Study of Decomposition Pattern duringAerobic Composting of Municipal Solid Waste by Physico-chemical and Spectroscopic methods

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Abstract : Composting process is one of the traditional waste management phenomena that produce a useful product of economic importance. This paper is concerned with structural changes at 10, 20, 30, 40, 50 and 60 days old composting samples (both municipal and pilot). From the results it was observed that pH was tending to neutral towards the 60th day of composting process. Electrical conductivity, organic carbon, moisture content, chloride, total soluble solids, sodium, potassium, carbonates, bicarbonates, alkalinity, available nitrogen, phosphorous and heavy metals were showing decreasing trend at the later stages. Solid state ^{13}C NMR spectra revealed depletion in alkyl-C, O-alkyl-C region, whereas aromatic-C concentration dominated at 60th day. FTIR spectra indicated intense peaks at 1500–1800 cm^{-1} and weak absorptions at 2800–3200 cm^{-1} region towards the 60th day of composting. X-ray diffraction spectra indicated decomposition of complex molecules into smaller fragments.
Keywords : Solid waste, Aerobic composting, Physico-chemical characteristics, FTIR, ^{13}C NMR, X-ray diffraction.

1 Introduction

Enhancedrate in migration of rural population to urban centers for better opportunities of livelihood led to overwhelming demographic growth in many cities worldwide and it is expected to continue for several more years. The increased rate of production and consumption of synthetic products and services is generating a bulkquantity of solid waste in cities. Solid waste management has become a global issue and needs a maximum attention.

The solid waste management involves waste collection, transportation, processing or disposal. Municipal solid wastesare wastes generated from municipal services like street sweeping, dead animals, market wastes, and also includes domestic wastes, commercial wastes and institutional wastes.The municipal solid waste contains large quantity of health hazardous, toxic and dangerous chemicals. Exposure of these wastes to water, soil and atmosphere causes environmental pollution. Several disorders like infections and chronic diseases may occur by direct contact of these wastes or by exposure to the regions polluted by the solid wastes. Burns and other injuries may occur from occupational accidents at waste disposal sites.

Recycling, incineration, composting, open burning, dumping in far-away places etc., are some of the common methods of solid waste management processes. Composting is a biological decomposition process that

converts active organic materials into stabilized nutrient rich products, which can be used for the enrichment of soil fertility.*Aerobic composting* process utilizes oxygen in a controlled condition to biologically decompose the solid wastes, whereas A*naerobic composting*is done in absence of oxygen. Aerobic composting takes shorter time for the degradation than anaerobic composting, and emission of unpleasant odor can also be reduced.

The variation in nutrient concentration and structural changes during the composting process can be evaluated through the analysis of different physico-chemical parameters and spectroscopic characterization. The aim of the present work is to determine the toxicity level in the municipal solid waste due to heavy metals like lead, chromium, etc and how the composition and the structural changes occur in the degradable fraction of municipal solid waste during the composting process through the determination of physico-chemical parameters like pH, temperature, EC, OC, moisture content, chloride, TSS, carbonates, bicarbonates, alkalinity, available nitrogen etc., and FTIR, ^{13}C NMR and X-ray Diffraction methods.

2 Materials and Methods

The study has been carried out in two pilot plants of 3ft×3ft×3ft size i.e., pile A and pile B. Municipal solid waste samples were collected from Municipal Solid Waste Composting site, Vidyaranyapuram, Mysore, and dumped into pile A. In pile B,grass clippings, dry leaves, green leaves and kitchen wastes (containing vegetables, rice materials, paper cups, tea waste and egg shells) were taken. Moisture content was maintained around 40–60%for the growth of microorganisms, which leads to faster degradation. Both piles were mixed periodically and samples were collected during10, 20, 30, 40, 50 and 60th day of composting process. Samples were first dried at 105ºC in hot air oven, crushed well and sieved through 0.2mm mesh. The powdered samples were then used for further physico-chemical and spectral characterization.

2.1 Physico-chemical parameters

Temperature (°C) was noted during the collection of compost samples. Moisture content (%) andTotal soluble salts (mg/g) were estimated by gravimetric method.pH and electric conductivity were found outfor the 1:5 compost-water suspensions.Organic carbon (%) and organic matter (%) were estimated using Walkey and Black method. Water holding capacity (%) was measured using filtration method.Chloride (%) was determined by titration of compost: water (1 : 5) extract with standard silver nitrate solution, using potassium chromate as the indicator. Phosphorus (ppm) was determined throughVanado-molybdate method. Carbonates, bicarbonates and alkalinity (mg CaCO$_3$/L) were estimated by titration of compost : water (1 : 5) extract with standard H$_2$SO$_4$ solution using methyl orange and phenolphthalein as indicators.Calcium and magnesium were estimated by titration of compost : ammonium acetate (1 : 5) extract with standard EDTA solution using Eriochrome Black-T and Patton-Reeder's indicators.Brucine method was used for the estimation of nitrate–nitrogen whereassodium and potassium were determined using Flame photometry. Humification Index was estimated through UV-visible spectrophotometry.

For estimation of heavy metals like lead, manganese, zinc, copper, iron etc.,triacid (nitric acid : sulphuric acid : perchloric acid in 9 : 2 : 1 ratio) extract of the compost sample was used for Atomic Absorption Spectrophotometer.

2.2 Fourier Transform Infra-red (FTIR) spectroscopy

Different bonds (C–C, C=C, C–O, O–H, etc.,) have different vibrational frequencies. These bonds present in the organic matter can be detected by identifying this characteristic frequency as an absorption band in the infrared spectrum.The dry composting samples were finely ground and pressed to tablets with dry KBr powder and analyzed through Shimadzu IR Prestige21 FTIR Spectrophotometer.

2.3 C^{13} Nuclear Magnetic Resonance (^{13}C NMR) spectroscopy

Composting process leads to transformation of organic wastes into stable humic like substances. To understand the transformation of organic matter during composting process, the compost samples were analyzed through 300MHz solid state ^{13}C FT NMR spectrophotometer.The overall chemical shift range was divided into following main regions: Alkyl C (0–50 ppm); O-alkyl-C (60–110 ppm); aromatic-C and aromatic-substituted-C (110–160 ppm); carboxyl-C and carbonyl-C (160–200 ppm).

2.4 X-Ray diffraction method:

The overall structural changes during the decomposition can be studied using X-ray diffraction method. Samples were ground to fine powder and spectra were recorded on Bruker D8 Powder XRD Instrument using the source Copper K alpha.

3 Results and Discussion

3.1 Physico-chemical parameters:

Physico-chemical parameters of the samples from pile A (municipal solid waste) and pile B (known composition) are shown in Tables 3.1 and3.2 respectively. Temperatures of both the piles increased at the beginning of the composting process indicating the decomposition of organic matter and further decrease towards 60th day of composting process indicates the stabilization of the decomposed organic matter.

Compost samples from both the piles showed alkaline pH, which was tending to neutral value along with progress of composting process.During different degradation stages, decrease in pH wasobserved, which can be attributed to the production of CO_2 from organic acids and loss of nitrogen as reported by Lugtenberg (2009), and ammonia volatilization could be one of the most important reasonsfor pH drop (Kim *et al*., 2008; Elango*et al*., 2009). Decrease in the value of electrical conductivity towards later stages of the process was due to lowering of ionic concentration, indicating the growth in maturity of the compost.

Table 3.1Physico-chemical parameters of compost samples for pile A (MSW)

S. No.	Sampling days	10	20	30	40	50	60
1	Temperature (^{o}C)	56	40	38	31	30	28
2	Moisture (%)	57	65	54	63	55	48
3	pH	7.47	7.80	7.92	7.80	7.72	7.47
4	Electric Conductivity (dS/m)	8.3	8.2	6.7	5.0	3.0	3.1
5	Calcium (mEq/L)	15.617	14.453	13.871	16.102	14.55	18.042
6	Magnesium (mEq/L)	8.536	8.73	8.148	7.857	7.372	6.79
7	Organic carbon (%)	12.86	17.14	10.52	9.944	9.93	8.76
8	Organic matter (%)	22.17	29.55	18.14	17.14	17.12	15.10
9	TSS (mg/g)	3.76	3.54	2.76	3.10	1.37	1.3
10	Chloride (%)	0.256	1.282	0.996	0.384	0.236	0.233
11	Carbonates ($mgCaCO_3$/L)	0.238	0.238	0.143	0.095	0.095	0.048
12	Bicarbonates ($mgCaCO_3$/L)	0.475	1.188	1.14	0.38	0.38	0.333
13	Alkalinity ($mgCaCO_3$/L)	0.951	1.664	1.426	0.57	0.57	0.429
14	Water holding capacity (%)	44.23	40.49	46.60	51.31	55.63	55.99
15	Nitrate–Nitrogen (ppm)	68	73	55	42	39	27
16	Available-Nitrogen (g/kg)	0.711	0.778	0.736	0.814	0.829	0.832
17	Phosphorous (%)	1.05	1.03	1.03	1.0	0.9	0.9
18	Potassium (mg/g)	12.8	183.	13.0	8.1	5.9	5.8
19	Sodium (mg/g)	6.5	7.3	6.7	2.9	1.5	1.3
20	Humification Index	8.35	8.43	8.62	8.88	8.94	9.08

Calcium, one of the important nutrients for the growth of microorganisms, got decreased at the beginning of the composting process and increased towards 60th day of composting process,where as magnesium goes on decreasing from 10 to 60th day .Since degradation process results in liberation of carbon dioxide and methane gas from the activity of microorganisms, percentage of organic carbon (OC) and hence percentage of organic matter (OM) lowered during the process. Fares *et al*. (2005) reported that carbon loss accounted for initial total carbon during the composting process.

Table 3.2 Physico-chemical parameters of compost samples from pile B (Pilot)

S.No.	Sampling days	10	20	30	40	50	60
1	Temperature (^{o}C)	40	30	29	27	26	26
2	Moisture (%)	39	51	45	49	46	42
3	pH	7.42	7.18	7.20	7.13	7.14	7.04
4	Electric Conductivity (dS/m)	1.8	2.0	1.5	1.03	1.02	1.0
5	Calcium (mEq/L)	14.065	14.55	13.774	12.804	13.58	14.356
6	Magnesium (mEq/L)	5.141	3.686	5.432	5.238	4.656	4.656
7	Organic carbon (%)	9.94	8.38	7.99	8.18	7.98	7.43
8	Organic matter (%)	17.14	14.45	13.77	14.10	13.76	13.43
9	TSS (mg/g)	1.08	0.76	0.87	0.70	0.56	0.49
10	Chloride (%)	0.256	0.202	0.175	0.027	0.032	0.013
11	Carbonates (mgCaCO$_3$/L)	0.143	0.238	0.048	0.095	0.095	0.048
12	Bicarbonates (mgCaCO$_3$/L)	0.238	0.333	0.285	0.285	0.238	0.428
13	Alkalinity (mgCaCO$_3$/L)	0.524	0.809	0.381	0.475	0.428	0.524
14	Water holding capacity (%)	39.29	42.51	44.53	50.13	53.25	62.53
15	Nitrate-Nitrogen (ppm)	33	43	37	31	32	25
16	Available Nitrogen (g/kg)	1.624	1.638	1.694	1.684	1.750	1.750
17	Phosphorous (%)	0.65	0.71	0.71	0.53	0.5	0.5
18	Potassium (mg/g)	2.5	2.9	2.5	1.9	1.7	1.5
19	Sodium (mg/g)	0.3	0.8	0.5	0.5	0.4	0.3
20	Humification Index	5.80	6.31	6.37	6.42	6.44	6.74

Water holding capacity of compostwas the ability of compost to hold water against the force of gravity. For both pile A and pile B it got increased towards 60th day(pile A 55.99% and pile B 62.53%). The high

er quantity of water holding capacity can be utilized to increase the water holding capacity in soil.

Total water soluble solids got decreased as the solid waste underwent degradation. Samples from pile A indicated the variation from 3.76 to 1.3 mg/g and samples from pileB varied from 1.08 to 0.49 mg/g. Since composting process ends up with formation of stable humic like substances, the concentration of soluble solids decreased during the process.

Alkalinity is a measure of the capacity of water or any solution to neutralize or "buffer" acids. The decrease in the concentration of carbonates and bicarbonates caused lowering of alkalinity towards 60th day of

composting. Since carbonates and bicarbonates decreased towards the end of composting process, alkalizing effect will not occur when it is applied to fields.

The concentration of chloridecontent in solid waste showed decreasing trend during composting process. For pile A, it decreased from 1.282% to 0.233%, whereas for pile B, it decreased up to 0.013% from 0.256%. This may be due to formation of volatile chlorine formation during the decomposition of solid waste and liberation of chlorine gas to the atmosphere.

Nitrogen is an essential macronutrient needed by all the plants to thrive. Nitrate nitrogen concentration towards the 60th day of composting process got decreased, whereas concentration of available nitrogen was increased during the composting phenomena. From 10th day to the 60th day of composting process for pile A, it was increased from 0.711 to 0.832 g/kg and for pile B, from 1.624 to 1.750 g/kg. Other nutrients like potassium, phosphorous and sodium resulted in decrease of concentration

3.2 Heavy metals analysis

Various heavy metal concentrations for the composting samples from piles A and B are listed in Tables 3.3 and 3.4.

Table 3.3 Heavy metal concentrations for the composting samples from Pile A

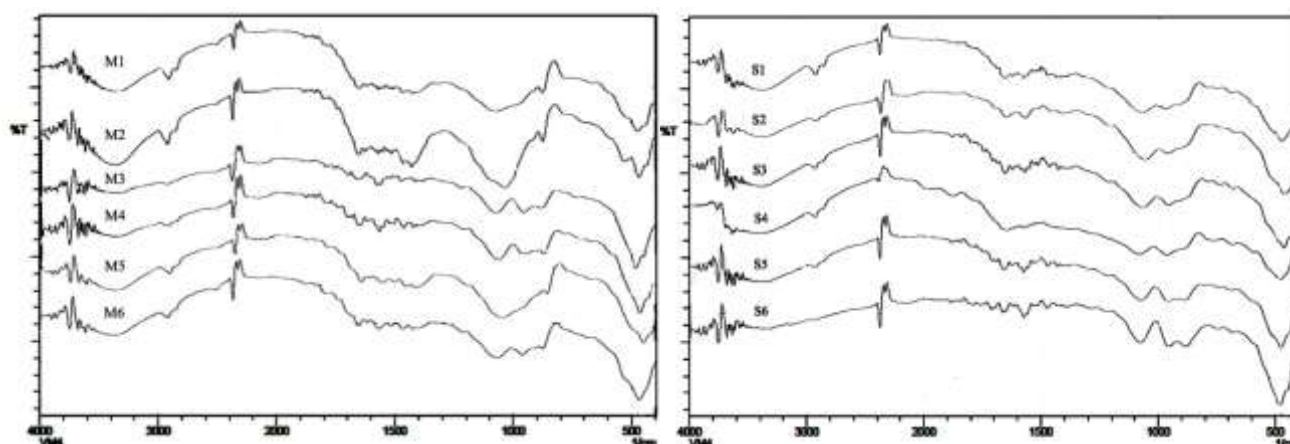| S.No.	Sampling days	10	20	30	40	50	60
	Table 3.3 Heavy metal concentrations for the composting samples from Pile A						
1	**Copper(g/kg)**	0.203	0.204	0.216	0.186	0.170	0.170
2	**Zinc(g/kg)**	0.197	0.198	0.205	0.190	0.187	0.175
3	**Iron(g/kg)**	4.81	5.17	5.19	8.48	7.95	6.92
4	**Manganese (g/kg)**	0.244	0.254	0.238	0.250	0.230	0.230
5	**Lead (g/kg)**	0.051	0.035	0.040	0.050	0.23	0.21
6	**Chromium(g/kg)**	0.078	0.067	0.65	0.79	0.73	0.69
7	**Nickel(g/kg)**	0.029	0.27	0.028	0.29	0.028	0.023

Samples from piles A and B were rich in iron content compared to other materials (3.795 to 8.48 g/kg).

Metals like chromium and nickel were found at lower concentrations whereas lead concentration was found to be below detectable limits for the samples from pile B.

Heavy metal concentrations got increased up to 30th day of composting process and at the later stages got decreased. This was due to release of metal ions from larger solid wastes materials during the decomposition process, and further decrease was due to leaching of metal ions by water.

Table 3.3 Heavy metal concentrations for the composting samples from Pile B

S. No.	Sampling days	10	20	30	40	50	60
1	**Copper(g/kg)**	0.043	0.032	0.034	0.032	0.032	0.031
2	**Zinc(g/kg)**	0.085	0.077	0.091	0.077	0.078	0.076
3	**Iron(g/kg)**	3.815	3.795	4.65	4.285	4.2	4.02
4	**Manganese (g/kg)**	0.368	0.332	0.360	0.366	0.332	0.322
5	**Lead (g/kg)**	BDL	BDL	BDL	BDL	BDL	BDL
6	**Chromium(g/kg)**	0.033	0.027	0.031	0.026	0.025	0.024
7	**Nickel(g/kg)**	0.023	0.021	0.022	0.021	0.018	0.014

Fig 3a: FTIR spectra of composting samples at different maturity stages for pile A and B

3.3 Fourier Transform Infra-red (FTIR) spectroscopy

Figure 3a showsthe FTIR spectra of composting samples from piles A and B at different maturity stages. M1, M2, M3, M4, M5 and M6 represent the spectra of 10th, 20th, 30th, 40th, 50th and 60th days old samples, respectively, for pile A. Similarly S1, S2, S3, S4, S5 and S6 represent the spectra of 10th, 20th, 30th, 40th, 50th and 60^{th}days old samples of pile B.

A broad absorbance band was observed around 3300–3400cm^{-1} (H-bonds, -OH groups) and two distinct peaks were at 2850, 2950cm^{-1} (C–H asymmetric, C–H stretching for –CH group). Sharp peaks were observed at 1650 cm^{-1} (C=C in aromatic region), 1560 cm^{-1} (amide bonds) and 1450cm^{-1}.(C–H$_{def}$ for CH$_2$ and CH$_3$ groups). A weak absorbance band was observed at 1160cm^{-1} (aliphatic CH$_2$, OH or C–O stretch of various groups) and broad peak at 1040–1080 cm^{-1} region represents C–O$_{str}$ of polysaccharides,Si–O$_{str}$ (Jenn-Hung Hsu *et al.*, 1998).

From FTIR spectra of composting samples at different maturity stages, it was observed that peaks in the aliphatic region (2850–2950cm^{-1})got reduced towards 60th day of composting process, and for pile B it got almost disappeared. The absorbance at aromatic region (1650 cm^{-1}) becomes stronger towards the 60th day, indicating the formation of stable aromatic compound after the decomposition of long chain aliphatic compounds. Peaks in the aliphatic, polysaccharide region got reduced towards 60th day of composting process, indicating the formation stable products.

3.4 ^{13}C NMR spectroscopy

The ^{13}C NMR spectra for composting samples at different maturity stages for pile A (MSW) is represented in Figure 3b.Since pile B had only vegetables and readily degradable materials, clear spectra was not obtained.Since structure of compost is very complex, it is difficult to find out to which molecule or compound the functional group belongs. Hence different regions of ^{13}C NMR spectra were analyzed for compost samples at different maturity stages.
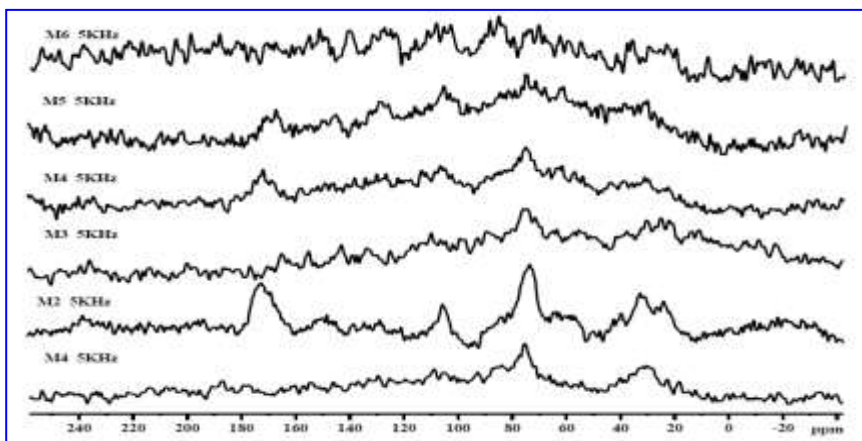

Fig 3b: ^{13}C NMR spectra for composting samples at different maturity stages for pile A

The depletion in the alkyl–C (0–60 ppm) and O–Alkyl–C (6–110ppm) was observed towards the formation of mature 60th day compost sample. Less mature compost sample (10 days) was dominated by the signal in carboxyl-C and carbonyl-C region(160–200 ppm) whereas aromatic-C and aromatic substituted-C (110-160ppm) dominated at 60th day composting sample. As indicated in FTIR spectra, the formation of stable aromatic compounds during composting process was clear. The depletion of carboxyl-C and carbonyl-C is possible due to liberation of carbon dioxide during the decomposition of active organic matter by microorganisms.

3.5 X-Ray diffraction analysis

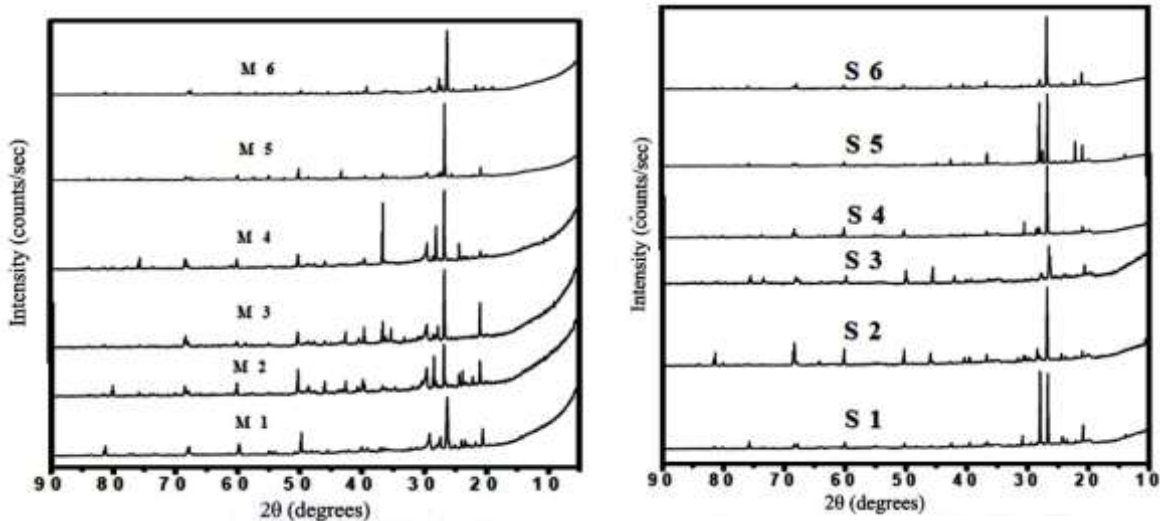X-ray diffraction spectra of composting samples from piles A and B at different maturity stages are shown in Fig. 3c.

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Fig 3c: XRD spectra of composting samples at different maturity stages for piles A and B

X-Ray diffraction is a useful tool to get the structural information of crystalline compounds. Each signal in XRD represents the plane of a crystal. Spectra of both pile A and pile B revealed intense peaks for composting samples of 20 and 30th days. Most of the signals almost disappeared towards the 60th day of composting process. From the overall data obtained from the X-ray diffraction spectra, it is clear that particle size decreases during the degradation of solid waste.

4 Conclusions

Increase in temperature at the earlier stage of composting process and further decrease revealed the decomposition of organic matter followed by the formation of stable products after decomposition of organic matter. Variation in different physico-chemical parameters was observed during the degradation of municipal solid waste by aerobic composting. Increase in the parameters like water holding capacity, available nitrogen during the composting process and availability of most of the required nutrient for plants makes compost as a good fertilizer.

Both FTIR and 13C NMR revealed the formation of stable aromatic compounds from the decomposition of long chain aliphatic compounds and liberation of carbon dioxide and methane gas. Degradation of complex molecules into smaller constituents was indicated by X-ray diffraction method. From the above study it is clear that structural changes take place during the composting phenomena leading to the formation of stable nutrient rich product.

Acknowledgement

References

1.   Almendrosa G, DoradoaJ, González-VilabFJ, BlancocMJ, LankesdU: *^{13}C NMR assessment of decomposition patterns during composting of forest and shrub biomass,*2000;*32(6)*.
2.   Castaldi P, Alberti G, Merella R, Melis P: *Study of the organic matter evolution during municipal solid waste composting aimed at identifying suitable parameters for the evaluation of compost maturity*, 2005; *25(2)*, 209.

3.   FaridBarjea, Loubna. El Felsa, Houda. El Hajjoujia, Soumia. Amirb, Peter Wintertonc, Mohamed Hafidia: *Molecular behaviour of humic acid-like substances during co-composting of olive mill waste and the organic part of municipal solid waste,* 2012;*74,* 17.

4.   HuangGF, WuQT, WongJWC, NagarBB: *Transformation of organic matter during co-composting of pig manure with sawdust,* 2006;*97,* 1834.

5.   Giovanni Gigliotti, Klaus Kaiser, Georg Guggenberger, Ludwig Haumaie: *Differences in the chemical composition of dissolved organic matter from waste material of different sources,Biology and Fertility of Soils* 2002, *36,* 321.

6.   Hogarh JN, Fobil JN, Ofosu-Budu GK, Carboo D, Ankrah NA,Nyarko A: *Assessment of Heavy Metal Contamination and Macro-Nutrient content of Composts for Environmental Pollution Control in Ghana,Global Journal of Environmental Research*2008, *2(3),* 133

7.   Jenn-Hung Hsu, Shang-Lien Lo: *Chemical and spectroscopic analysis of organic matter transformations during composting of pig manure,*1999;*104,*189.

8.   Lucimar Lopes Fialhoa, b,Wilson Tadeu Lopes da Silvaa,Débora MBP Miloria, Marcelo LuizSimõesa, Ladislau Martin-Neto: *Characterization of organic matter from composting of different residues by physicochemical and spectroscopic methods,* 2010; *101(6),* 1927.

9.   Mahdi Ahmed, AzniIdris, Syed Omar SR: *Physicochemical characterization of compost of the industrial tannery sludge, Journal of Engineering Science and Technology*2007;*2(1),* 81.

10.   Maria Rosaria Provenzano, Sandra Cristina de Oliveira, Mary Rosa Santiago Silva, Nicola Senesi: *Assessment of maturity degree of composts from domestic solid wastes by fluorescence and fourier transform infrared spectroscopies,*2001, *49(12),* 5874.

11.   Martinpichler, Heikeknicker,Ingridkogel-Knabner: *Changes in the chemical structure of municipal solid waste during composting as studied by solid-state dipolar dephasing and PSRE ^{13}C NMR and Solid-State NMR Spectroscopy. Environmental Science & Technology,* 2000;*34(18),* 4034.

12.   Mohammad AshikIqbal Khan,Kihachi Ucno, Sakae Horimoto,Fuminori Komai, Kinji Tanaka, Yoshitaka Ono: *Physicochemical, including spectroscopic, and biological analyses during composting of green tea waste and rice bran,*2009;*45,*306.

13.   Neil Glagovich M, Timothy D. Shine organic spectroscopy laboratory: *Utilizing IR and NMR in the identification of an unknown substance,Journal of Chemical Education*2005;*82,* 9.

14.   AlbrechtR, ZiarelliF, Alarcón-GutiérrezE, Le PetitJ, TerromG, PerissolC: *^{13}C solid-state NMR assessment of decomposition pattern during co-composting of sewage sludge and green wastes,* 2008;*59,*442.

15.   Riccardo Spaccini, Alessandro Piccolo: *Spectroscopic characterization of compost at different maturity stages.www.clean-journal.com,*2008,*36(2),* 152.

16.   Sharma AK, GuptaDP: *Physico-chemical characteristics of municipal solid waste of Bhopal city. Enviromedia*2006, *25(4),* 871.

17.   Slomczynska B, Slomczynski T: *Physico-chemical and toxicological characteristics of leachates from MSW Landfills, Polish Journal of Environmental Studies*2004;*13(6),* 627.

18.   TechnischeUniversitat Mu¨nchen, 85350 Freising–Weihenstephan, Germany. *Environmental Science & Technology*, Vol. 34, 18.

19.   Jayarama ReddyP: *Municipal solid waste management:Processing - Energy Recovery - Global Examples,* 2011, *1,* 27.

20.   JanakiramT,SrideviK: *Conversion of waste into wealth:A study in solid waste management,* 2010;*7(4),*1340.

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