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## Production and characterization of vermicompost and biochar from rice straw

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**Abstract**

“Soil Quality” is the capacity of a specific kind of soil to function within natural or managed ecosystem boundaries to sustain plant and animal productivity, maintain or enhance water and air quality and support human health and habitation. One of the major threats for soil quality is the intensive use of agrochemicals coupled with soil degradation processes. Vermicomposting has emerged as a promising eco-friendly approach for recovering degraded soils and equally good is the application of biochar, a carbonaceous material produced from pyrolysing biomass for both remediation and for soil carbon storage potentials. The vermicompost and biochar mentioned in the present study are rice straw based products. The lower bulk density of straw and its products compared to soil shows its promising role in reducing the soil bulk density and increasing the porosity besides its capability to hold more water when applied to soil. The process of vermicomposting helped to increase the nutrients viz., N, P, K, Ca, Mg, S, and silicon and decrease that of carbon, cellulose and lignin thereby narrowing down the C: N ratio. Conversion of residues into biochar helped to increase content of most of the nutrients in the final product, while nitrogen, cellulose and lignin content were found to decrease after pyrolysis. Pyrolysis process imparted more recalcitrant character by increasing aromatic compounds as evidenced from FT-IR analysis, thus ensuring its suitability for carbon sequestration.

**Keywords:** Rice straw, vermicompost, biochar, physico-chemical properties, surface morphology, structural chemistry

**Introduction**

There is a growing interest of late in the agricultural sector to explore the possibility of crop residue based organic amendment application with thrust on its merits and demerits. Ideally the crop residue management systems should be chosen in a way with minimal adverse effects on the environment at the same time optimising crop yields, resembling the site specific nutrient management.

Rice, the staple food across Asia is the most important human food crop in the world that has fed more people over a larger time than has any other crop. It also is the most important residue producing crop in Asia contributing to 84 per cent of total world production. Assuming a harvest index of 0.5, nearly 200 mt of rice straw is produced in India annually (Benbi and Yadav, 2015) [2].

Crop residues are good sources of nutrients and primary source of organic matter. Rice straw at harvest contain 0.5-0.8 per cent N, 0.07-0.12 per cent P<sub>2</sub>O<sub>5</sub>, 1.16-1.66 per cent K<sub>2</sub>O, 0.05-0.1 per cent S, and 4-7 per cent silicon. This translates to about 40 per cent of the nitrogen, 30-35 per cent of the phosphorus, 80-85 per cent of the potassium, 40-45 per cent of sulphur and 80 per cent silicon taken up by the plant and which remain in the vegetative parts at maturity (Dobermann and Fairhurst, 2000)<sup>[7]</sup>. Rice straw stand out from other straws with its higher silicon and lower lignin content which designates it as a ligno-cellulosic biomass with 35-40 per cent cellulose, 25-30 per cent hemicellulose, and 10-15 per cent lignin (Thygesen *et al.*, 2003) [26].

In principle, rice straw can be put into varied uses such as for soil fertility improvement through carbonisation and composting, in bio energy production, in the making of bio fibre and other industrially useful products. Soil incorporation of straw is a good proposition for enhancing soil fertility, but the current intensive cropping systems leaves too little time for its proper decomposition and related effects. With hardly few viable options, open field burning is very commonly practiced for straw disposal and this has increased dramatically over the last decade causing emission and persistence of toxic gases and smog that extends even to adjoining places. In addition, it leads to nutrient losses and killing of beneficial soil flora and fauna.

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It is in this context that vermicomposting and pyrolysis turn out as effective technologies for conversion of rice straw into quality products capable of enhancing soil quality and reducing the environmental footprint together with increasing income generation from rice production systems.

Composting is an excellent waste management strategy, which yields biologically stable organic matter. Crop residues contain the nutrients in their recalcitrant forms which on composting get transformed into humified matter through the activity of soil biota. Biochar on the other hand is a novel technology for agriculture productivity and is a unique weapon to combat against climate change and global warming via sequestration of atmospheric CO<sub>2</sub>. The most prominent benefit of biochar is its longevity; it can remain in the soil for years. Thus, biochar application helps to reduce the repeated addition of soil amendments and minimise the possibility of new contaminants reaching the soil through addition of synthetic soil amendments. Present investigation is an earnest attempt on rice straw management through vermicomposting and pyrolysis undertaken in the Department of Soil Science and Agricultural Chemistry during 2017-2020.

### Materials and Methods

Straw was collected from the farmers in Thrissur district after the harvest of rice. Further materials required for the research work viz., vermicompost and biochar were produced from the straw using the methodology furnished underneath.

Vermicomposting of the rice straw was carried out in ferrocement tanks of 1m<sup>3</sup> diameter and 300 kg capacity. The bottom portion of the tank up to one foot height was filled with a layer of coconut husk, positioned with their concave side facing upwards. Rice straw and cowdung was mixed in 8:1 ratio and this mixture was transferred into the ferrocement tank to form a layer of 30-45 cm thickness. Cowdung slurry was sprinkled over this layer. This process was continued till the tanks were filled to their fullest capacity maintaining a top layer of cowdung slurry which was then covered using a moistened gunny bag. The material was left as such to allow partial

decomposition with occasional turning at weekly interval followed by cowdung slurry application to ensure proper aeration and moisture content. After three weeks, the composting worm *Eisenia foetida* was introduced into the tank @2000 Nos. per tank. Turning was done once in five days to maintain homogeneity. Care was taken to ensure an optimum moisture content of 40 to 50 per cent by sprinkling water. The materials gained maturity by 62 days as evidenced by the change in appearance, colour and odour. Sprinkling of water was stopped at this point to enable the worms to migrate down and cling to the vermi bed. Composted material was collected from the top of the ferrocement tanks without disturbing the vermi bed and kept in shade for two days. The composted rice straw was sieved and stored in the laboratory in plastic containers for analysis.

The biochar used in the present study was produced from straw utilising kilns specially designed and fabricated for the purpose using metallic drums of 87 cm height and 57 cm diameter. Straw was loaded through the inlet at the top and the process of pyrolysis was initiated using a little diesel. With the reduction in intensity of smoke produced, closed the inlet to slow down air entry thus preventing the material getting converted into ash. After one hour duration the kiln was allowed to cool and the finished product 'rice straw biochar' was collected from the outlet located towards the bottom side. Pyrolysis temperature was recorded using an Infrared thermometer and it was found to vary between 350 to 600°C throughout the process. The product was crushed and passed through 2 mm sieve and characterised using standard procedures detailed in Table 1.

The information on surface composition and topography of the straw and its products were studied using Scanning Electron Microscope (SEM) that enabled for creating a high resolution image. The samples were smeared on a small piece of adhesive carbon tape which was fixed on a brass stub. The samples then subjected to gold coating using sputtering unit for 10 seconds at 10 mA of current. The gold coated samples were placed in the chamber of SEM and secondary electron or back scattered electron images are recorded.

**Table 1:** Standard procedures employed for characterization

| Parameters              | Methods   |                              |                              |
|-------------------------|---|------------------------------|------------------------------|
| Moisture                | Moisture meter (Model: MB23)  |                              |                              |
| Bulk density            | Cylinder method (Piper, 1966) <sup>[22]</sup>   |                              |                              |
| pH                      | Potentiometry   | Jackson, 1958 <sup>[9]</sup> |                              |
| Electrical conductivity | Conductometry   |                              |                              |
| Total carbon            | CHNS Analyzer (Model : Elementar's vario EL cube)   |                              |                              |
| Total Nitrogen          |   |                              |                              |
| Total Phosphorus        | Microwave digestion system with HNO <sub>3</sub><br>(Model: MARSX 250/40)                                     | Colorimetry                  | Jackson, 1958 <sup>[9]</sup> |
| Total Potassium         |   | Flame photometry             |                              |
| Total Calcium           |   | ICP-OES                      |                              |
| Total Magnesium         |   | (Model: Optima® 8x00 series) |                              |
| Total Sulphur           | CHNS Analyzer (Model : Elementar's vario EL cube)   |                              |                              |
| Silicon                 | Digestion (Ma <i>et al.</i> , 2002) <sup>[18]</sup> and estimation using ICP-OES (Model: Optima® 8x00 series) |                              |                              |
| Cellulose               | Sadavivam and Manickam (1996) <sup>[23]</sup>   |                              |                              |
| Lignin                  | Klason (1923) <sup>[12]</sup>   |                              |                              |

Structural chemistry of straw and their products were characterized using Fourier Transform Infra-Red spectrometer equipped with Attenuated Total Reflectance (FTIR-ATR) containing diamond crystal (Model: Perkin Elmer spectrum 100 FT-IR spectrometer with ATR). The methodology included transferring samples to the small crystal area located on the ATR top plate, followed by positioning the pressure over crystal/ sample area and applying force till the pressure gauge registered force sufficient enough to push the sample on the diamond surface. An infra-red (IR) beam with a high refractive

index was then directed at a certain angle on to the optically dense diamond crystal. This reflectance helped to create an evanescent wave that extended beyond the surface of the crystal on to the sample held in contact with it. The evanescent wave got alternated in those regions of the IR spectrum where the sample absorbed energy. These alienated beam then returned to the crystal, exist via opposite side of the crystal and got directed to the detector in the IR spectrometer. The detector recorded the alienated IR beam as an interferogram signal which could be used to generate an IR spectrum. FT-IR spectra

were acquired at the middle infra-red region of 4000-400 $\text{cm}^{-1}$ . Organic compounds have fundamental vibration bands in the mid infra-red region, because of which this region is widely used in IR spectroscopy.

## Results and Discussions

Vermicompost and biochar was produced from rice straw and it could be seen that the recovery was more (74.38%) when straw was converted into compost with the help of residue feeding earthworms than as biochar (19.86%) through pyrolysis. Reports say that the biochar yield is highly dependant on the pyrolysis conditions such as temperature, heating rate and residence time (Uzun *et al.*, 2006; Tsai *et al.*, 2007) [29, 28] and is also greatly influenced by physical, chemical and biological properties of the raw materials used (Lehmann, 2007; Chan and Xu, 2009; Basta *et al.*, 2011; Conz *et al.*, 2017) [16, 3, 1, 6]. Elangovan (2014) [8] reported recovery percentage of 12 to 40, when pyrolysis was done using different biological residues. Phuong *et al.* (2015) [21] concluded that the decrease in biochar yield might be due to the thermal decomposition of organic material present in the residues. The properties of straw, vermicompost, and biochar are given in Table 2.

### Physical properties

Comparatively, higher moisture content was observed in vermicompost (23.68%) than straw (7.24%) and biochar (3.62%). Pyrolysis process reduced the moisture content of final product than the raw materials. However, composting increased the moisture content.

Straw is yellow in colour whereas the resultant vermicompost was brown in colour which might be due to the presence of humic substances in vermicompost. With the progress in composting a series of organic acids are produced that changes the colour of the matured compost. Research results conclusively indicates the role of fulvic and humic acids in colour development. Biochar produced are black in colour due to the high carbon content. No foul odour was experienced either from the straw or its products.

**Table 2:** Characterization of straw, vermicompost, and biochar

| Parameters                            | Straw                 | Vermicompost | Biochar |
|---------------------------------------|-----------------------|--------------|---------|
| <b>1. Physical properties</b>         |                       |              |         |
| Moisture (%)                          | 7.24                  | 23.68        | 3.62    |
| Colour                                | Yellow                | Brown        | Black   |
| Odour                                 | Absence of foul odour |              |         |
| Bulk density ( $\text{Mg m}^{-3}$ )   | 0.80                  | 0.78         | 0.64    |
| <b>2. Electro-chemical properties</b> |                       |              |         |
| pH                                    | 7.81                  | 8.71         | 9.24    |
| EC ( $\text{dSm}^{-1}$ )              | 0.50                  | 1.15         | 0.86    |
| <b>3. Chemical properties</b>         |                       |              |         |
| Carbon                                | 36.45                 | 18.25        | 42.17   |
| Nitrogen                              | 0.52                  | 1.23         | 0.44    |
| Phosphorus                            | 0.18                  | 0.34         | 0.22    |
| Potassium                             | 1.29                  | 1.31         | 1.41    |
| Calcium                               | 543.12                | 582.45       | 548.26  |
| Magnesium                             | 249.20                | 370.17       | 260.02  |
| Sulphur                               | 523.08                | 540.00       | 528.98  |
| Silicon                               | 5.08                  | 13.87        | 15.38   |
| Cellulose                             | 38.10                 | 12.26        | 2.81    |
| Lignin                                | 12.06                 | 8.84         | 4.74    |
| C/N ratio                             | 71.20                 | 14.83        | 95.84   |

The increase in particle size during vermicomposting due to the amalgamation of small particles resulted in reducing the bulk density of vermicompost (0.78  $\text{Mg m}^{-3}$ ). Pyrolysis process also

reduced the bulk density of biochar (0.64  $\text{Mg m}^{-3}$ ). The lower bulk density of straw and products compared to soil indicated its promising role in reducing the soil bulk density and increasing the porosity thus its ability to hold more water when applied to soil.

### Electro-chemical properties

pH is an important electro-chemical property controlling the availability of nutrients. Straw, vermicompost, and biochar were alkaline in nature, having a pH value 7.81, 8.71, and 9.24 respectively. The increase in pH after vermicomposting probably resulted from the release of ammonia due to the proteolytic process. These results are in agreement with the findings of Thiyageshwari *et al.* (2018) [25]. High solubility of nutrients in earthworm casts could be another reason for the rise in pH in the present study. The pH of biochar was comparatively higher than the straw as well as vermicompost. This might be due to the production of alkali salts during pyrolysis process. At a higher temperature, the alkali salts begin to separate from the organic matrix thus increasing the pH consequently. Highest pH recorded in biochar could be supported by high calcium and magnesium content as shown in the results of the present study.

Electrical conductivity is a measure of concentration of soluble salts. Electrical conductivity of straw, vermicompost, and biochar was 0.50, 1.15, and 0.86  $\text{dSm}^{-1}$  respectively. The higher electrical conductivity might be due to the presence of soluble salts. The present study revealed that electrical conductivity increased on vermicomposting. Decomposition of substrates and subsequent release of exchangeable bases would have increased electrical conductivity of the compost. In a study on composting using agricultural by-products, Chandna *et al.* (2013) [4] also reported an increase in initial substrate electrical conductivity on composting. Loss of biomass through the biotransformation of organic materials and subsequent mineralization of nutrient elements could have attributed to the increment in electrical conductivity. The electrical conductivity of biochar was also higher than the residual biomass but comparatively lower than vermicompost because of lower nutrient composition in biochar than compost.

### Chemical properties

The process of vermicomposting helped to concentrate the nutrients *viz.*, N, P, K, Ca, Mg, S, and silicon. The increase in nitrogen and decrease in lignin helped to narrow down the C: N ratio from 71.20 to 14.83. The process of pyrolysis that yielded biochar also proved to be a nutrient accumulating method. Much alike vermicomposting, the content of lignin and cellulose got reduced here also. The difference between biochar production and vermicomposting in terms of nutrients was the reduction in nitrogen following pyrolysis

After vermicomposting, carbon content of straw got reduced remarkably due to the combined action of earthworm ingestion and decomposition by microbes. The carbon content in compost is the major source of energy for the microorganisms. The values on carbon content of biochar obtained from the present study revealed its highly carbonaceous nature. The increased carbon of biochar indicates that pyrolysis temperature promotes carbonization (Chun *et al.*, 2004) [5]. This promotion was due to high degree of polymerization leading to more condensed carbon structure in the biochar (Lehmann and Joseph, 2009) [17].

The increased nitrogen content of the compost is due to the mineralization of proteins present in the substrates to nitrate and ammoniacal forms. The nitrogen content in the cowdung

also contributed to increase in total nitrogen of vermicompost. It is normally seen that when organic matter reduction is more than the loss of  $\text{NH}_3$ , nitrogen concentration usually increases. Total nitrogen content was found to decrease with pyrolysis process. This might be due to the volatilization loss of nitrogen during pyrolysis. When plant biomass is subjected to pyrolysis, their nitrogen containing structures, i.e., amino sugars, amino acids and amines, get transformed into heterocyclic aromatic structures (Koutcheiko *et al.*, 2006) [14].

The phosphorus content of the vermicomposts was higher than the straw. The phosphorus content in the straw as well as in cowdung might have contributed to increase in phosphorus in final vermicompost. Mineralization and mobilization of phosphorus by bacterial and phosphatase activity of earthworms could be the main reason of phosphorus increase in vermicompost (Tripathi and Bhardwaj, 2004) [27]. When organic matter passes through the gut of earthworm, some phosphorus is converted into more available form. The release of phosphorus in the available form is performed partly by earthworm gut phosphatase and further release of phosphorus can be ascribed to the phosphorus solubilizing microorganisms present in the worm casts (Suthar, 2008) [24]. Charring enhances P availability from residues. This is because with combustion, there is disproportionate volatilization of carbon which leads to cleavage of organic phosphorus bonds thus yielding biochar rich in soluble salts of phosphorous (Knoepp *et al.*, 2005) [13].

The increase in potassium content in the vermicomposts suggests that earthworms has symbiotic gut microflora with secreted mucus and water to increase the degradation of ingested substrates and release of metabolites (Khwairakpam and Bhargava, 2009) [11]. Chandna *et al.* (2013) [4] also opined that during the composting of agricultural substrates, organic carbon decreased, whereas total N, P and K increased with time. The nutrient content in biochar was comparatively lower than the vermicomposts. Whereas, the potassium content was found to be more in biochar. This might be due to the ash content in the biochar.

Upon vermicomposting, calcium content was found to be increased. Calcium enrichment occurs when the substrates pass through the digestive tract of earthworms. Earthworms were reported to captivate calcium in excess from their food and transfer it to calciferous glands, which contain carbonic anhydrase enzyme which catalyse the fixation of  $\text{CO}_2$  as  $\text{CaCO}_3$  concretions before being excreted through the digestive tracts (Padmavathiamma *et al.*, 2008) [20]. The bicarbonates produced in excess of earthworm metabolic requirement were excreted as cast material, thus increasing the calcium content in the final vermicompost. The indistinguishable significance of composting and vermicomposting in enriching the compost with calcium content was earlier reported by Mayadevi (2016) [19]. Pyrolysis process increases the calcium content in the final product. The increase in calcium content in the biochar might be due to the release of calcium during pyrolysis.

Magnesium content was highest in vermicompost than biochar and straw. Only slight variation in sulphur content was observed among the straw and their products such as vermicompost and biochar. Both vermicomposting and pyrolysis go in favour of increasing nutrient content in the final product, though its often comparatively higher in vermicompost. This might be due to the biological as well as thermal decomposition of straw during vermicomposting and charring respectively.

Silicon is considered as a beneficial element for crop growth, especially for crops under *Poaceae* family. Rice is a typical silicon accumulating plant and it benefits from silicon

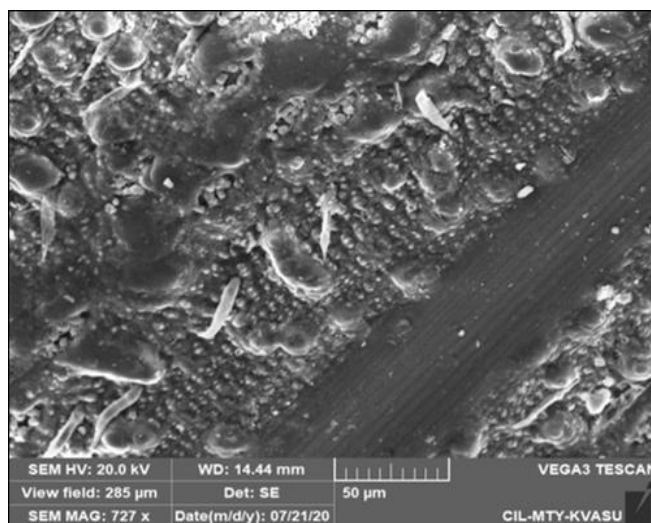
nutrition. Rice residues contain high quantity of silicon. Vermicomposting and charring enhanced the silicon content. Compared to vermicomposting, charring has a great influence on the release of silicon. Xiao *et al.* (2014) [30] reported that pyrolysis temperature caused the intense cracking of carbon components, and thus the silicon located in the inside tissue was exposed to cause enhancement of silicon content in the final product "biochar".

Lignin and cellulose content decreased after composting and charring. The results are in line with the findings of Zhang *et al.* (2015) [31], who reported that thermal degradation of cellulose and lignin occurs under high temperature during pyrolysis. The extent of reduction in cellulose was 67.80 per cent in vermicompost. Compared to the vermicomposts, the per cent reduction of cellulose was high after charring (92.62 %). The extent of reduction in lignin was lower compared to cellulose in both vermicompost (26.69 %) and biochar (60.69 %). Lignin is a relative complex compound having a cross-linked phenolic-type structure which does not easily breakdown. Due to its aromatic structure, it is more chemically stable and heat resistant than cellulose.

Carbon to nitrogen ratio serves as a reliable parameter for the maturity of compost. A remarkable change in the C: N ratio was noticed after composting. The C: N ratio of vermicompost was 14.83. The improvement in nitrogen and lowering of carbon resulted in the lowering of the C: N ratio, which is an important criterion for a compost to be fully mature. The results are in conformity with the findings of Thiyareshwari *et al.* (2018) [25]. The C: N ratio of biochar was higher than the vermicompost and straw. The increase in carbon content and decrease in nitrogen by pyrolysis process might be the reason for high C: N ratio.

### Surface morphology

The SEM micrograph of straw exhibited a complex morphology with cell wall composition (Figure 1).



**Fig 1:** SEM micrograph of rice straw

SEM image of vermicompost (Figure 2) showed a highly fragmented, porous and disaggregated structure contrary to the rice straw. This might be due to the activity of earthworms during vermicomposting.

Biochar (Figure 3) exhibited a highly disordered and complex morphology with longitudinal channels and pores under 50µm resolution. The particles gave a broken or distorted appearance thus resembling the plant structure with remains of vessels, the larger diameter tubes used for the transport of fluids and

nutrients. The results are in conformity with the findings of Phuong *et al.* (2015) [21].

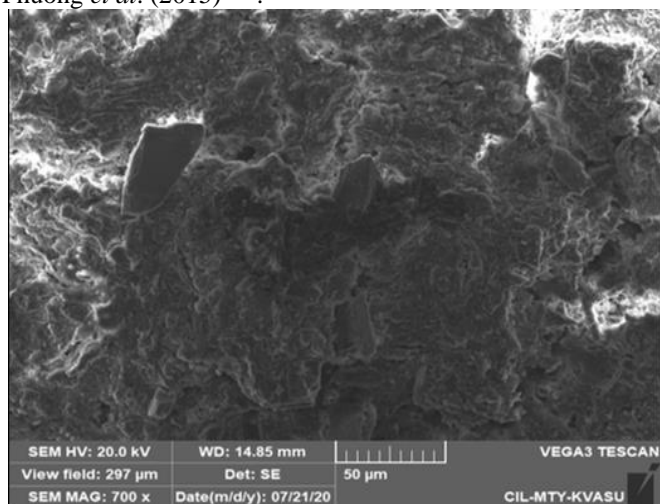


Fig 2: SEM micrograph of vermicomposted straw

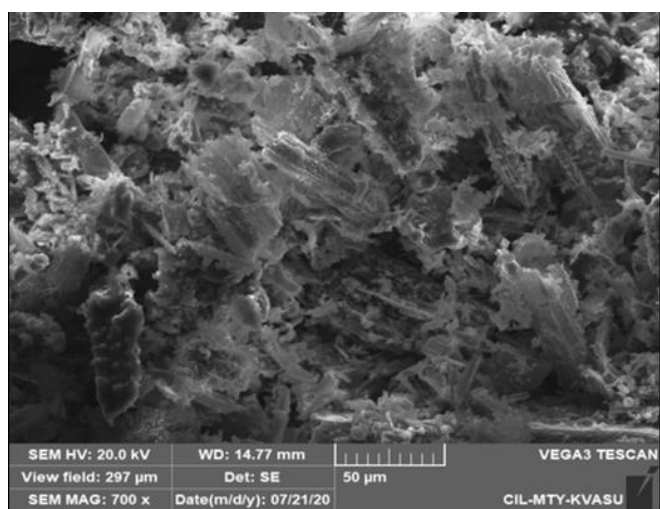


Fig 3: SEM micrograph of rice straw biochar

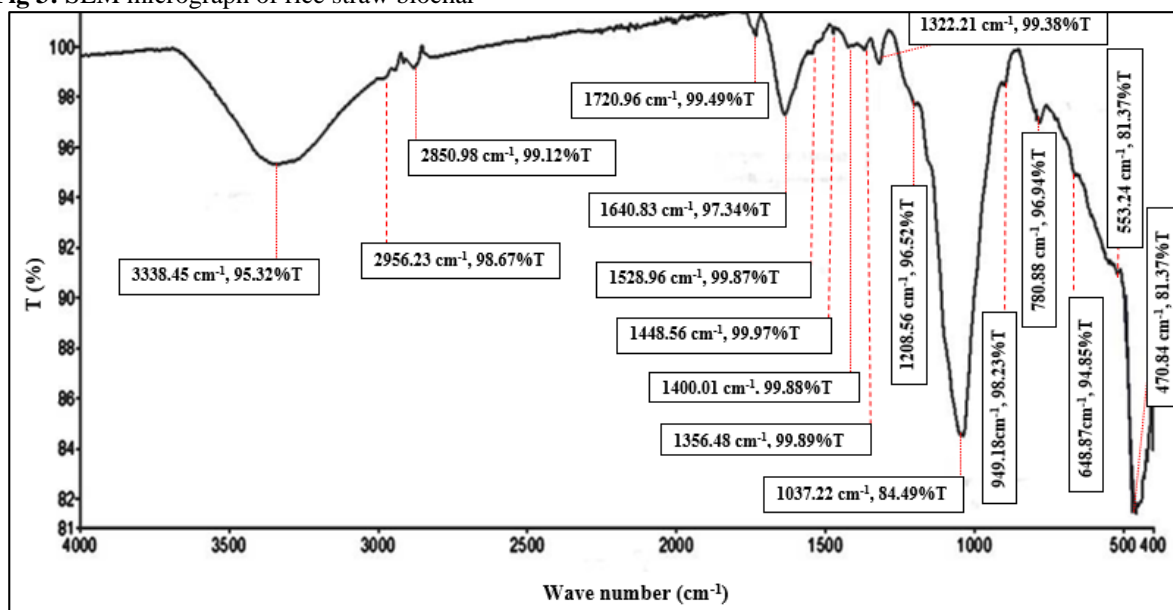


Fig 4: Fourier-transform infrared (FT-IR) spectrum of rice straw

### Structural chemistry

The structure of straw, vermicompost, and biochar were analysed using FT-IR. Each peak in FT-IR is assigned with corresponding functional groups. The functional group of cellulose, hemicellulose and lignin could be seen in the spectrum. In FT-IR spectrum presence of silicon is illustrated by Si-O-Si and Si-H bond. In the present study such bonds were identifiable in both the straw and its products (Figure 4-6). Silicon is a major component in chemical structure of rice, and is typical of its recalcitrant property (Jindo *et al.*, 2014) [10].

In vermicompost, the O-H stretching of hydroxyl groups from alcohols and carboxylic acid, and N-H stretching vibrations from amides and amines are indicated by a band from 3300-3500  $\text{cm}^{-1}$ . Vermicompost had significant level of nitrogen rich compounds and low level of aliphatic or aromatic compounds compared to straw, which was confirmed by the FT-IR analysis. The peaks at 2943.75  $\text{cm}^{-1}$  and 2896.31  $\text{cm}^{-1}$  are assigned to aliphatic methylene groups, found to be decreased in vermicompost compared to the straw.

The reduction in methylene peaks might be due to the decrease in  $\text{CH}_2$  and  $\text{CH}_3$  groups, which suggested the decomposition of aliphatic compounds after composting. The easily biodegradable compounds are decreased after vermicomposting. The presence or absence of spectral peaks for functional groups indicated the stabilization or degradation of residue during bioconversion process (Mayadevi, 2016) [19]. The complete disappearance of O-H stretching ( $>3000 \text{ cm}^{-1}$ ) and almost disappearance of aliphatic C-H stretching ( $3000-2500 \text{ cm}^{-1}$ ) was noted in the FT-IR spectrum of biochar. While, peaks arising from the aromatic stretching became more apparent. This implies that greater dehydration and increased aromatization occurred during pyrolysis process. Lee *et al.* (2010) [15] reported that charring temperature modifies the functional groups, and thus aliphatic carbon groups decreases but aromatic carbon increases. Pyrolysis process created more recalcitrant character by increasing aromatic compounds, and is thus suitable for carbon sequestration.

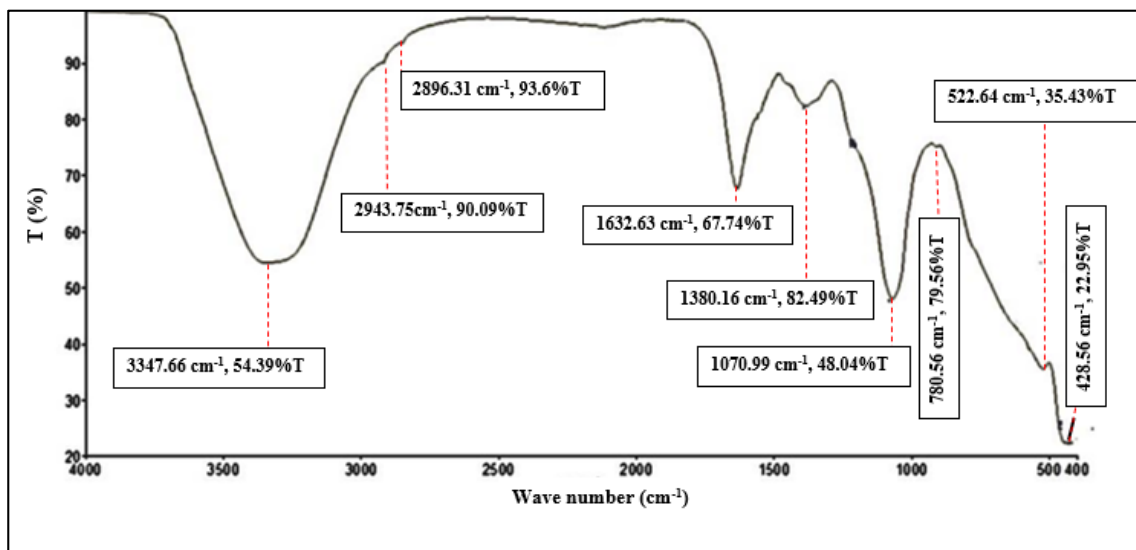


Fig 5: FT-IR spectrum of vermicomposted rice straw

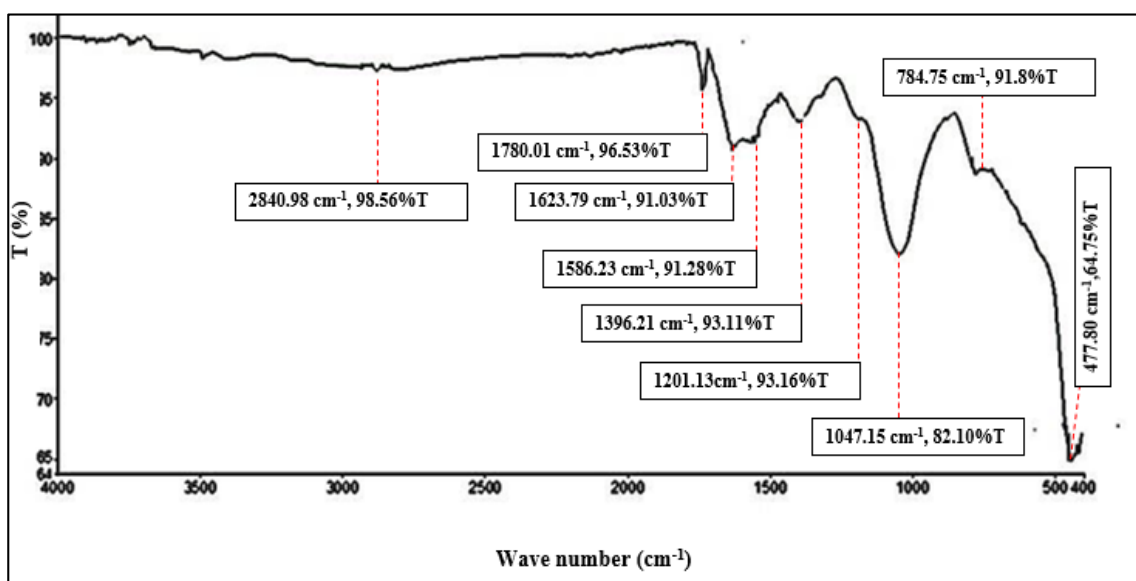


Fig 6: Fourier-transform infrared (FT-IR) spectrum of rice straw biochar

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