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Investigation on changes in fly ash based vermicompost during vermicomposting utilizing SEM/EDAX and FTIR

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Abstract
In the present paper, the chemical changes due to vermicomposting with partially decomposed cow dung (PCD) and fly ash (FA) mixture was described. Vermicomposting was carried out with different combinations of PCD and fly ash *viz.,* PCD: FA (1:1), PCD: FA (1:2), PCD: FA (1:2:5), PCD: FA (1:3), PCD: FA (2:1), PCD: FA (2:5:1) and PCD: FA (3:1). *Eisenia fetida* (red earthworm) was released to these mixtures for vermicomposting at the rate of six per kg of material. 60 per cent moisture was maintained gravimetrically throughout the study. Variations in temperature during the process of vermicomposting was monitored regularly by using temperature sensor. Samples were taken periodically at an interval of 14 days for studying the morpho - chemical changes that occurred during different stages of vermicomposting using Fourier Transform Infrared Spectroscopy (FTIR) spectrum and Scanning Electron Microscope (SEM) with energy dispersive X – ray spectroscopy (EDAX) analysis. The result of FTIR showed that certain functional group like gaseous water molecule (3900 – 3750 cm^{-1}), free alcohol (3800 - 3700 cm^{-1}) and aliphatic ether groups (1880 cm^{-1}) disappeared with increasing period of vermicomposting. Similarly with the increase in period of vermicomposting, increase in carboxylic acid group at the wavelength of 3380 -3370 cm^{-1} and increase in aromatic group or acid polymers at 1000 - 1020 cm^{-1} were observed. Due to the conversion of alcohol and ethers into acids during vermicomposting which may decreases the pH of the vermicompost sample and also increase the nutrient availability by chelating the nutrients in its aromatic structure. SEM with EDAX of before and after vermicomposting of fly ash with PCD showed that there was a decline in heavy metal concentration with the period of vermicomposting. It is concluded that fly ash as fly ash based vermicompost can be utilized as manure for crop production.

Keywords: fly ash, vermicomposting, FTIR, SEM, manure, cow dung

1. Introduction

Fly ash is a byproduct from thermal power plants due to the combustion of coal. With the increasing problem in disposal of fly ash due to increase in thermal power production for power generation creates the need for utilization of fly ash. In India, around 65 million tons of fly ash produced annually (Usmani and Kumar, 2017) [11]. Since it contains nutrients like nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg) and micronutrients (MNs) which are essential for growth of the plants, it can be utilized for agriculture purpose. However, the presence of heavy metals like chromium (Cr), cadmium (Cd) and lead (Pb) in fly ash hinders the utilization of fly ash for crop production. To alleviate the heavy metals contamination in soil from fly ash, an efficient tool of vermicompost technology was adopted. Since the morpho - chemical changes occurred during the period of vermicomposting can't be visible to naked eye, it can be observed by using fourier transform infrared spectroscopy (FTIR) spectrum and its elemental composition and size of the particles were observed with scanning electron microscope (SEM) image with EDAX at sub-micron scale (Avinash and Murugesan, 2017) [1]. In this present study, the morphological and chemical changes occurred during the period of vermicomposting was determined by using SEM with EDAX and FTIR spectrum images.

2. Materials and Methods

The present investigation was conducted in Radioisotope Laboratory, Tamil Nadu Agricultural University, Coimbatore to study the changes occurred during vermicomposting utilizing fly ash. The material fly ash utilized for vermicomposting was taken from Mettur thermal power plant. Cow dung was obtained from the nearby village which bolstered the natural vegetation. Foreign particles present in cow dung was evacuated and the large clumps were smashed into fine particles. The cow dung which was used in the study was partially decomposed by incubating for 30 days to diminish the production of heat during thermophilic phase.

Then it was blended with fly ash at various combinations for vermicomposting. Night crawler (*Eisenia fetida*) utilized for vermicomposting were picked from the nearby commercially produced vermicompost unit and around 30 numbers of earthworm was released in to each treatment.

2.1 Experimental Design
Seven distinct combinatioin of fly ash and partially decomposed cow dung was prepared to fed *Eisenia fetida* on dry weight premise *viz.,* PCD: FA (1:1), PCD: FA (1:2), PCD: FA (1:2.5), PCD: FA (1:3), PCD: FA (2:1), PCD: FA (2.5:1) and PCD: FA (3:1). Trays of 10 kg capacity was taken and were filled with mixtures of around 5.0 kg for each treatments and 30 earthworms (night crawlers) were released to each treatment for vermicomposting. About 60 per cent moisture was maintained using distilled water throughout the study on weight basis and the trays were kept in a concealed region in Radioisotope Laboratory, TNAU, Coimbatore. To maintain the required moisture content, water was sprayed intermittently depends on the temperature. Changes in temperature has been monitored throughout the investigation using temperature monitoring sensor. Mortality of worms were also recorded in all treatments throughout the study. Characterization of the partially decomposed cow dung and fly ash used for the experiment were delineated in Table 1.

Table 1: Characterization of Partially decomposed cow dung (PCD) and Fly ash

Parameters	Partially Decomposed cow dung (PCD)	Fly ash (FA)
pH	8.50	10.94
EC (dS m^{-1})	4.20	2.39
N (%)	0.84	0.22
P (%)	0.14	0.04
K (%)	0.43	2.49
Ca (%)	3.04	18.40
Mg (%)	1.19	7.2

2.2 Sample collection
To determine the chemical changes occurred during vermicomposting process, samples were collected at 14 days interval until maturity of the compost based on C:N ratio (upto 42 days). The composite sample was prepared by uniformly mixing of nine samples, three samples each from top, center and bottom of the tray. The samples were air dried, sieved (for SEM imaging) and ground for FTIR analysis.

2.2.1 Sample preparation for Scanning electron microscope (SEM) Imaging.
For imaging the sample material using scanning electron microscope (SEM), sample was placed in a carbon tape present in sample holder using thin brush by dusting, then the excess dust material present in the sample holder was removed by blower. Then it was kept in a sample holder present in SEM for imaging.

2.3. Analytical methodology
2.3.1. SEM / EDAX
A Scanning Electron Microscope (SEM) was used to evaluate the texture and morphology of the sample. Before scanning the image of a sample, high vacuum condition was created and by increasing the voltage sample was scanned. By adjusting the focus and magnification of an image, sample images of different magnification based on need were captured. The elemental composition of the sample in percentage was characterized by energy dispersive X-ray spectroscopy (EDAX). After capturing the image of particular sample, it was subjected to identify the peaks of elements present in the sample. After peak identification, the composition of elements present in the sample on percentage basis was computed.

2.3.2. Fourier Transform Infrared Spectroscopy (FTIR)
Various functional groups present in vermicompost sample was characterized by Fourier transform infrared spectroscopy in the wavelength range of 4000 – 400 cm^{-1} for good characterization. FTIR spectrometer with Attenuated Total Reflectance (ATR) technique was used for recording the change in functional group of a sample at room temperature which enables the samples to be studied under solid or liquid phase without potassium bromide pellet preparation. Switched on the instruments for an hour before getting spectrum for sample and the background check was done to eliminate the peaks developed due to noise, then samples such as FA, PCD, FAV at initial and final stages were analyzed for FTIR spectrum. Bio rad software was used to identify the functional group present in the sample.

3. Result and Discussion
3.1 Scanning Electron Microscope (SEM)
The morphology of fly ash and partially decomposed cow dung were depicted in Fig. 1(a) and 1(b). The size and morphology of the vermicompost sample before and after vermicomposting were depicted in the Fig. 2(a) and Fig. 2(b) respectively.
The spherical structure present in Fig. 2(a) indicate the presence of fly ash material with partially decomposed cow dung at 5000 times magnification whereas Fig. 2(b) shows the rod-shaped structure and spherical shaped structure indicate the presence of bacteria due to the secretion from earthworm and fly ash material (Stimoniaris *et al.*, 2019) [10] respectively.

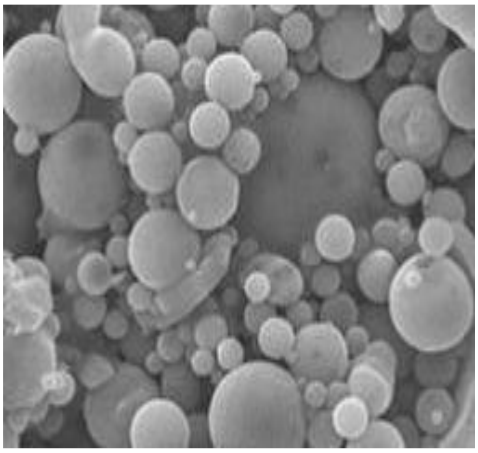

Fig 1(a): Fly ash

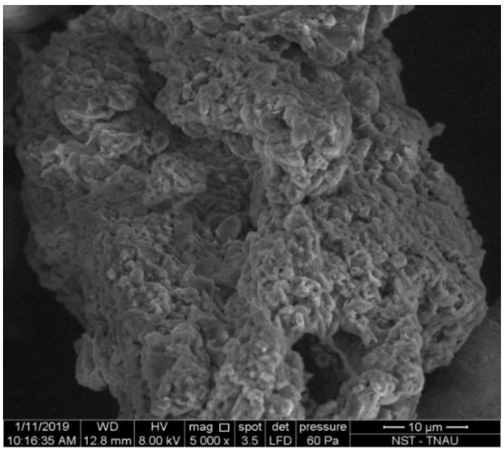

Fig 1(b): Partially decomposed cow dung

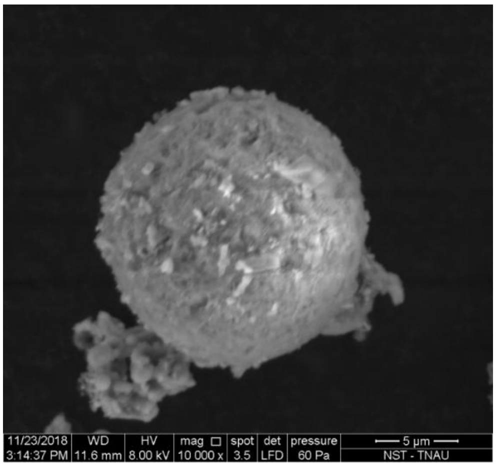

Fig 2(a): FAV before vermicomposting

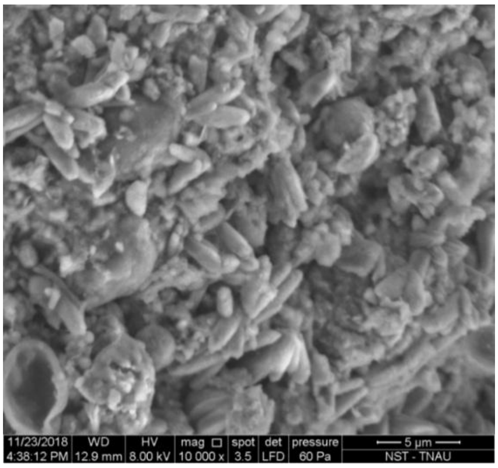

Fig 2(b): FAV after vermicomposting

3.2. EDAX

The elemental composition of PCD in percentage was presented in the Fig. 3 showed that the major peak of PCD was Carbon (C) around 64.15 per cent followed by Oxygen (O) of 26. 43 per cent, Nitrogen (N) of 7.20 per cent, Silica (Si) of 1.48 per cent, Sodium (Na) of 0.54 per cent and Magnesium (Mg) of 0.19 per cent.

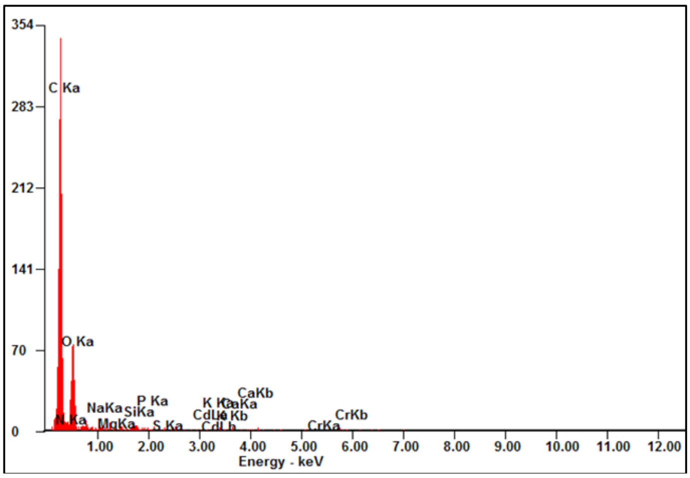

Fig 3: EDAX spectrum showing the elemental composition of PCD

The composition of various elements present before and after vermicomposting of PCD: FA in the ratio of 3:1 was characterized by EDAX. The EDAX spectrum of before and after vermicomposting was depicted in Fig. 4(a) and Fig. 4(b). Before vermicomposting the sample shows the major peak of Chromium (Cr), Aluminium (Al), Silica (Si), Cadmium (Cd) and Calcium (Ca) peak.

The elemental composition present in FAV after maturity showed the peaks of Carbon (C), Nitrogen (N), Oxygen (O), Aluminium (Al), Silica (Si), Phosphorus (P), Sulphur (S) and Calcium (Ca) (Fig 4 (b)). The reduction in heavy metal concentration after vermicomposting observed in Fig. 4(b) might be due to the accumulation of heavy metals in earthworm (Gupta *et al.*, 2005) [5]. There was an increase in nutrient content also observed in Fig. 4(b) might be due to the secretion of mucous and other excreta from earthworm gut enhance the nutrients after vermicomposting (Lukashe *et al.*, 2019) [6].

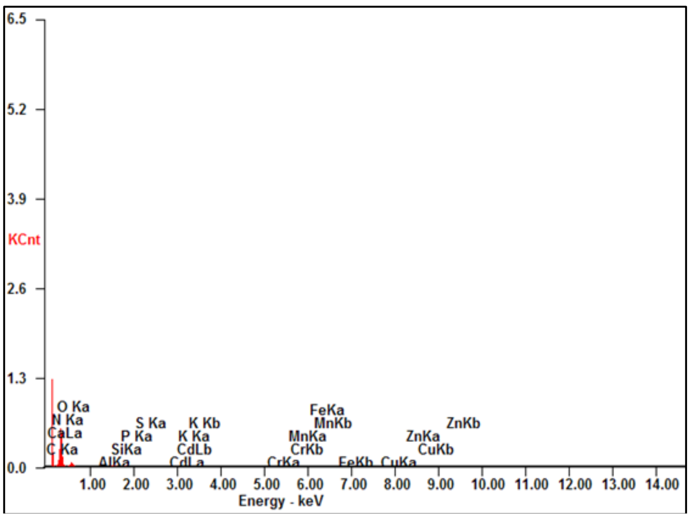

Fig 4 (a): EDAX spectrum before vermicomposting

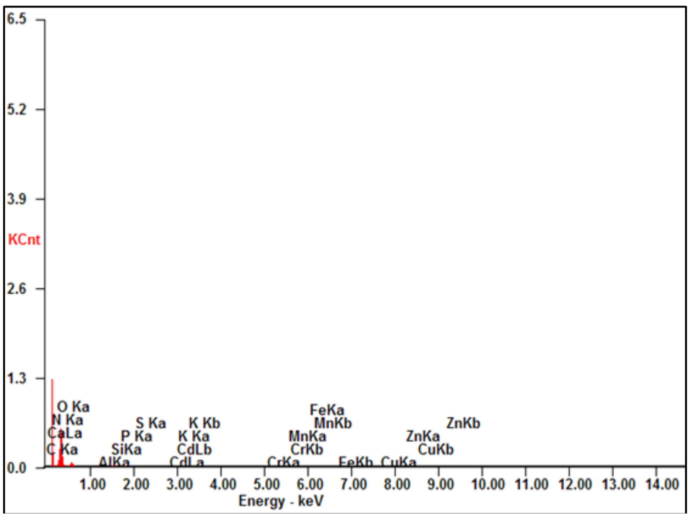

Fig 4 (b): EDAX spectrum after vermicomposting

3.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 5 showed the infrared spectrum of fly ash and partially decomposed cow dung sample. FTIR shows peak at 3985 cm^{-1}, 1220 cm^{-1} and 772 cm^{-1} for fly ash sample. The peak at the wavenumber of 3985 cm^{-1} indicates the presence of gaseous water molecule due to the valence vibration (Novak *et al.*, 2001) [7]. There was a strong band occurs at 1220 cm^{-1} indicate the strong asymmetric phosphate stretching and the band at 772 cm^{-1} due to the presence of calcium carbonate (Clara and Sugirtha, 2016) [2] and silica minerals (Sivakumar *et al.*, 2012) [8]. The peak at 1000 cm^{-1} indicate the presence of strong alkene compound or polymers with C= O stretching (Fong *et al.*, 2006) [4].

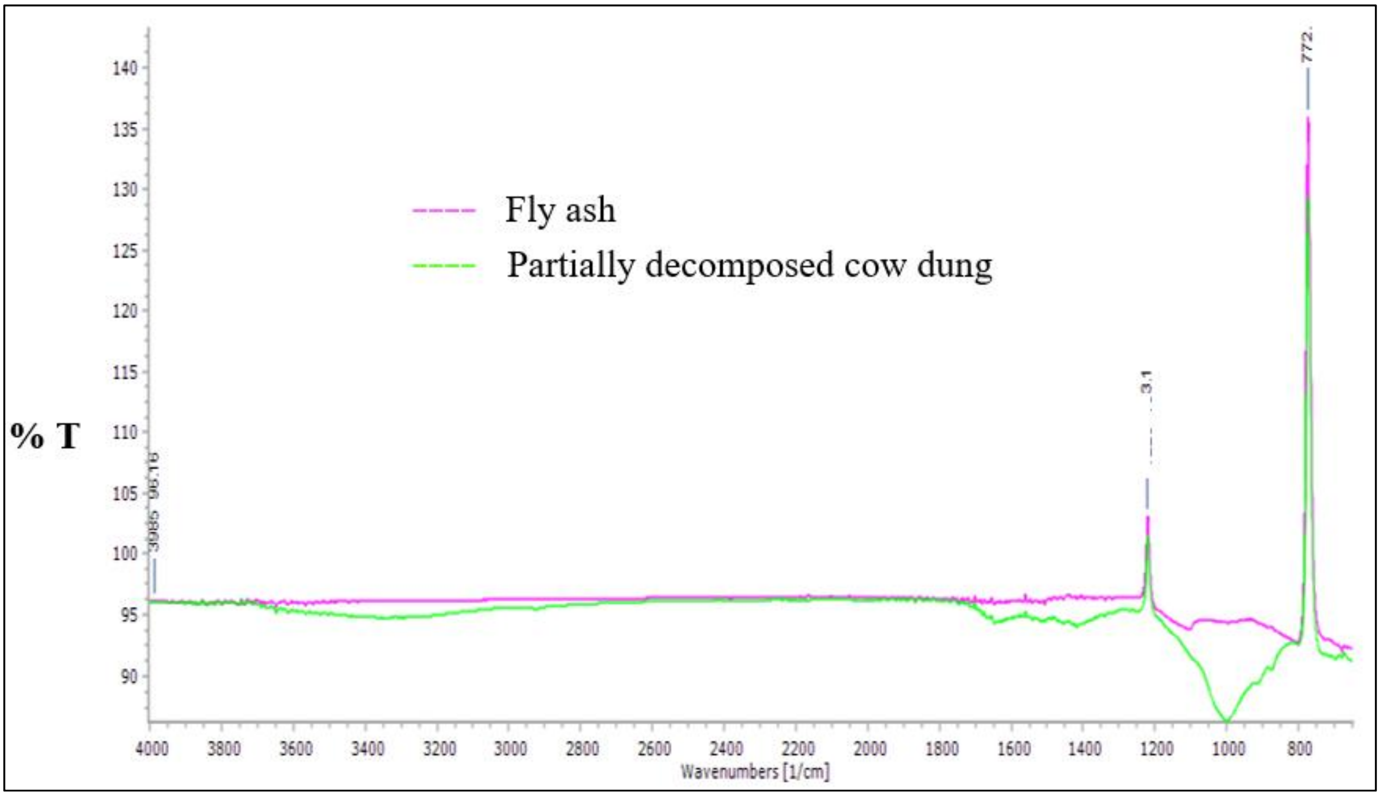

Fig 5: FTIR spectrum of fly ash and partially decomposed cow dung

There was broad stretching occurs in partially decomposed cow dung at 3200 - 3600 cm^{-1} indicates the presence of alcohol group due to O – H bond stretching. The bend occurs at 1650 cm^{-1} indicate the presence of nitrogen compound due to C=N stretching whereas the dip occurs at 1400 cm^{-1} indicate the presence of sulphur compound. Certain compounds like C=N, phosphorus compound, Si compound, Halogens, Phenolic and alcoholic groups are present in FAV throughout the period of vermicomposting was shown in Fig. 6 and Fig. 7. But the intensity was increased with increase in period of vermicomposting especially with phosphorus, nitrogen and organic acid content. With the increasing period of vermicomposting certain functional groups like gaseous water molecule present at the peak region of 3782.69 cm^{-1} was disappeared due to the weak interaction of O-H-O molecule with its environment through hydrogen bonding (Novak *et al.*, 2001) [7] and also the organic functional groups of anhydride or ketones observed at 1884.11 cm^{-1} are disappeared after vermicomposting might be due to the conversion of alcohol and ketones to carboxylic acid group during vermicomposting (Dahlan *et al.*, 2008) [3].

Table 2: Peak Assignments for different functional groups and minerals

Wavelength (cm^{-1})	Compounds	Tentative group	Band appearance	Reference
3800 - 3700	Gaseous water molecule or free alcohol group	Valence vibrations of water molecule, O – H bonding	Weak	Novak *et al.*, 2001; [7] Socrates, 2001 [9]
1420 -990	Sulphinic acids or esters, sulphates	S = O stretching	Medium	Socrates, 2001 [9]
3300 - 2500	Carboxylic acid	OH – stretching (intermolecular bonded)	Strong and broad	Socrates, 2001 [9]
1655 - 1610	Amine, organic nitrate compounds	N – H bending O – NO_2 asymmetric stretching	Medium	Socrates, 2001 [9]
2075 – 2100	Isothiocyanate	N=C=S stretching	Strong	Socrates, 2001 [9]
1884.11	Esters, Ketones, Carboxylic acid and their salts, acid anhydride	C= O stretching	Strong	Socrates, 2001 [9]
1220	Phosphorus as phosphates	Asymmetric PO_4^- stretching	Strong	Clara and Sugirtha, 2016 [2]
1000 - 1020	Aromatic ethers and polymers	C – O-C stretching	Medium	Socrates, 2001 [9] Fong *et al.*, 2006 [4].
868 – 873 770 -780	Calcite	C-O bending for carbonates	Medium	Dahlan *et al.*, 2008 [3]. Clara and Sugirtha, 2016 [2]

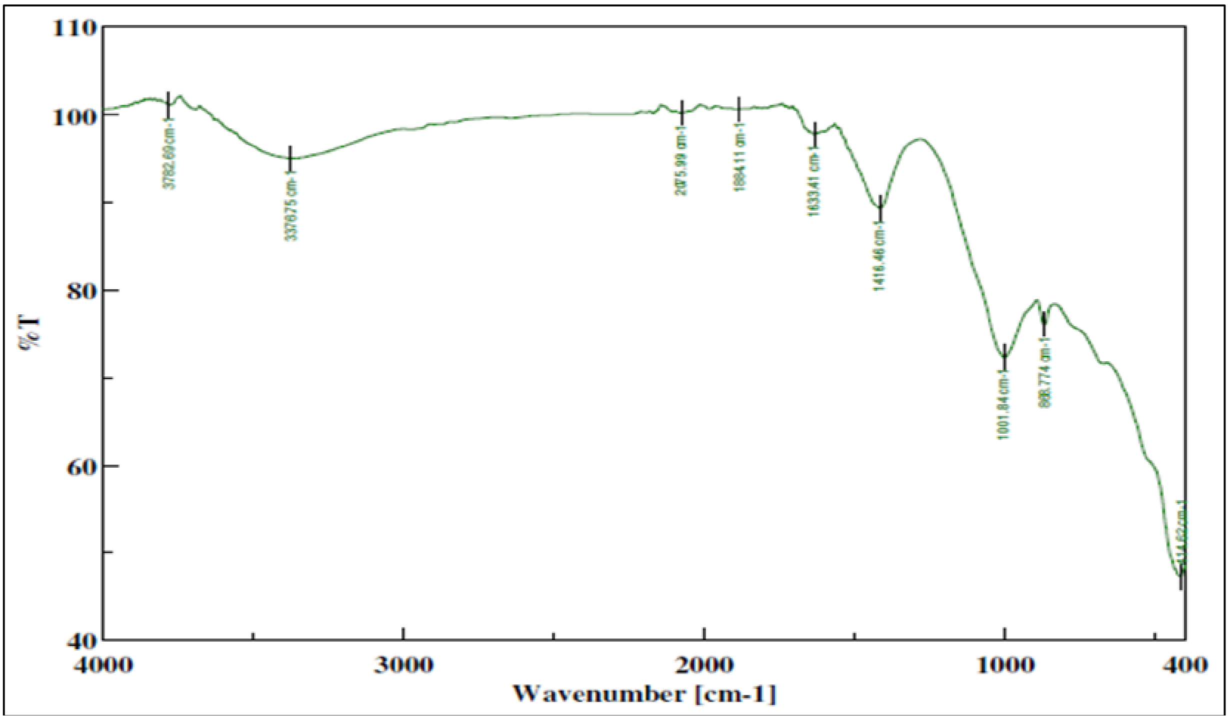

Fig 6: FTIR spectrum of Fly ash based vermicompost in the ratio of 3:1 as PCD: FA before vermicomposting

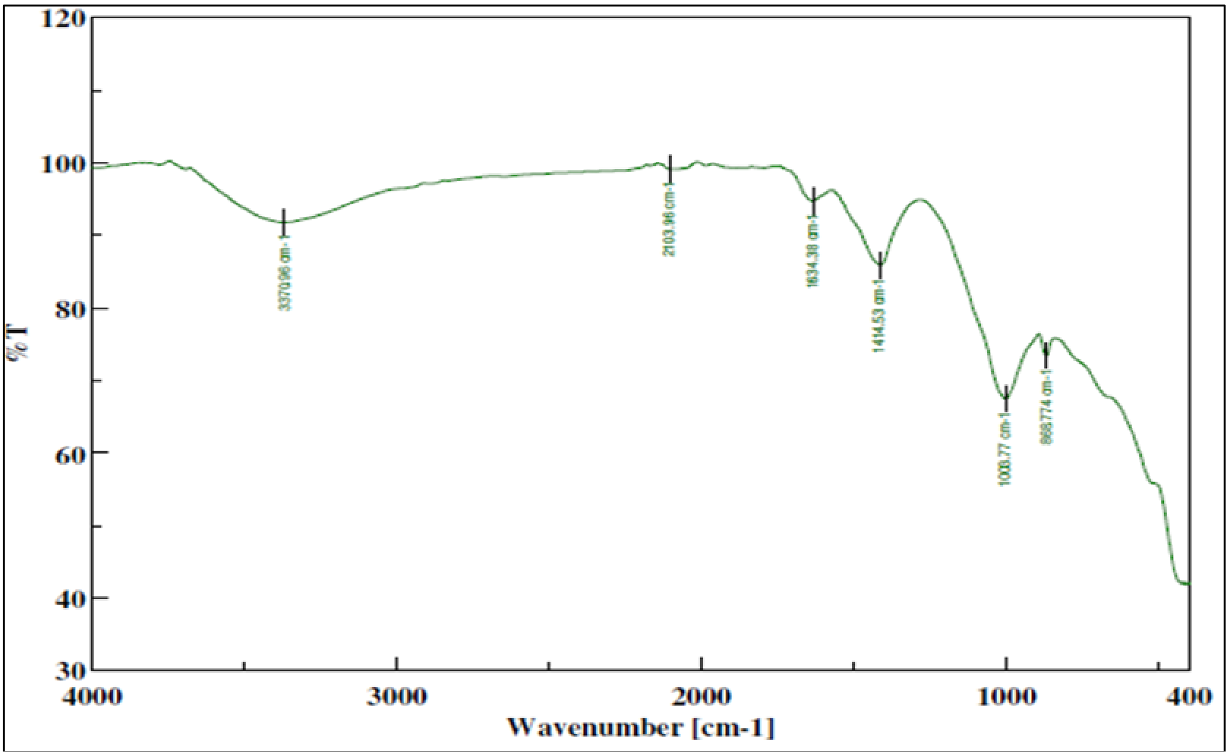

Fig 7: FTIR spectrum of Fly ash based vermicompost in the ratio of 3:1 as PCD: FA after vermicomposting (42 days)

4. Conclusion

Based on the results of investigation on morpho - chemical changes occurs during vermicomposting, the following conclusions were drawn:

FTIR spectroscopy was a helpful method to visually classify the highly correlated spectra for rapid detection of the functional groups present in fly ash based vermicompost before and after vermicomposting which causes the change in pH and other nutrient concentration. The FTIR spectrum of FAV after maturity clearly indicate that there was an increase in carboxylic acid group, calcium content, phosphorus and nitrogen compound which helps in crop production.

In this study, fly ash based vermicompost was considered as one of the techniques to alleviate heavy metal contamination from fly ash. It was evident from the results of EDAX spectrum that the fly ash based vermicompost showed an excellent result for removal of heavy metals from fly ash after vermicomposting. Though it contains lot of nutrients like N, P, S, Ca and Silicon with reduced heavy metal concentration (*i.e.*, within the critical limit), it can used as a manure for cultivation of crops in agriculture.

The infrared bands of certain peak range with their possible functional groups were shown in the Table 2. By comparing the frequency of fly ash-based vermicomposting with the available literature, peaks in the region of 868 – 873 cm^{-1} indicate the presence of calcium (Calcite) as carbonates whereas the presence of peak in the region of wavelength 1655 – 1610 cm^{-1} indicate the nitrogen compound (C=N). The presence of organic compounds like O-H, C-O and aromatic ethers and acid polymers was indicated by the broad peak in the region of 3200 -3400 cm^{-1} and 1000 – 1075 cm^{-1} respectively which is an indication the compost process came to maturity.

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