Identification of organic functional groups and proximate analysis of crop residues

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ABSTRACT

The study was conducted during 2019 at Tamil Nadu Agricultural University to identify the functional groups, nutrient and proximate composition of residues such as groundnut (Arachis hypogaea L.) shell, coir (Cocos nucifera L.) pith and rice (Oryza sativa L.) husk. Proximate analysis of the residues showed that, moisture, ash content, cellulose, hemicelluloses and lignin were in the range of 2.11–12.6, 6.1–17.3, 24.6–32.5, 13.1–21.4, and 15.6–30.2% respectively. Furthermore, nutrients including N, P, K, Ca, Mg, Mn, Fe, Zn and Cu were also analysed in all residues. The functional group analysis revealed the presence of significantly different hydroxyl and carbonyl groups. The results showed that, cation-exchange reactions, water-retention capacity and other properties were attributed to the functional groups present in the crop-residual composition. Hence these residues turn out to be an environmental friendly and relatively simple to use in agriculture.

Key words: Crop residues, Nutrients, FTIR, Functional Groups, Organic Agriculture

Excessive use of chemicals and concerns over the environment has driven the scientists, farmers and policy-makers around the world to think of an alternative farming technology which triggered the attention on alternative farming. Alternative integrated farming relies on the use of farm wastes (animal and crop), and on farm-based inputs for the sustained crop production. Crop residues are the major wastes that are generated during harvesting of various crops. Burning of these residues in field has resulted in environmental pollution and accounts for the loss of organic carbon, nitrogen and other nutrients, which would otherwise be retained in soil (Jain et al. 2014). If these resources are rationally utilized, they save and replace a lot of externally purchasable fertilizers, besides reducing the environmental pollution. Crop residues like straw, stalk, haulm, trash, shell, coir pith are some of the main resources available copiously on a farm. In recent years, farmers have shown interest in crop-residue recycling for maintenance of soil fertility maintenance, consequently attributing to higher crop productivity. These crop residues contribute to the soil stability and fertility by composting. Thus, farmers and scientists focus on crop residues to make it as a valuable resource in soil fertility.

India generates on an average 500 million tonnes of crop residue per year (NPMCR, 2019). However, most of the crop residues are burnt in the fields without knowing their alternative values. Compost and mulching are considered as a promising alternative technology that converts residue into viable, nutri-rich and soil conditioner. The amounts of nutrients in post-harvest crop residues are highly variable due to differences in the availability of nutrients present in individual plant species. Availability of nutrients in crop residues varies greatly with respect to nitrogen and potassium. During the decomposition process, these nutrients are made available to subsequent crops at a rate depending on C : N ratio. Knowledge of the amounts of nutrients in different crop residues and their use in terms of plant nutrition within a crop rotation is critically important, particularly in integrated farming. In general, crop residues provide a number of benefits when left in the field, including soil carbon sequestration, preventing erosion, reducing evaporation from the soil surface, improving soil structure, improving the activity of soil fauna, contributing nutrients to the soil, increasing water filtration and...
retention capacity and reducing weed infestation. The agronomic value of these crop residues is closely related to the functional groups present in its composition. Therefore, an in-depth investigation of the organic functional groups of these residues could provide information on the quality and suitability to use as mulch and compost.

Fourier Transform Infrared (FTIR) spectroscopy is an important analytical technique, which detects various characteristic functional groups present in the sample. Ossman et al. (2014) studied the functional groups (carboxyl, carbonyl, hydroxyl and amino) in peanut shell. Lazim et al. (2015) reported that, those functional groups on the surface of the adsorbents were involved in the adsorption process. Keeping in view, the present study was undertaken to characterize the organic functional groups in crop residues using FTIR methodology and to characterize their nutrient and proximate composition. The study was aimed to explore the potential of crop residues to use as base input for crop production.

MATERIALS AND METHODS

During residues were collected randomly from the farm of Eastern block, Tamil Nadu Agricultural University Coimbatore, and nearby farmer’s field. The crop residues collected were pooled together and air-dried. Samples of each residue were milled using agate mortar and used as a base material for further analysis.

The crop residues were analyzed to determine the proximate composition of the samples collected in triplicates. Moisture, ash, dry matter, nitrogen, crude protein, sugar and crude wax contents were estimated as per standard methods (AOAC, 1990).

Nutrient composition

Collected crop residues were shade dried and then oven-dried, powdered in a Wiley mill. The finely ground sample was used for estimating nutrient contents. All the macro and secondary nutrients were analysed by following the standard procedures (Singh et al., 1999).

Each 1 g of the crop residues was predigested overnight using 10 mL triple acid mixture (HNO₃ : H₂SO₄ : HClO₄) in the ratio of 9 : 4 : 1 in digestion tubes. Then digestion tubes were heated up to 260°C until the solution became clear. After cooling the sample to room temperature, the tubes were filled to 20mL Millipore water. Volume was made up to 100 mL and is filtered through Whatman No. 1 filter paper. Aliquots were analysed in Atomic Absorption Spectrometer using the method adopted by Chen et al. (2009) with modifications.

The FTIR analysis was performed using a Thermo Scientific FTIR spectrophotometer (Nicolet iS10 series) with smart iTR transmission accessory. Detector used in this study was Deuterated Triglycine Sulfate (DTGS) KBr. Attenuated Total Reflection (ATR) technique was used in this spectrometric analysis to identify the functional groups of various residues by collecting its infrared spectra. The experiment was conducted thrice to ensure the infrared spectra of each investigated inputs. The observed spectra are the transmittance of the different inputs versus the wave number in the range of 4,000–400/cm with a resolution of 4. Thirty-six scans were recorded, averaged for each spectrum and corrected against ambient air as background. Data collection and processing were performed by using the OMNIC software.

RESULTS AND DISCUSSION

Proximate composition

The ash contents recorded for groundnut shell, coir pith and rice husk were 6.1, 6.85 and 17.3% respectively (Table 1). The cellulose composition ranged from 24.6 to 32.5% of the crop residues investigated. The proximate analysis revealed that, coir pith had the lowest proportion of cellulose content (24.6%) and high composition of lignin content (30.2%).

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Groundnut shell</th>
<th>Coir pith</th>
<th>Rice husk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>6.3</td>
<td>12.6</td>
<td>2.1</td>
</tr>
<tr>
<td>Ash content</td>
<td>6.1</td>
<td>6.85</td>
<td>17.3</td>
</tr>
<tr>
<td>Cellulose</td>
<td>32.5</td>
<td>24.6</td>
<td>32.1</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>16.8</td>
<td>13.1</td>
<td>21.4</td>
</tr>
<tr>
<td>Lignin</td>
<td>26.1</td>
<td>30.2</td>
<td>15.6</td>
</tr>
<tr>
<td>C : N ratio</td>
<td>34:1</td>
<td>104:1</td>
<td>85:1</td>
</tr>
</tbody>
</table>

The C : N ratio is an indicator of organic matter origin, stability, maturity and nutrient availability. A significant variation was found in the C : N ratio among the residues under study. The C : N ratio for groundnut shell and rice husk were 34 : 1 and 85 : 1, respectively. However, the coir pith recorded a higher C : N ratio (104 : 1). This might be owing to the presence of carbon-rich, long-chain polymeric organic compounds, characteristics of natural fibre. The high C : N ratio found in coir pith has greater potential to increase N immobilization due to low residue nitrogen (Oladayo, 2010) hence partially decomposed coir pith with lesser C : N ratio is advisable for mulching.

Higher lignin content was found in coir pith followed by groundnut shell. Dijkstra et al. (2004) reported that, the lignin content of plant litter was a crucial factor, determining C stabilization in a grassland ecosystem. Similarly, Mandal et al. (2008) reported that, high lignin content of soil amendments such as compost was considered as a factor leading to stabilization of soil organic C in non-labile
 pools under flooded rice ecosystem. This might have favoured the formation of biochemical complexes with proteins of plant origin under submergence, which made them resistant to microbial decomposition, resulting in a comparatively higher proportion of the carbon in the passive (Chan et al., 2001).

**Nutrient composition**

The N and K contents varied according to the type of crop residues, while the P content was almost consistent (Table 2).

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Groundnut shell</th>
<th>Coir pith</th>
<th>Rice husk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.13</td>
<td>0.49</td>
<td>0.61</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.22</td>
<td>0.21</td>
<td>1.21</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.36</td>
<td>1.13</td>
<td>0.56</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.21</td>
<td>0.02</td>
<td>9.2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.43</td>
<td>0.51</td>
<td>1.5</td>
</tr>
<tr>
<td>Copper (ppm)</td>
<td>2.87</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Iron (ppm)</td>
<td>0.38</td>
<td>0.38</td>
<td>4.6</td>
</tr>
<tr>
<td>Manganese (ppm)</td>
<td>17.75</td>
<td>0.45</td>
<td>0.13</td>
</tr>
<tr>
<td>Zinc (ppm)</td>
<td>7.7</td>
<td>0.12</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Higher N content was noticed in rice husk (0.61%) than the other residues. Nwite et al. (2011) report that rice husk ash can be effectively used as a soil amendment for improving the nutrient status, as it has more N content. Matos et al. (2011) stated that, around 32% of the total amount of nitrogen in plant material is released in the first 15 days. This helps in retaining a reasonable amount of nitrogen in soil at the time of incorporation. In the present study, the average potassium concentration was higher in coir pith than rice husk and groundnut shell. According to Matos et al. (2011) phosphorus is the most rapidly released nutrient from plant residues and 60% of the total P in plant residues is released in the first 15 days. The potassium content recorded for groundnut shell, coir pith and rice husk were 0.36, 1.13 and 0.56%, respectively. The micronutrients, viz. zinc (7.7 ppm), copper (2.87 ppm) and manganese (17.75 ppm), contents were higher in groundnut shell, whereas iron content was higher in rice husk (4.6).

**FTIR analysis of crop residues**

Band assignments indicated that the 3 agricultural residues contain a number of atomic groupings and structures. Like all biomass, crop residues are composed of cellulose, hemicellulose and lignin. Band intensities revealed that, the most abundant chemical bonds were O–H, C–H, and C–O. the C O and aromatic C C bonds were also detected in these residues.

**Coir pith**

The broad component at 3,462.69/cm for coir pith might have been formed due to stretching of O-H hydroxyl groups and it affirms the presence of cellulose as a major component of coir pith (Fig 1). When the OH functional group content increases in soil, it leads to the solubility of phosphate and provides favourable environment for H-
bonding which ultimately results in the increase of moisture content (Donisa et al., 2003). Hence coir pith naturally holds more moisture when applied to the soil and thus improves the water-holding capacity of the soil. The bands absorbed at 2,923.58 and 2,851.06/cm might be due to the stretching of CH, CH2, and CH3 groups with the indication of alkanes which reflect the aliphatic nature of the coir pith. The peak at 2,348.02/cm indicates the stretching of O=C=O bond and shows the presence of carbonates-related compounds. Carboxyl and hydroxyl groups found in the coir pith have the good metal-binding capacity and forms chelation with heavy metal like Chromium (Cr) and thereby reducing the toxicity of Cr in the contaminated site (Hu et al., 2004; Vidhya et al., 2018). The absorption bands are at 1,647.73/cm that show the characteristic of CP%C groups and shows the presence of alkenes, COO, H-bonded C=O (Lin et al., 2008). This reconfirms the formation of organic ester linkage of hemi-cellulose and p-coumeric acids of lignin (Seki et al., 2013), and upon degradation lignin is converted to humic and fulvic acids by microorganisms (Stevenson, 1982); thus increase the soil organic matter in turn organic carbon. In addition, the band at 1,096.15/cm was due to the stretching vibrations of the C-O bond indicating the presence of secondary alcohols. The peaks at 776.51, 693.83 and 628.62/cm show the C-H bending patterns. Applied coir pith has functional groups such as COO-, O-H, C=O and others possess cation-exchange properties similar to those of clay particles and adsorb cations on their surfaces (Bianchi et al., 2008).

**Groundnut shell**

The hydroxyl group produced characteristic deep absorption peak at 3,322.07/cm corresponding to O-H link confirms the presence of alcohols (Fig. 2). The band at 2,921.70/cm indicates the stretching of aliphatic C-H, mainly CH3 of methyl groups in cellulose and hemi cellulose components (Dolatkhah et al., 2019) and this C-H bands mark the presence of labile carbon (Calderón et al., 2011). Short band at 2,162.90/cm confirms the stretching of alkenes. The small stretching at 1,730.61/cm is owing to the presence of carbonyl groups (Zhu et al., 2009) which strongly affects the microbial activity (Li et al., 2015). A medium peak at 1,634.47/cm indicates C=C stretching vibration. The absorption band at 1,509.21/cm indicates N-O stretching, confirming the presence of nitro-compound in groundnut shell. Carboxylic acid had a characteristic bending of O-H vibration at 1,422.76/cm. This acid has the ability to dissolve insoluble fixed nutrients in the soil through acidification (nutrients becomes soluble which facilitates the nutrient uptake of plants), chelation (form complex group with nutrients and improve their solubility) and exchange reactions (displace the nutrients adsorbed with colloids) (Adeleke et al., 2012a, b). The peaks at 1,362.34 and 1,314.42/cm ascribed to O-H bending and confirm the presence of phenols and it forms chelates with polyvalent metal ion which aids in metallic detoxification.

![Fig. 2. FTIR of groundnut shell](image-url)
of soil (Haynes and Mokolobate, 2001). The absorption band at 1,258.96/cm indicates C-N stretching link that confirms the presence of amine groups. The infra-red peak at 1,022.91 is assigned to C-O stretching links the alkyl aryl ether. The spectrum of 891.33/cm indicates the presence of C=C stretching of unsaturated alkenes and affirms the presence of vinylidene.

**Rice husk**

The peak around 2,996.80/cm (Fig. 3) indicates the existence of free hydroxyl groups which are involved in the formation of hydrogen bonding by using its residual water (Fu et al., 2010). Thereby it absorbs more water and improves the water-holding capacity of the soil. The weak band at 2,878.57/cm can be attributed to the aliphatic C-H stretching (Kim et al., 2012) and may be the presence of hydrocarbons (Fu et al., 2010). The band at 2,323.85/cm, which is ascribed to O=O=C vibrations in carbonyl groups, shows the presence of ketones and the weak band at 1,873.66/cm is discerned as C-H bending vibration that indicates the existence of aromatic compound. The conjugated aldehydes with C=O stretching are detected by the band at 1,700.72/cm. Presence of cyclic alkenes was detected by C=C stretching vibrations in the region of 1,560.12/cm. The N-O stretching vibrations at 1,482.51/cm indicates nitro compound presence, whereas O-H bending vibrations at 1,397.35/cm detects the presence of alcohol. Characteristic band at 1,344.79/cm can be confirmed to the O-H bending and shows the presence of phenols in the form of lignin and polysaccharides, which make the husks structure (Cruz et al., 2013). Islabão et al. (2014) reported that, rice-husk ash serves as a corrective of soil acidity. The band at 1,191.65/cm is ascertained to C-O stretching vibration of tertiary alcohols. Existence of C=C bending vibration at 915.32/cm affirms the presence of alkenes. The band at 784.43/cm can be ascertained to the vibrations of Si-O bonds (Markovska and Lyubchev, 2007)

**CONCLUSION**

This research investigated crop residue as potential modulators for improving soil conditions. Decomposition of crop residue has strong effects on the soil-nutrient contents. Spectra of the samples focus on qualitative spectral features of residues. FTIR analysis also showed that, the crop residues exhibited cation-exchange reactions and the adsorption phenomenon, water-holding capacity due to the presence of functional groups on their surfaces. This, in turn, improves the overall properties of soil and facilitate a
better environment for crop production. If crop residues are utilized properly, it can warrant the improvements in soil physical, chemical and biological properties and sustain productivity of soil and ultimately crop production.

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