2015)
17. Baker, D. E. & Suhr, N.H. Atomic absorption and flame emission spectrometry. In Page et al.,(eds) Metods of Soil Analysis, Part 2(2nd ed.), pp 13–26, (1982)
18. Parker D. R. & Bertsch P. M. Formation of the “Al13”tridecameric polycation under diverse synthesis conditions. Environ. Sci. Technol. 26, 914–921, (1992)

19. Ma, J., Yuan, Y., Zhou, T. G. & Yuan, D. X. Determination of total phosphorus in natural waters with a simple neutral digestion method using sodium persulfate. Simple neutral digestion method. 15, 372–380, (2017)
20. Shi, J. H., Gao, H. W., Qi, J. H., Zhang, J. & Yao, X. H. Sources, compositions, and distributions of water-soluble organic nitrogen in aerosols over the China Sea. J. Geophys. Res. 115, 1–13, (2010)
21. Tsuda, K., Takata, A., Shirai, H., Kozaki, K., Fujitake, N. A. Method for Quantitative Analysis of Aquatic Humic Substances in Clear Water Based on Carbon Concentration. Anal Sci. 28, 1017–1020, (2012)
22. Silverstein, M. F., Mirer, F. E., Kotelchuk, D., Silverstein, B. & Bennet, M. Mortality among workers in a die casting and electroplating plant. Scand. J. Work Environ. Health. 7, 156–165, (1981)
23. Zhang, J. M., An, T. T., Chi, F. Q., Wei, D., Zhou, B. K., Hao, X. Y., Jin, L. & Wang, J. K. Evolution over years of structural characteristics of humic acids in Black Soil as a function of various fertilization treatments. J. Soils Sediments. 19, 1959–1969, (2019)
24. Chukov, S. N., Lodygin, E. D., Abakumov, E. V. Application of ^{13}C NMR Spectroscopy to the Study of Soil Organic Matter: A Review of Publications. Eurasian Soil Sci. 51, 889–900, (2018)
25. Dorado, J., Almendros, G. & González-Vila, F. J. Response of humic acid structure to soil tillage management as revealed by analytical pyrolysis. J. Anal. Appl. Pyrolysis. 2016, 117, 56–63.
26. Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D. & Engelhard, M. H. Oxidation of black carbon by biotic and abiotic processes. Org. Geochem. 37,1477–1488, (2006)
27. Iwegbue, C. M. A., Egun, A. C., Emuh, F. N. & Isirimah, N. O. Compost Maturity Evaluation and its Significance to Agriculture. Pak. J. Bio. Sci. 9, 2933–2944, (2006)
28. Reddy, S. B.; Nagaraja, M. S., Kadalli G. G. & Champa, B.V. Fourier Transform Infrared (FTIR) Spectroscopy of Soil Humic and Fulvic Acids Extracted from Paddy Land Use System. Int. J. Curr. Microbiol. Appl. Sci. 7, 834–837, (2018)
29. Shin, S. M., Park, J. K. & Jung, S. M. Changes of Aromatic CH and Aliphatic CH in In-situ FT-IR Spectra of Bituminous Coals in the Thermoplastic Range. ISIJ Int. 55, 1591–1598, (2015)
30. Xu, J., Xu, X. H., Liu, Y., Li, H. T. & Liu, H. J. Effect of microbiological inoculants DN-1 on lignocellulose degradation during co-composting of cattle manure with rice straw monitored by FTIR and SEM. Environ. Prog. Sustain. Energy. 35, 345–351, (2015)
31. Roobroeck, D., Palm, C. A., Nziguheba, G., Weil, R. & Vanlauwe, B. Assessing and understanding non-responsiveness of maize and soybean to fertilizer applications in African smallholder farms. Agric. Ecosyst. Environ. 305, 107165, (2020)
32. Ge, J. Y., Huang, G. Q., Yang, Z. L., Huang, J. & Han, L.J. Characterization of the Dynamic Thickness of the Aerobic Layer during Pig Manure Aerobic Composting by Fourier Transform Infrared Microspectroscopy. *Environ. Sci. Technol.* 48, 5043 – 5050, (2014)
33. Romanska, H., Tiziani, S., Howe, R., Gunther, U., Guizar, Z. & Lalani, E. N. Nuclear Magnetic Resonance Detects Phosphoinositide 3-Kinase/Akt–Independent Traits Common to Pluripotent Murine Embryonic Stem Cells and Their Malignant Counterparts. Neoplasia. 11, 1301–1308, (2009)
34. Al-Faiyz, Y. S. S. CPMAS ^{13}C NMR characterization of humic acids from composted agricultural Saudi waste. Arab. J. Chem. 10, 839–853, (2017)
35. Salvino, R.A., Celebre, G. & de Luca, G. Molecular Characterization of the Organic Fraction of Municipal Solid Waste and Compositional Evolution during Oxidative Processes Assessed by HR-MAS ^{13}C NMR Spectroscopy. Appl. Sci. 11, 2267, (2021)

Figures

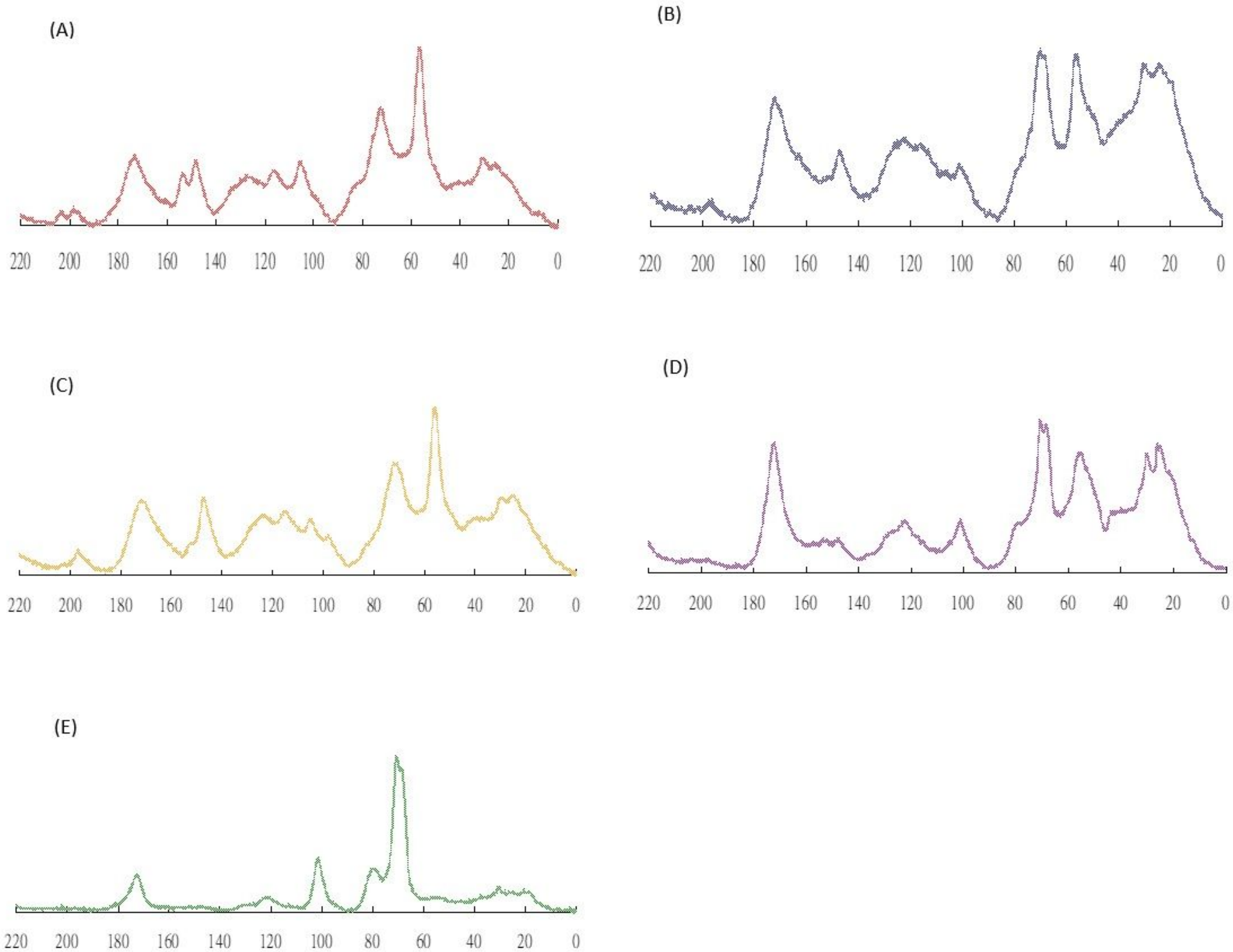

Figure 1

^{13}C NMR graphs of five types of compost. (A:chicken manure, B:cattle manure, C:pig manure, D:soybean manure, E:lemon manure)