Extraction and characterisation of humic acid from different organic wastes and its physico-chemical properties

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DOI: https://doi.org/10.22271/chemi.2020.v8.i1k.8359

Abstract
A study on characterization and extraction of humic acid collected from various agro-industrial and agricultural organic wastes from different locations viz., cocopeat, coffee pulp, pressmud, biofuel waste, distillery biocompost, sewage sludge, poultry manure, vermicompost, urban compost and farm yard manure (FYM). Results reveal that physical properties such as bulk density and water holding capacity of different organic wastes ranged from 0.22 Mg m\(^{-1}\) (85.50 %) in coco peat to 0.69 Mg m\(^{-1}\) (40.21%) of biofuel waste. Chemical properties like pH of poultry manure (pH 8.32) were alkaline in nature and biofuel waste (pH 5.28) slightly acidic in nature. Electrical conductivity was high 1.89 dSm\(^{-1}\) in coffee pulp followed by FYM 1.50 dSm\(^{-1}\). Organic carbon content was higher (40.99%) in biofuel waste. While it was lowest (14.13%) in sewage sludge. With respect to major and secondary nutrients poultry manure recorded higher total N, P, K and Ca (2.85, 1.56, 1.92 and 3.89 %) and iron, manganese, copper and zinc (3850, 541.30, 76 and 476 mg kg\(^{-1}\) respectively). Higher recovery of humic and fulvic acid, (8.92 and 4.21 %, respectively) was recorded in press mud and lowest was in coco peat with 3.43 and 2.45 per cent, respectively. Elemental composition (CHNO) of humic acid extracted from poultry manure had higher N (6.01 %) followed by pressmud and coffee pulp. Higher C (61.04 %) and H (8.89%) were recorded in biofuel waste and O (52.31 %) was higher in sewage sludge. Carboxyl (6.08 meq g\(^{-1}\)), phenolic hydroxyl (1.94 meq g\(^{-1}\)) groups and total acidity (8.02 meq g\(^{-1}\)) was higher in poultry manure followed by pressmud and coffee pulp. However, lower content of carboxyl (2.84 meq g\(^{-1}\)) phenolic hydroxyl group (1.32 meq g\(^{-1}\)) and total acidity (4.16 meq g\(^{-1}\)) was observed in biofuel waste. Slightly higher concentration of nickel (21.8 mg kg\(^{-1}\)) and chromium (17 mg kg\(^{-1}\)) was observed in humic acid of sewage sludge.

Keywords: Humic acid, fulvic acid, organic wastes, physical and chemical properties, percent recovery, elemental composition

Introduction
Organic matter is considered as the “Life of soil” due to its importance in maintaining fertility of the soil, the depletion of the same will become a major threat to food security in the years to come. Hence, there is a need to improve the soil fertility in a sustainable manner by utilizing the locally available agro-industrial and other organic wastes because these wastes contains substantial amount of nutrients which are necessary for the plant growth in addition to maintaining of soil health. Utilization of these agro industrial wastes and other organic wastes as a source of nutrients reduces the reliance on chemical fertilizers and these organic wastes provides substantial quantity of nutrient elements as well as humus which helps in improving the physical, chemical and biological properties of soil. However, to improve the organic matter content of soils many management techniques have been adopted such as crop rotation, plough techniques, green manuring and application of animal residues, application of humic acids and humates (Doran, 2003) [2]. Use of bulky organic manures has been considered as a burden by the farmers as it requires large number of labourer for transportation and application. Also, use of bulky organic manures results in spreading of weed seeds in crop land and control of weeds would also be a major problem. In this context, extraction of humic substances from bulky organic manures and their use may help solve many problems associated with use of bulky organic manures.
Many of the agro industrial units viz., sugar mills distilleries etc., generate large quanties of organic wastes which pose problems of disposal and transport. In this context extraction of humic acid from these agro industrial wastes would be a very valuable alternative. The industry would benefit in overcoming disposal and transportation. Composition of the organic waste varies due to many factors. The composition mainly depends on the type of waste, which is dependent on the raw materials used in the industry or the human population and how often waste is collected and how it is disposed.

Humic acids are heterogeneous, which include macromolecule, hydrophilic acidic functional groups and hydrophobic groups. Humic acid hydrophilic groups promotes hydration and thus increases the water retention capacity in soils. Humic acid (HA) is the main fractions of humic substance (HS) and the most active components of soil and compost. Physically, it promotes good soil structure and increases the water holding capacity of the soil, biologically it enhances the growth of useful soil organisms, and chemically it serves as an effective adsorption and retention complex for inorganic plant nutrients and there by enhances nutrient uptake and yield by improving the quality and production of crops.

Keeping all these factors in view present investigation entitled “Extraction and charactrisation of humic acid from different organic wastes and its physico-chemical properties” was carried out with an objective of Extraction and characterization of humic acid from different organic wastes.

Material and Methods
Characterization of organic wastes
Various agro-industrial and agricultural organic wastes were collected from different locations and the details of collection are furnished in Table 1. The organic waste samples were air dried, powdered and stored for further analysis.

Nutrient content of organic waste
Powdered samples of organic material was analyzed for pH and electrical conductivity in 1:10 and 1:100 ratio of organic waste and distilled water. Kjeldhal digestion cum distillation method was adopted for total N estimation. For other macro, secondary and micro nutrients estimation organic waste samples were digested separately using diacid mixture. The methods adopted for estimation are presented in Table 2.

Extraction, fractionation and quantification of humic substances
Extraction of humic substances
Ten gram of air dried organic sample was weighed in to 250 ml conical flask 100 ml of 0.1 N NaOH was added (Schnitzer and Skinner, 1968) and shaken for 24 hours. Dark colored supernatant solution was separated by centrifugation and collected. The extraction procedure was repeated thrice using 50 ml of extractant each time for complete extraction of the humic substances.

Fractionation and purification of humic substances
Precipitated humic acid fraction was separated by centrifugation. Precipitation and centrifugation was repeated to attain partial purification of humic acid fraction as described by Stevenson (1981) (20). The fractions were further purified by treating with HCl-HF mixture (5 ml of each HCl and HF acids were dissolved in 990 ml of double distilled water) for 24 hours and this acid mixture was separated by centrifugation. The residue so obtained was thoroughly washed with distilled water and freeze dried to obtain humic acid.

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Table 1: Organic wastes from different locations

| Humic acid sources                  | Sources                                      |
|------------------------------------|----------------------------------------------|
| Coco peat                          | Cocopeat industry, Doddaballapur             |
| Coffee pulp                        | Farmers field, Chikkamagalur                |
| Pressmud                           | Chamundeshwari Distillery, K.M Dodd, Mandya  |
| Biofuel waste                      | Organic farming unit, UAS, GKV, Bangalore    |
| Distillery bio compost             | Chamundeshwari Distillery, K.M Dodd, Mandya  |
| Sewage sludge                      | Sewage treatment plant, Jakkur, Bangalore    |
| Poultry manure                     | Poultry farm, Doddaballapur                 |
| Vermicompost                       | Zonal agricultural research station, UAS, GKV |
| Urban compost                      | Karnataka compost development corporation, Bangalore |
| Farmyard manure                    | Farmer’s field, Harohalli                   |

Table 2: Methods adopted for the analysis of organic wastes

| Parameter          | Method                                 | Reference         |
|--------------------|----------------------------------------|-------------------|
| MWHC (%)           | Keen’s Cup                             | Piper (1966)      |
| pH                 | Potentiometry                          | Jackson (1973)    |
| EC (dS m⁻¹)        | Conductometry                          | Jackson (1973)    |
| Organic carbon (%) | Dry combustion                         | Jackson (1973)    |
| Total nitrogen (%) | Micro kjeldahl digestion and distillation | Piper (1966)  |
| Total phosphorus (%) | Vanadomolybdic yellow colour spectrophotometry | Piper (1966)  |
| Total potassium (%) | Flame photometry                       | Piper (1966)      |
| Total calcium (%)  | Versenate titrimetry                   | Piper (1966)      |
| Total magnesium (%) | Versenate titrimetry                   | Piper (1966)      |
| Total sulphur (%)  | Turbidimetry                           | Piper (1966)      |
| Total Fe, Mn, Zn and Cu (ppm) | Atomic absorption spectrophotometry   | Lindsay and Norvell (1978) |
| Total B (ppm)      | Colorimetry using Azomethane-H reagent with continuous flow analyzer | Page et al. (1982) |
| Heavy metals content (Pb, Ni, Cr, Cd) | Atomic absorption spectrophotometry | Lindsay and Norvell (1978) |
Purification of fulvic acid

The purification of fulvic acid was done by following the procedure as outlined by Wander and Traina (1996) [23]. The aqueous solution obtained after centrifugation was passed through exchange resin (Sera lite SRC-120) in the H⁺ form. For this, an adsorption column of 20 cm length with a porcelain perforated bed was used. Over this, a glass wool packing of 0.5 cm was placed. The resin was uniformly packed up to 15 cm height using wet packing method. Over the column again a glass wool packing of 0.5 cm was again placed. The aqueous solutions were eluted through this column four times and the fulvic acid fraction eluted was directly transferred to 100 mwco dialysis bags and dialyzed against double distilled water for 24 hours. The dialyzed fraction was evaporated under low temperature and freeze dried to obtain fulvic acid.

Characterization of humic acid

Purified samples of humic acid extracted from different organic wastes were subjected to elemental analysis, total acidity, E₆/E₅ ratio and other nutrient analysis.

Elemental analysis

Humic acid extracted from different organic wastes were subjected to elemental analysis. Carbon, hydrogen, nitrogen and sulphur content of the humic acid was estimated by dry combustion method using CHNS analyser. The oxygen content was computed by recording the difference between the sum of the C, H, and N percentages from hundred. The molar ratio of elements was computed by dividing the content of elements present in percentage by their atomic mass (Orlov et al., 1992) [14].

Total acidity

Total acidity of humic acid was determined by Ba(OH)₂ method by Schnitzer and Gupta (1964) [17]. The sample was allowed to react with an excess of Ba(OH)₂. The unreacted Ba(OH)₂ was determined by back titrating with standard acid as per the following reactions.

\[
\text{Ba(OH)}_2 + 2 \text{HA} \rightarrow \text{BaA}_2 + 2 \text{H}_2\text{O}
\]

Fifty milligrams of HA and a blank (Ba(OH)₂) was taken in separate stoppered flasks and 20 mL of 0.2 N Ba(OH)₂was added. The flasks were shaken for 24 hours, the suspension was filtered and the residue washed with CO₂ free distilled water. The filtrate and washings were titrated against 0.5 N HCl to pH 8.4 potentiometrically.

\[
\text{Total acidity (meq g}^{-1}\text{)} = \frac{\text{(TV for sample - TV for blank)} \times 0.1 \times 1000}{\text{Wt. of the sample (mg)}}
\]

Carboxyl groups

The method is based on liberation of acetic acid when acids are treated with calcium acetate and its titration was carried out with standard 0.1 N NaOH (Schnitzer and Khan, 1972) [18].

\[
2\text{R-COOH} + (\text{CH}_3\text{COO})_2\text{Ca} \rightarrow (\text{RCOO})_2\text{Ca} + 2\text{CH}_3\text{COOH}
\]

To fifty milligrams of HA in a stoppered flask, 10 ml of 1 N (CH₃COO)₂Ca and 40 ml of CO₂-free distilled water were added. A blank was also set up simultaneously. The flakes were shaken at room temperature for 24 hours and the residue was washed with CO₂-free distilled water. The filtrate and washings were titrated potentiometrically with standard 0.1 N NaOH to pH 9.8.

\[
\frac{\text{COOH group (meq g}^{-1}\text{)}}{\text{Wt. of the sample (mg)}} = \frac{\text{(TV for sample - TV for blank)} \times 0.1 \times 1000}{\text{Wt. of the sample (mg)}}
\]

Phenolic –OH groups

The phenolic –OH groups was calculated as the difference between total acidity and –COOH acidity.

\[
\text{Phenolic –OH groups (meq g}^{-1}\text{)} = \frac{\text{(Total acidity) - (COOH acidity)}}{\text{(me g}^{-1}\text{)}}
\]

E₆/E₅ ratio

The degree of humification and aromaticity of humic acid was measured using E₆/E₅ ratio. A known quantity of the sample was taken and dissolved in 10 ml of 1x10⁻² M NaHCO₃ solution. The absorbance and ratio was recorded at wavelength 465 and 665 nm using UV-VIS spectrophotometer.

Digestion of humic acid sample for determination of other elements

A known weight of humic acid sample was taken in a 250 ml conical flask and was predigested by adding 10 ml of HNO₃ and keeping it overnight. Diaacid mixture (10 ml) in 9:4 proportion (HNO₃:HClO₄) was added and heated on sand bath until a snow white residue was obtained. Residue was cooled and diluted to a known volume with distilled water, filtered and made up to 100 ml using distilled water it was further used for estimation of all other elements. The methods adopted are same as outlined in Table 2.

Result and discussion

Characterization of organic wastes

Physical and physicochemical properties of organic wastes

The data on the characteristics of organic waste used for extracting humic acid are presented in Table 3 and 4. Bulk density of different organic wastes ranged from 0.22 Mg m⁻³ in coco peat to 0.69 Mg m⁻³ of biofuel waste. Water holding capacity was more in coco peat (85.50 %) and lowest in biofuel waste (40.21 %). The analysis of the samples revealed that poultry manure (pH 8.32) and distilled bio-compost (pH 8.03) was alkaline in nature, while coffee pulp (pH 7.78) and FYM (pH 7.12) was slightly alkaline compared to vermin compost. Coffee pulp (pH 7.18) urban compost (pH 7.59) and FYM (pH 7.12) were slightly alkaline compared to vermin-compost, sewage sludge, coco peat and biofuel waste with pH value of 6.52, 5.95, 5.68 and 5.28, respectively which were acidic to slightly acidic in nature. Electrical conductivity was high 1.89 dSm⁻¹ in coffee pulp followed by FYM 1.50 dS m⁻¹. Increase in water holding capacity was due to decreased bulk density and increase in finer particle size which resulted in higher surface area thereby high moisture holding capacity. Similar results were observed by Soumare et al. (2003). The change in pH may be attributed to the presence of fairly good source of cations particularly calcium (Gajanand et al., 1999). The alkaline nature and high salt content of organic waste material might be due to the presence of basic cations. Similar results were reported by Kasongo et al. (2011). The higher electrical conductivity was due to accumulation of higher concentration of salts as a result of decomposition of organic matter or
higher organic carbon content as reported by Francou et al. (2005)\(^1\).

The organic carbon content was higher (40.99\%) in biofuel waste while it was lowest (14.13\%) in sewage sludge. With respect to major nutrients poultry manure recorded higher total N, P, K and Ca (2.85, 1.56, 1.92 and 3.89\%, respectively) followed by higher N (2.01\%), in coffee pulp and P (1.27\%) in pressmud. Similar findings were recorded by Mohamed et al. (2010). However lowest N (0.42\%) was in FYM. P content was low (0.12\%) in coco peat and sewage sludge recorded low K (0.2\%). Among secondary nutrients higher calcium content was recorded in poultry manure (3.89\%). With respect to magnesium and sulphur higher (5.84 and 0.75\%) was recorded in sewage sludge. Low magnesium (0.86\%) and sulphur (0.24\%) was in FYM. This might be due to variations in composition of different waste materials used for decomposition. Higher content of sulphur in sewage sludge can be attributed to presence of chemical alkyl benzene sulfonate which is a widely surfactant in detergent formulations which is a common commodity used in households (Smith, 2009). Higher concentrations 3850, 541.30, 76 and 476 mg kg\(^{-1}\) of iron, manganese, copper and zinc, respectively was observed in poultry manure followed by higher iron and manganese content in pressmud (3642 and 525 mg kg\(^{-1}\), respectively) and coffee pulp (3407 and 480.7 mg kg\(^{-1}\), respectively). However, higher copper (93 mg kg\(^{-1}\)) and zinc (370 mg kg\(^{-1}\)) was in sewage sludge. Lower concentration of 1602, 182.20, 27.20 and 25.10 mg kg\(^{-1}\) of iron, manganese, copper and zinc was in biofuel waste. The sewage sludge recorded higher boron content (85.40 mg kg\(^{-1}\)) followed by poultry manure (72.28 mg kg\(^{-1}\)) and it was lower (25.87 mg kg\(^{-1}\)) in biofuel waste. Similar results were obtained by Gomez et al. (1993)\(^6\) who reported that the nutrient contents of different organic materials act as an alternative nutrient source with beneficial effect in improving soil properties and supply of nutrients for adequate plant growth and development.

Among heavy metals in organic wastes higher (41.7 mg kg\(^{-1}\)) of nickel was observed in urban waste while cadmium (8.75 mg kg\(^{-1}\)), lead (36.1 mg kg\(^{-1}\)) and chromium (33.91 mg kg\(^{-1}\)) were higher in sewage sludge. Lead and cadmium were not detected in other organic samples except sewage sludge and urban compost. The results are in agreement with studies conducted by Manju et al. (2013)\(^12\) on characterization of MSW and also by (Gomez et al., 1993)\(^6\).  

Table 3: Physico-chemical properties, major and secondary nutrient composition of different organic wastes used for extracting humic acid

| Organic wastes      | BD (Mg m\(^{-1}\)) | WHC (%) | pH 1:50 | EC (dSm\(^{-1}\)) 1:100 | OC (%) | Major nutrients | Secondary nutrients |
|---------------------|-------------------|---------|---------|------------------------|--------|----------------|---------------------|
|                     |                   |         |         |                        |        | N (\%)         | P (\%)             | K (\%)   | Ca (\%) | Mg (\%) | S (\%)  |
| Coco peat           | 0.22              | 85.50   | 5.68    | 1.19                   | 35.61  | 0.43           | 0.12               | 0.49     | 1.64     | 0.79     | 0.26    |
| Coffee pulp         | 0.53              | 40.86   | 7.78    | 1.49                   | 38.36  | 2.01           | 0.52               | 1.56     | 3.44     | 1.05     | 0.41    |
| Pressmud            | 0.54              | 41.78   | 7.18    | 1.12                   | 36.11  | 1.75           | 1.27               | 1.25     | 3.72     | 1.15     | 0.46    |
| Biofuel waste       | 0.69              | 40.21   | 5.28    | 1.05                   | 40.99  | 0.61           | 0.16               | 0.47     | 2.00     | 0.85     | 0.20    |
| Distillery biocompost| 0.51             | 47.42   | 8.03    | 1.59                   | 18.56  | 1.59           | 1.04               | 1.40     | 3.20     | 1.42     | 0.31    |
| Sewage sludge       | 0.55              | 42.50   | 5.95    | 1.12                   | 14.13  | 0.43           | 1.03               | 0.20     | 3.54     | 5.84     | 0.75    |
| Poultry manure      | 0.52              | 48.05   | 8.32    | 1.26                   | 34.29  | 2.85           | 1.56               | 1.92     | 3.89     | 1.93     | 0.48    |
| Vermicompost        | 0.58              | 44.00   | 6.52    | 0.99                   | 18.26  | 0.74           | 0.30               | 0.47     | 1.76     | 0.89     | 0.28    |
| Urban compost       | 0.56              | 45.23   | 7.59    | 1.36                   | 24.01  | 1.24           | 0.49               | 1.15     | 3.08     | 1.62     | 0.42    |
| FYM                 | 0.49              | 43.29   | 7.12    | 1.50                   | 17.43  | 0.42           | 0.35               | 0.51     | 1.52     | 0.86     | 0.24    |

Table 4: Micronutrients and heavy metals content of different organic wastes used for extracting humic acid

| Organic wastes      | Micronutrients | Heavy metals |
|---------------------|----------------|--------------|
|                     | Fe  | Mn  | Cu  | Zn  | B  | Ni  | Cd  | Pb  | Cr  |
|                     | (mg kg\(^{-1}\)) |              |         |    |    |     |     |     |     |
| Coco peat           | 2049| 309.20 | 29.40 | 32.30 | 45.20 | 29.98 | BDL | BDL | 24.20 |
| Coffee pulp         | 3407| 480.70 | 63.50 | 225.00 | 56.80 | 30.19 | BDL | BDL | 25.03 |
| Pressmud            | 3642| 525.00 | 67.50 | 182.40 | 64.20 | 33.80 | BDL | BDL | 23.57 |
| Biofuel waste       | 1602| 182.20 | 27.20 | 25.10 | 25.87 | 26.09 | BDL | BDL | 20.41 |
| Distillery biocompost| 2091 | 312.00 | 66.90 | 101.00 | 59.15 | 29.10 | BDL | BDL | 25.90 |
| Sewage sludge       | 3450| 365.60 | 93.00 | 370.60 | 85.40 | 31.24 | 8.75 | 36.1 | 33.91 |
| Poultry manure      | 3850| 541.30 | 76.00 | 476.00 | 72.28 | 27.87 | BDL | BDL | 19.23 |
| Vermicompost        | 2897| 282.30 | 48.00 | 83.60 | 51.65 | 34.48 | BDL | BDL | 26.29 |
| Urban compost       | 3025| 319.10 | 71.20 | 112.00 | 69.48 | 41.70 | BDL | 14.6 | 20.26 |
| FYM                 | 1968| 264.40 | 41.90 | 85.00 | 43.27 | 30.24 | BDL | BDL | 23.45 |

Note: BDL – Below detectable limit

Percent recovery of humic acid and fulvic acid from different organic wastes

The results of the recovery percentage of humic acid and fulvic acid from different organic wastes are presented in Table 5. Higher recovery of 8.92 and 4.21 per cent humic and fulvic acid was recorded for press mud followed by coffee pulp and poultry manure. The results are in concurrence with work carried out by Satisha and Devarajan et al. (2011)\(^16\) and Gayathri et al. (2011)\(^5\). However lower humic and fulvic acid 3.43 and 2.45 per cent was recorded in coco peat, respectively. Scheild et al. (1989) reported low recovery of humic acid in sewage sludge materials. The humic acid extracted from different organic wastes is dark brown to black in color, which might be due to elemental configuration and melanin pigment (Kumuda, 1987)\(^{11}\).
The elemental composition and molar ratios of humic acid extracted from different organic wastes

The elemental composition and molar ratios of humic acid extracted from different organic wastes are presented in Table 6. The humic acid extracted from biofuel waste recorded higher content of carbon (61.04 %) followed by coco peat (50.91 %) and distillery biocompost (48.48 %) followed by coffee pulp and pressmud (47.10 and 46.4 %, respectively). Sathisha and Devarajan (2011) also reported 46.36 per cent of organic carbon in the humic acid extracted from pressmud which may be due to higher organic carbon content of the test materials in present study. With respect to hydrogen, higher (8.89 %) concentration was recorded in biofuel waste sample and lower concentration (4.08 %) was observed in poultry manure. The nitrogen content of humic acid was affected by nature of raw material. Poultry manure recorded higher (6.01 %) nitrogen followed by pressmud (5.37 %), coffee pulp (5.07 %) and urban compost (4.95 %) while least was in FYM (2.32 %). Similar findings were observed with respect to urban compost and sewage sludge (Atiyeh et al., 2002 and Keiji Jindo et al., 2012). With respect to oxygen content, higher value (52.31 %) was recorded in sewage sludge followed by FYM (52.19 %) and vermi compost (47.56 %).

The results of the molar ratios of elements suggest the stoichiometric relationship that exist among the elements. The H/C ratio in different organic samples ranged from 0.09 to 0.15. Lower H/C ratio in poultry manure (0.09) followed by coffee pulp, press mud and urban compost suggest that polymerisation and or condensation takes place well, due to introduction of carbohydrate and oxidation of phenolic compounds with methoxyl groups or aliphatic side chain in the humic acids (Vila et al., 1982). With respect to O/C ratio higher (1.30) was recorded in sewage sludge and FYM, and lower (0.44) was recorded in biofuel waste. The presence of C, H and O in humic acid is accounted in the form of carboxyl, methoxyl and carbonyl groups (Govindasamy et al., 1989). These values are highly helpful in judging the extent of the role dehydrogenation as well as removal of alkyl or carboxyl groups during the operational process of extracting humic acid. The difference in the ratios studied could be attributed to the dissimilar splitting of the peripheral aliphatic chains as well as to an increase in the number and length of aliphatic chains (Govindasamy et al., 1989; Kononova, 1966). The N/C ratio was higher in poultry manure (0.13) followed by press mud (0.12), coffee pulp (0.11) and urban compost (0.11) indicating that acid insoluble humin nitrogen increased considerably.

### Table 6: Elemental composition and molar ratios of humic acid extracted from different organic wastes

| Organic wastes | Contents of elements (%) | Molar ratios of elements |
|----------------|--------------------------|--------------------------|
|                | C | H | N | O | H/C | N/C | O/C |
| Coco peat      | 50.91 | 5.80 | 3.05 | 40.24 | 0.11 | 0.06 | 0.79 |
| Coffee pulp    | 47.10 | 4.40 | 5.07 | 43.43 | 0.09 | 0.11 | 0.92 |
| Press mud      | 46.40 | 4.35 | 5.37 | 43.88 | 0.09 | 0.12 | 0.95 |
| Biofuel waste  | 61.04 | 8.89 | 3.01 | 27.06 | 0.15 | 0.05 | 0.44 |
| Distillery biocompost | 48.48 | 4.91 | 4.09 | 42.52 | 0.10 | 0.08 | 0.88 |
| Sewage sludge  | 40.35 | 4.39 | 2.95 | 52.31 | 0.11 | 0.07 | 1.30 |
| Poultry manure | 45.06 | 4.08 | 6.01 | 44.85 | 0.09 | 0.13 | 0.99 |
| Vermicompost   | 44.54 | 5.06 | 2.84 | 47.56 | 0.11 | 0.06 | 1.07 |
| Urban compost  | 46.57 | 4.39 | 4.95 | 44.09 | 0.09 | 0.11 | 0.95 |
| FYM            | 40.02 | 5.47 | 2.32 | 52.19 | 0.14 | 0.06 | 1.30 |

### Functional groups of humic acid extracted from different organic wastes

The data on functional groups and E/Eo ratio of humic acid extracted from different organic wastes are presented in Table 7. Higher content of carboxyl group (6.08 meq g⁻¹), phenolic hydroxyl group (1.94 meq g⁻¹) and total acidity (8.02 meq g⁻¹) was recorded in poultry manure, this was followed by pressmud and coffee pulp. While lower content of carboxyl (2.84 meq g⁻¹), phenolic hydroxyl group (1.32 meq g⁻¹) and total acidity (4.16 meq g⁻¹) was observed in biofuel waste. Higher content of carboxyl group compared to phenolic hydroxyl group suggest that the carbohydrates and phenolic compounds present in these substances are easily degradable and are readily converted to carboxyl group on subsequent oxidation (Masaaki et al., 1992). Similar results were reported by Satisha and Devarajan (2011); Ushashree et al. (1989). The higher acidity or exchange-capacity of these humic substances could be attributed to the occurrence of ionisable H⁺ ions of carboxyl and hydroxy groups found in aliphatic chains or aromatic rings of molecules (Schnitzer, 2000). It is also evident from the present study that carboxylic and phenolic hydroxyl groups were present in varying quantities and these findings corroborate with that of Prasad and Sinha (1981) who reported that the variation in molecular weight may be responsible for the difference in the quantities of functional groups.
The E₄/E₆ ratio is a valid and informative index for characterization of humic substance with respect of aromaticity (Kononova, 1966) [10]. In the present study, the E₄/E₆ ratio was high in humic acid extracted from poultry manure (5.21) followed by press mud (5.12), coffee pulp (5.10) and urban compost (5.01) lower E₄/E₆ ratio was recorded in biofuel waste (4.58). Higher E₄/E₆ ratio indicates more aliphatic nature of the fractions (Garcia et al., 1991) [4] and in turn also reflects a low degree of aromatic condensation. Similar observations were also reported by Kadalli et al. (2000) [4].

| Organic wastes | Total acidity (meq g⁻¹) | Carboxylic group (COOH) (meq g⁻¹) | -OH (Phenolic groups) (meq g⁻¹) | E₄/E₆ ratio |
|----------------|-------------------------|----------------------------------|---------------------------------|-------------|
| Coco peat      | 5.03                    | 3.60                             | 1.43                            | 4.70        |
| Coffee pulp    | 7.68                    | 5.89                             | 1.79                            | 5.10        |
| Pressmud       | 7.84                    | 5.97                             | 1.87                            | 5.12        |
| Biofuel waste  | 4.16                    | 2.84                             | 1.32                            | 4.58        |
| Distillery biocompost | 5.57                  | 3.79                             | 1.58                            | 4.95        |
| Sewage sludge  | 5.40                    | 3.73                             | 1.47                            | 4.78        |
| Poultry manure | 8.02                    | 6.08                             | 1.94                            | 5.21        |
| Vermicompost   | 5.12                    | 3.78                             | 1.34                            | 4.85        |
| Urban compost  | 7.41                    | 5.75                             | 1.71                            | 5.01        |
| FYM            | 4.92                    | 3.53                             | 1.39                            | 4.61        |

**Summary**

Present study revealed that utilization of agro industrial wastes and other organic wastes as a source of nutrients reduces the reliance on chemical fertilizers and these organic wastes provides substantial quantity of nutrient elements as well as humus which helps in improving the physical, chemical and biological properties of soil. Intern soil health by decreasing demand on chemical fertilizers and also reduce soil pollution. Thus, humic acid derived from organic wastes like cocopeat, pressmud, coffee pulp, sewage sludge, poultry manure, urban compost etc. which have substantial quantities of humic materials are of great importance in maintaining soil organic matter levels especially in semi-arid tropics of India.

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