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Characterization of organic compounds in soil irrigated with treated paper board mill effluent using FTIR

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Abstract

Paper and paper board industry contributes to largest waste water disposal problems all over the world. Yet the effluent contains huge load of organic materials which may end up in soil contributing to increase in soil organic matter contents. The soils which are irrigated with paper and board mill effluent are characterized using FTIR. This shows the dominance of C compounds and sulfur compounds. The results also indicate that the soils have sufficiently high load of organic matter owing to the irrigation by effluents from the board mill industry.

Keywords: Organics, board mill effluent, subtractive FTIR, hydrolysable pool

Introduction

The paper industry consumes large amount of water and hence releases large quantities of wastewater. Irrigating the farming area with treated has been a far reaching practice utilized for either wastewater discharge or as a recharging of water source due to worldwide changes in precipitation pattern and demand and even in some cases increase in crop yield has also been reported. This ongoing demand for water of water scarcity can be overcome by irrigating farmlands with the effluent from waste paper based paper board industry since it contains sufficiently good quantities of nutrients.

Soil is a very complex medium and is one of the most important factors for agriculture. It contains minerals, organic matter, micro-organisms, air and water. The use of treated WW for agriculture adds more of organic compounds to the soil. The dynamics or the presence of organic compounds in these soils need to be studied. Fourier transform infrared spectroscopy (FTIR) can provide fundamental information on the molecular structure of organic and inorganic components (Margenot *et al.*, 2016) [8] and is one of the most versatile analytical techniques for the non-destructive, chemical characterization of geological samples, such as coal, shale, fluid and melt inclusions, silicate glass, minerals, and microfossils. The absorbance of molecular vibrations under IR radiation are proportional to the abundance of the functional groups. Transmission FTIR is a fast and relatively cost-efficient technique which has been used extensively in chemistry, geology, and other scientific fields (Raphael, 2011) [12].

The quality of soil organic matter (OM) depends on its distribution among labile and recalcitrant pools (Rovira and Vallejo, 2002) [13]. An attempt was made to identify the organic materials other than carbohydrates since they represent 5 to 30% of the organic materials in soil (Oades *et al.*, 1970) [10]. The aim of the study is to characterize the organic compounds present in the soil irrigated with treated effluent from the waste paper based paper board industry. Since they constitute the labile pools, acid hydrolysis approach was followed for the removal of carbohydrates from the soils.

Materials and Methods

Experimental design

The present study was carried out in M/s. TNPL Unit II, a waste paper based paper board industry located at Mondipatti, Tiruchirappalli, Tamil Nadu. The treated effluent is used for irrigation to agro-forestry systems using drip irrigation. The Agroforestry system comprises tree species like Kadamba, Melia, Neem, Casuarina etc. Soil samples were collected from agro forestry plantations and pooled to make a composite sample. Five replications were made to characterize the soil samples.

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Physico-chemical characteristics

The soil samples were assessed for color, pH (Jackson, 1973)^[5], EC (Jackson, 1973)^[5], organic carbon (Walkley and Black, 1934)^[16], Available Nitrogen (Subbaih and Asija, 1956), Available Phosphorus (Olsen *et al.*, 1954), Available Potassium (Stanford and English, 1949)^[15].

Sample preparation

To understand the general character of the FTIR spectra of the organic matter present in the sample different nature of soil sample were employed. Such differences were given below.

1. Original sample (without pyrolysis)
2. Soil sample after pyrolysis
3. Unhydrolysable pool obtained after acid hydrolysis.

The collected soil sample was dried for 105°C, grinded with mortar, sieved and approximately 5 g of soil sample was taken, passed through 0.2 mm sieve and stored in closed glass vial.

The carbohydrate free pool was isolated from the soil by the procedure described by Oades *et al.*, 1970^[10]. The soil samples were analyzed in Fourier Transform Infrared Spectroscopy to identify the organic components present in the soil based in the procedure described by (Cox *et al.*, 2000)^[11]. The subtractive FTIR technique offers advantages in analyzing the soil organic matter since in this method the soil sample to be analyzed is subjected to pyrolysis or thermal treatment by which the combustion of organic compounds takes place leaving the inorganic matter (Gezici *et al.*, 2012)

^[3]. The resultant spectra will represent the absorption by organic components present in the soil (Cox *et al.*, 2000)^[11].

FTIR spectroscopy

The soil sample was pressed into a KBR pellet and the spectra was collected on a Nicolet iS10 FTIR, using Nicolet Omnic software. Then the pellet was reground in a mortar, placed in a glass vial heated for 15 min at 650 °C in a muffle furnace to decompose the organic compounds. After cooling the sample was again pressed into pellets and the spectra was recorded. This spectrum was subtracted from the previous spectrum which was recorded before pyrolysis. This represents the absorbance by the organic components in the soil.

Results and discussion

The characteristics of the soil used for the study are as follows; the color of the soil when dry is 5YR4/4 (reddish brown) and when wet is 5YR 3/4 (dark reddish brown). The pH of the soil was 7.33 and it was near neutral. The EC was 0.05 dS m⁻¹. The Organic carbon content of the soil is 0.52% (medium), the soil available Nitrogen is 257.6 kg of N/ha, the soil available phosphorus is 10.1 kg/ha, the soil available Potassium is 284 kg/ha.

FTIR spectra

Fig 1 and 2 represents the spectra obtained from the soil sample before and after pyrolysis, respectively. The spectra obtained after subtractive technique is given in fig 3. Fig 4 represents the spectra for the unhydrolysable pool.

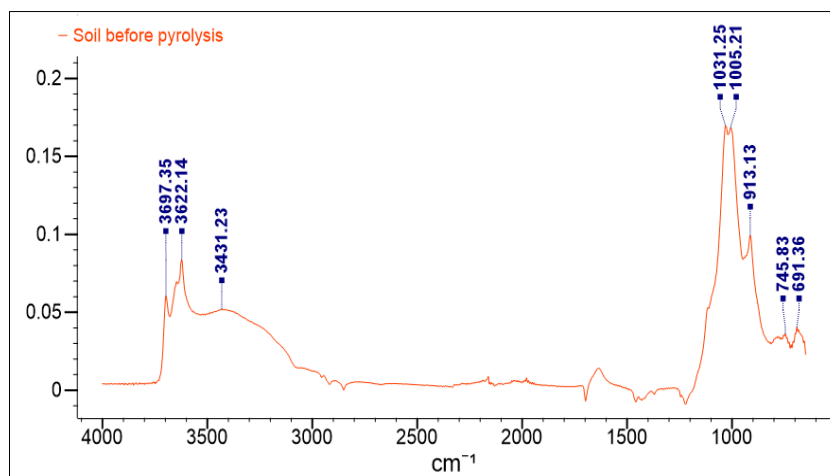


Fig 1: FTIR spectra of the original soil sample before pyrolysis

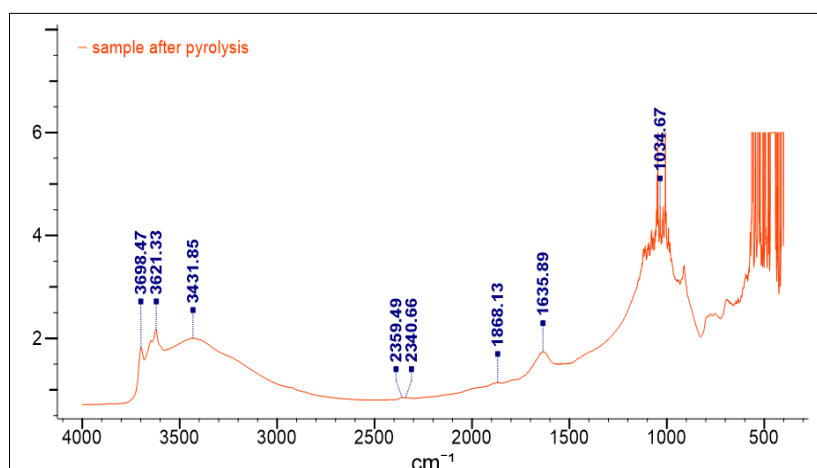


Fig 2: FTIR spectra of the sample after pyrolysis

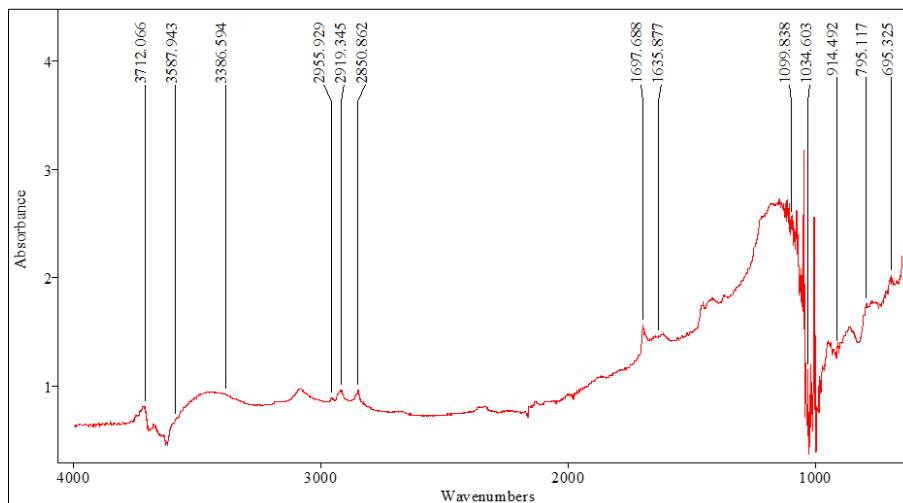


Fig 3: FTIR spectra subtracted

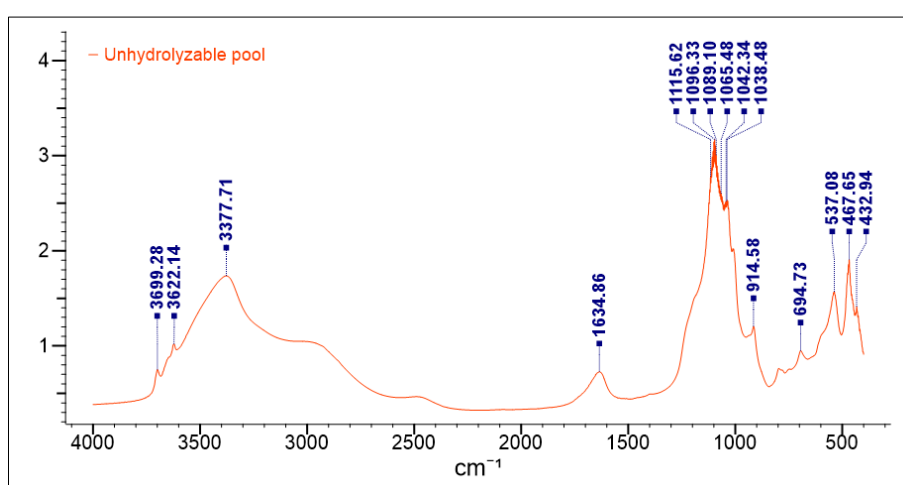


Fig 4: FTIR spectra of the unhydrolyzable pool

Organic spectra peak assignment

The most important peak assignments of aliphatic groups were the C-H stretching around 3000 cm^{-1} and the -CH deformation modes around 1460 cm^{-1} and 1380 cm^{-1} . The CH_3 asymmetric stretching vibration occurs at $2975\text{--}2950\text{ cm}^{-1}$, while the CH_2 absorption occurs at about 2930 cm^{-1} . The symmetric CH_3 vibration occurs at $2885\text{--}2865\text{ cm}^{-1}$ while the CH_2 absorption occurs at about $2870\text{--}2840\text{ cm}^{-1}$. Carboxylic acids absorption occurs from about $3100\text{ to }2200\text{ cm}^{-1}$. C=O stretching was found between $1725\text{--}1700\text{ cm}^{-1}$, C-O stretching between $1440\text{--}1395\text{ cm}^{-1}$ and $1320\text{--}1210\text{ cm}^{-1}$ and OH deformation between $950\text{--}900\text{ cm}^{-1}$. Aromatic C=C vibrations and stretching can be assigned to peaks in the wavelength between 2000 and 1700 cm^{-1} . Similar observation and interpretation of the organic functional groups was made by (Lehmann and Solomon, 2010) [6]. The strong band between 1150 and 1000 cm^{-1} of FTIR spectra taken from soils is usually due to the C-OH stretching of polysaccharides. However, this band overlaps with the Si-O-Si stretching of silicate bands ($1200\text{--}970\text{ cm}^{-1}$) in soil, and may undermine the identification of the polysaccharide peak position, as well as the quantification of this functional group from the peak intensity (Lehmann and Solomon, 2010) [6]. Intensity of other absorbance peaks reflecting possible vibrations is weak (stretching or bending) in case of organic molecules present in soil samples and also they are often superimposed by most intense vibration of Si-O group of silicates. This is applicable

mainly to polysaccharides and polysaccharide-like substances, whose absorption bands occur in a relative broad range from 1170 to 950 cm^{-1} ((Madari *et al.*, 2006, Chapman *et al.*, 2001) [7, 1]).

Table 1: Functional group frequencies of the main FTIR bands of soil components

Peak positions (wavenumber cm^{-1})	Soil components
3000 cm^{-1}	C-H stretching of aliphatic groups
$2975\text{--}2950\text{ cm}^{-1}$	Asymmetric stretching vibrations due to CH_3 groups.
$1725\text{--}1700\text{ cm}^{-1}$	C=O stretching of carboxylic, quinones, amides, ketones, esters, aldehydes
$1440\text{--}1395\text{ cm}^{-1}$ and $1320\text{--}1210\text{ cm}^{-1}$	C-O stretching O-H bending of COOH
$2000\text{--}1700\text{ cm}^{-1}$	Aromatic C=C vibrations and stretching
$3500\text{--}3200\text{ cm}^{-1}$	O-H stretching of carboxylic acids, phenols, alcohols
$2925, 2858\text{ cm}^{-1}$	Soil humic compounds
1635 cm^{-1}	Alkenes, amides, amines
2340 cm^{-1}	Amine salts, Phosphorus, sulfur compounds
3431 cm^{-1}	Urea, Urethanes
3621 cm^{-1}	Silicon compounds

FTIR spectra of unhydrolyzable pool

The FTIR peak near $3350\text{--}3180\text{ cm}^{-1}$ are caused by the stretching NH amide groups. CO groups are responsible for

the peaks near 1650 cm^{-1} . NH_2 deformations are responsible for the bands near $1650\text{--}1620\text{ cm}^{-1}$. The spectrum contains more absorption bands in particular spectral regions, they are caused by the vibration of Si–O group in silicates at 1080 and 1035 cm^{-1} . The peaks near 3622 cm^{-1} and 3697 cm^{-1} were due to the presence of kaolinite clay content (Mckissock *et al.*, 2003)^[9]. The broad absorption bands near 3400 cm^{-1} is due to OH vibration (Haberhauer *et al.*, 1998; Chapman *et al.*, 2001)^[4, 1]. The area consisting of the two adjacent absorbance peaks ($1640\text{--}1620\text{ cm}^{-1}$) can be due to lignocellulose material (Ellerbrock and Kaiser, 2005; Smidt and Schwanninger, 2005)^[2, 14]. The peaks near $1650\text{--}1530\text{ cm}^{-1}$ corresponds to Lignin. The peaks between $550\text{--}400\text{ cm}^{-1}$ relates to the O-Si-O deformation or bending.

Table 2: Functional group frequencies of the main FTIR bands of soil components for the unhydrolysable pool or recalcitrant fractions

Peak positions (wavenumber cm^{-1})	Soil components
$3350\text{--}3180\text{ cm}^{-1}$	Stretching of NH amide groups
$1650\text{--}1620\text{ cm}^{-1}$	NH_2 deformations
1080 and 1035 cm^{-1}	Si–O group in silicates
$1640\text{--}1620\text{ cm}^{-1}$	Lignocellulosic materials
3400 cm^{-1}	OH vibrations
3622 cm^{-1} and 3697 cm^{-1}	Kaolinite clay minerals
$1650\text{--}1530\text{ cm}^{-1}$	Aromatic C=C vibrations and C=C stretch of aromatic C in lignin

Conclusion

The combustion and subsequent spectra subtraction in FTIR technique offers the advantage of eliminating the shielding effect of bands with respect to inorganic matter present in the soil samples and the method is solvent free. The soil sample irrigated with paper and board mill effluent contains more of organic compounds added through the irrigation of the effluent. Hence the soil spectra is dominated by Carbon compounds including like alkenes, amides, amine salts, urea, humic acids etc., added through effluent irrigation and sulfur compounds added to the soil from mineral weathering, atmospheric deposition, and organic matter decomposition. Thus subtractive FTIR technique offers a rapid, useful and easy approach for soil organic matter studies. To improve the understanding of changes in SOM composition further research to should is to be added by combining FTIR with other spectroscopic techniques such as NMR spectroscopy or pyrolysis Gas Chromatography–Mass Spectrometry (PY-GC/MS) that will provide complementary information on SOM composition.

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