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Spectroscopic evaluation of Temperature affecting humification and maturity of MSW composting

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Abstract: Composting of municipal solid waste is practiced to obtain a more suitable and pathogen free marketable fertilizer for agricultural recycling. The humic acids were extracted from compost of the municipal solid wastes collected from Rohtak, Haryana that was treated aerobically. The municipal waste (15 kg), and bulking agents were added to treatment Cw1 (waste), Cw2 (waste+ consortia), Cw3 (waste+ cow dung) and trial Cw4 (waste+ consortia+ cowdung), composted using drum composter in winter season. A bacterial consortia and cow dung was inoculated to the treatments to evaluate the significant effects of temperature on humification (E2/E3, E4/E6 ratio) and to check if the compost has attained maturity was estimated by UV and FTIR spectroscopy. The results indicated that treatment Cw4 (bacterial inoculation and cow dung) depicted maximum degree of humification and maturation, in order: (Cw4>Cw3>Cw2>Cw1) compared to control and other treatment. To conclude, the degree of compost humification on substrate indicates compost maturity for MSW compost samples was incomplete and temperature played a major role in waste composting

Index Terms: humic acids, FTIR, UV-Vis spectroscopy, aliphatic, humification, Municipal solid waste.

1. INTRODUCTION:

Composting is defined as an aerobically occurring thermophilic microbial degradation or a biological oxidative exothermic process which stabilizes and humidifies the organic matter present in waste material [1] aided by microorganisms leading to stabilization, maturing, deodorizing, abundance of humic substances with a final pathogen free hygienic marketable product [2-4]. In India, around 51% of the generated solid waste is organic in nature and so has a good potential for composting. Also, recycling of these wastes to a fertilizer or soil conditioner through composting is reliable method to combat the problem of enormous quantity of waste being generated in India [5]. Humic acids (HA) are the polymeric complexes of organic acids ranging widely in molecular weights and are resistant to microbial degradation in soil. These polymeric complexes are heterogeneous functional groups that depending on origin and age, may be phenolic, aromatic, quinolic and aliphatic with different molecular sizes, structural and chemical properties [6-8]. 1995; Chin et al. 1998) affecting their biological, physical and chemical reactions. Therefore, investigating the changes developing in the organic matter may be used for compost maturity assessment. The humification degree of organic matter signifies the production of humic-like substances, acknowledged as a measure of maturity. Various studies like the humification index- ratio, HA: FA (humic acid to fulvic acid ratio), spectroscopic analysis, humic acid percentage and the physico-chemical characterization of humic-like

substances denote maturity of compost. HAs being the most active fractions improve the tendency of nutrient absorption by plants and help soil microorganisms, stimulate respiration and photosynthesis in plants and positively affect the N and P dynamics favoring soil aggregate formation [9]. During composting of municipal solid waste as the treatment proceeds, there is relative increase in the aromatization and unsaturation of the humic acids with the unstable organic aliphatic and protein compounds being transformed to more stable humic compounds through microbial oxidative processes producing polycondensed olefinic/aromatic structure. The humic acid (HA), fulvic acid (FA) and humin compose SOM that are measured depending on solubility of these in alkaline and acidic solutions [10]. The humification index (HI), which is described as the Humic substances to non-HSs ratio is affected by the atomic ratios of C/H, O/C and C/N, the acidic functional groups and spectroscopic parameters. All of these play a defining role in determining the HS quality that influences the degree of humification to evaluate compost maturity [11-14]. For evaluation of SOM quality E4/E6 and E2/E3 ratios are determined by characterization of HA and FA in humification process to indicate the molecular size or degree of chemical complexity. Fourier transform infrared (FT-IR) spectroscopy is utilized frequently for environmental analysis being a nondestructive method for analysis and elucidates the structure and quantification of a large variety of biological, organic, and inorganic samples. It is majorly used for determination of soil organic matter [15], humic and fulvic acids [16-17] and to characterize humic substances for compost maturity [18]. In this study, inoculation of microbial consortia and cowdung was used to enhance the MSW composting by increasing the degree of humification in the process. Investigations were conducted at the plant screen house, Department of Environmental Sciences, M.D.U, Rohtak. The characteristics of Humic Acids were studied by using UV spectroscopy and FTIR during the composting of MSW. The routine profiling of the parameters for inoculated and non-inoculated treatments was done for the composting process. It was clear that microbial inoculation with cow dung affects positively during initial thermophilic stage of composting and enhance the waste stabilization process. The results could provide a useful theoretical and practical foundation for MSW composting in India when applied on larger scale in field.

2. MATERIALS AND METHODOLOGY:

The compost material derived from the four MSW treatments (Cw1 to Cw4): were used for extraction of HA's, purified afterwards. The procedure of composting was carried out in triplicates in closed bins of height 1.5ft with appropriate bedding material. The piles were turned every three days for initial two weeks and then turning was done after 1 week for rest of the composting period. Sampling was done at regular intervals (15, 30, 60 and 90 days) until the waste was stabilized.

2.1 *Extraction of the humic acids*:

The humic substances were extracted from the samples (30 g) by initial treatment with 40 ml of distilled H2O to remove non-humic, water-soluble substances, to avoid the interferences [10]. Then addition of 40 ml of NaOH (0.1M) was done and extraction was repeated until all the color from solutions disappeared followed by centrifugation at 4000 × g for 15 min. The supernatants were filtered through Whatman paper and precipitated by acid treatment with 1.5M H2SO4 for 24 h at 4 °C. The humic acids were separated from fulvic acid solution by filtration through Whatman paper and redissolved in 0.1M NaOH. The lyophilized humic acids were analyzed by various chemical techniques: a) Elemental analysis was performed for C, H, O and N on Perkin-Elmer 2400 Series; (b) The E4/E6 ratio was determined by measuring the absorbance at 465 and 665 nm as described by [19] and (c) FTIR spectra were recorded as KBr pellets with using a FTIR Perkin-Elmer 2000 spectrophotometer over the 4,000–400 cm-1 range at a rate of 0.5 cm/s.

3. RESULTS AND DISCUSSION:

3.1 Elemental analysis and E2/E3, E4/E6 Absorption Ratio:

Humic substances are considered the most essential part of organic fraction of compost. The degree of humification and compost maturity is represented by the increase in HA level [20]. Humic and fulvic acids extracted from composts after 90 days of degradation, were subjected to elemental analysis following procedure suggested by [21]. The elemental composition and absorbance measurements (E2/E3, E4/E6 Ratio) of the HA fractions obtained from MSW compost at initial and final stages of treatments are shown in Table1. It was observed that in all the treatments the C/N and O/C ration declined due to decrease in C, H and increased O percentage while nitrogen remained constant except in Cw3 treatment at final stages of composting process. This is attributed to the intense microbial activity and cow dung addition that causes reorganization of degraded molecules and form highly condensed aromatic compounds. A decreasing value of C may be attributed to organic material decomposition while a decrease in H is explained by substitution of aliphatic chains by aromatic groups. The C/H ratio was highest in treatment Cw4; depicting that HA and FA increase was highest after composting, indicating a relative highest increase in unsaturated structures while there was a relative decrease in C/O ratio of HA and FA indicated an increase in O-containing group. Average molecular weight or particle size defines the E4/E6 ratio which is related to the condensation degree of the aromatic C network, low ratio associated with high degree of aromatic HA condensation while a high ratio relates to high aliphatic character. The UV absorbance spectrum for E4/E6 ratio of excluded HA fraction (Table 1) shows a parallel decrease initially that may be associated with increasing molecular weight or decreasing acidity of the excluded fractions [19, 22] and an increase in later stages due to decreasing molecular weight of HA, aliphatic compound or increase in O content and carboxylic acids. As could be seen from the table below, the E2/E3 absorption ratio (Table 1) of excluded HA fraction decreases with time as the composting proceeds, this absorption ratio correlates the aromatic character and molecular size [23]. The compost maturity is evaluated by humification Index [24] which considered as an important indicator. The degree of polymerization/humification is calculated for humic substances by Humification Index (HI) = $C_{HA/}C_{FA}$ ratio, and HI>1, is a sign of maturity of the compost [25]. As seen from the table 1, the values for Cw4 treatment was not in accordance with the index that evaluates the compost stability as the percentage of TEC transformation into humic acids. Also, degree of humification does not correlate with the assigned value > 60% during the composting process indicating an immature compost with not possessing HA-like fraction characteristics as required for a standard soil HA.

Also, $\Delta \log K = \log A_{465} - \log A_{665}$ [26] as depicted in table 2 is estimated.

3.2 HA FTIR Spectroscopy:

Infrared Spectroscopy is considered a qualitative tool for chemical group and HA complexes structure characterization by indicator bands. Figure 1 illustrates the absorption bands marked by arrows for evaluation of progression in MSW composting process. The HA extracted from MSW show broad banding in comparison to pure compounds that generate sharp absorption peaks. This may be attributed to overlapping absorption of similar functional group. Three major wave number regions signalizing quick evaluation of the MSW composting process are: a) A reduction and then attainment of fluctuating aliphatic methylene bands at 2850 cm^{-1} indicating degradation of easily degradable substances, (b) a decreasing weak shoulder at 1230 cm-1 (C-O-C and C-N stretching), (c) an increasing band at 1590 cm-1 due to building of aromatic skeleton and d) appearance of the nitrate band at 1359 cm-1 in the compost spectrum at initial stage of composting corresponds to nitrate evolution in the biological process . A decreasing, not very sharp but distinct band in the wavenumber region 1220 cm- depicts cellulose degradation. The absence of bands at (2920 cm-1/1640 cm-1) and 1745-1685, 1610-1567 indicates instabilityof compost [27] suggesting that the humification is not yet complete. The emerging and disappearing band at 1310 cm-1 can be ascribed the typical behavior of metabolic products derived due to aromatic amines. The band at 960 cm^{-1} cm^{-1} depict C-O stretch due to decreasing polysaccharides. Lastly, a unrelative and lowering band peaks at 3395 cm^{-1}, 1080 cm^{-} imputes silica, and quartz and carbonates at wave number 713 cm^{-1} indicating a decrease in polysaccharides with an increase in aromatic condensation and aliphatic carbon. The FTIR spectral pattern of HA at final treatment stages for all treatments were not very different except certain absorption peaks indicating similar structural formation of HA but variable structure unit with different number of functional groups. The treatment Cw-4 indicated that microbial inoculation with dung could enhance the increase in aromatic content with decrease in polysaccharide and aliphatic content. The microbes also generated condensation molecules as indicated by loss of alky chains, carbohydrates, nitrogen containing functions, carboxylic acids. Comparative assessment of the atomic E4/E6 ratio's, elemental composition and FTIR spectra of all treatments ascertain that HA aromatization and condensation rates was in following order: (Cw-4>Cw-3>Cw-2>Cw-1). Similar results were reported by [28-32] where the microbial inoculation highly enhanced and affected the composting process. Overall it can be seen that microbial inoculation would enhance the humification degree and stabilize the process for MSW treatment if optimum temperature is available, via composting on larger scale.

Figure 1: HA- FTIR spectra at the initial and final stages of MSW composting

5. Conclusion"

The results obtained from elemental, UV and FTIR Spectra analysis showed that MSW composting with microbial inoculation and cow dung addition leads to development of early maturity with increase in aromatization degree and decompose the large molecular weight aliphatic, lipolic polysaccharides and peptide compounds to low molecular weight polycondensation compounds in HA fraction in comparison to treatment with no inoculation. These changes support the preferential oxidation of readily accessible moieties such as aliphatic side chains of lipidic and peptidic structures, leading to the production of highly functionalized aromatic macromolecules. So, the inoculated treatment had a clear advantage over non-inoculated MSW compost set. The degree of compost humification on substrate indicates compost maturity from MSW compost samples was incomplete and it was reported that temperature played a major role in waste composting.

Treatment	C (%)	N (%)	H (%)	O (%)	C/H	O/C	E_2/E_3	E_4/E_6	Δ Log K	HI(C_{HA} /C_{FA})	DH
Initial	59.3± 0.02	1.8 ±0.	8.2± 0.15	41.2±0. 05	0.8±0. 05	0.8±0. 04	8.3±0. 17	0.9±0. 12	1.9± 0.05	0.4±0.1 0	29.4±0.1 1

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Cw-1	54.3± 0.05	1.9 ±0. 03	7.6± 0.04	38.1±0. 15	0.8±0. 09	0.7±0. 02	6.1±0. 15	2.6±0. 14	1.8± 0.12	0.5±0.0 3	40.0±0.1 9
Cw-2	49.6± 0.09	2.2 ±0. 13	6.1± 0.05	46.3±0. 12	0.9±0. 22	0.6±0. 15	5.4±0. 15	3.3±0. 13	1.4± 0.14	0.7±0.1 5	46.1±0.3 2
Cw-3	47.1± 0.14	2.7 ±0. 01	6.2± 0.12	42.9±0. 02	0.9±0. 17	0.6±0. 01	4.1±0. 05	3.8±0. 08	1.5± 0.09	0.7±0.0 5	44.8±0.1 6
Cw-4	44.1± 0.03	2.6 ±0. 12	5.9± 0.17	45.8±0. 05	1.0±0. 19	0.6±0. 26	3.4±0. 25	4.2±0. 05	1.3± 0.15	0.8±0.0 9	50.4±0.1 8
Soil HA	54.6	3.2	4.8	35.5	1.0	0.5	2.7	5.0	1.1	>1	>60%

Table 1: Elemental composition, E2/E3, E4/E6 ratios, atomic ratios of HA at 90 days of the MSW composting

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