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FTIR spectroscopic study of fungal degradation of poly(ethylene terephthalate) and polystyrene foam

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ABSTRACT

The degradation of Poly(ethylene terephthalate) and polystyrene foam waste could be accelerated using microbes. The aim of the study was to determine the degree of biodegradation of poly(ethylene terephthalate) films and Polystyrene foam by Fourier transform infrared (FTIR) spectroscopy. Further, chemical changes like formation of ester group was observed in PET powder when buried in soil under laboratory conditions. C = C bond stretching in PET powder inoculated in soil, sewage and cowdung was evident in this study. On inoculation of PET flakes in soil, sewage and cowdung, FTIR spectral analysis reveal C-H and C=C bond stretching. Except in PET flakes in cowdung , PET inoculation in soil and sewage elicited C=O bond stretching. PS powder inoculated in soil, sewage and cowdung underwent degradation which in reflected in the FTIR spectral analysis (C-O, bond stretching). Furthermore, PS powder on inoculation with sewage elicited C-H and C=C bond stretching, while in cowdung it resulted in O-H, C=O and C=C bond stretching. PS flakes when buried in soil, sewage and cowdung exhibited C=C bond stretching. In addition, O-H, C-H, C=O bond stretching was evident in PS flakes buried in cowdung. Thus fungal species (*Aspergillus sp., Penicillium sp. and Fusarium sp)* could be used as a biological agents to degrade PET and PS foam.

Introduction

FTIR spectroscopy has been well-known as a powerful tool to study polymer degradation quantitatively [1,2]. The high sensitivity towards the chemical changes and controlled probing depth of the technique are vital functionalities to capture the initial degradation characteristics at the polymer surface [3,4]. The degradation related chemical changes can be used as indicators for predicting the long-term performance of the material [5,6]. The degradation index can be calculated using measurements of the IR peaks of interest to indicate the degradation behaviour of the polymer.

Management of synthetic plastic waste is of growing concern in recent time. Polystyrene (PS) is a multipurpose polymer that is used in varied applications in rigid and foamed form. General purpose polystyrene (GPS) is clear and hard which is used in packaging, laboratory ware, and electronics. The excellent physical and processing properties make polystyrene suitable for a lot of applications than any other plastic [7]. Expanded polystyrene (EPS) is used in foam form for packaging as well as insulation in various industrial fields in the world [8].EPS is moulded into sheets for thermoforming into trays for packaging of fish, meat and cheese, egg crates, tubs and cups. Styrene and its metabolites are known to cause serious negative effects on human health (Mooney et al., 2006). Styrene causes neurological impairment, toxic effect on liver, central nervous system. Styrene is metabolised by a number of microbes in natural environments. Styrene biotransformation causes the production of styrene oxide that is more toxic to human health. Polyethylene Terephthalate (PET) is a semi crystalline thermoplastic polymer, which is used in the preparation of a variety of products differing widely in their physical characteristics and hence, the end uses. The varieties of prominence are fibres and filaments, sheets and soft drink bottles.

The microbial biodegradation of plastic is widely accepted option and is still underway for its enhanced efficiency. Several microorganisms have been reported to produce polyester degrading enzymes. Several microbial species associated with degrading plastics have been reported (bacteria : *Pseudomonas spp, Streptococcus spp, Staphylococcus spp, Micrococcus spp* and *Maoraxella spp;* fungi : *Aspergillus niger spp, Aspergillus galucus spp , Actinomycetes spp., and Saccharomonospora genus spp)*[10]. Excellent adherence and colonisation properties give advantage to the fungi for bioremediation. Once established on a surface, the fungi cover the whole area by forming mycellial mat. Fungi are able to withstand longer periods of stress conditions and due to saprotrophic nature they are capable of producing a diverse arsenal of enzymes that are able to degrade the recalcitrant compounds [11] The aim of the present study was to isolate fungal species able to colonise and biodegrade Polystyrene Foam and Polyethylene terephthalate waste and the morphological changes , further confirmation of degradation by FTIR studies

Materials and Methods

Samples collection

The plastic (PET water bottles and PS foam) samples were purchased from local market. Soil and Cow dung was collected from local area and Sewage was collected from TWAD (Tamil Nadu water supply and Drainage Board) in Tiruchirapalli, India.

Preparation of PS Foam and PET Powder

PET bottles and Polystyrene foam (Thermo coal) were cut into small flakes and they were kept in the hot air oven for 30 minutes at 100 ^{0}C and 10 minutes approximately at 100^{0}C for

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PS foam, respectively. Further, they were crushed and sieved by using 1mm mesh

Preparation of PS Foam and PET flakes

PET bottles and PS foam were cut into 0.5cm× 0.5cm, thereafter both samples were washed with 70% ethanol and distilled water. Each samples was then aseptically transferred to field (Soil, Sewage and Cow dung) and individually placed into sterile minimal salt medium (MSM) in laboratory.

Biodegradation of PS foam and PET powder under laboratory condition

250 mg of prepared plastic samples (PET and PS foam powder) separately were directly inoculated into 250 ml of minimal salt medium (Soil + Minimal Salt medium, Sewage + Minimal salt medium and cow dung + Minimal salt medium) . The culture was carried out for a month on a rotary shaker at 120 rpm. Fungal population was counted every week by pure plate method using Rose Bengal Chlormophenicol Agar. Further plates were incubated at 28^{o} C for 7 days and developed colonies were isolated and sub cultured to get pure colonies and stored in refrigerator of further studies. Further, Fungal isolates were identified by using Lacto-phenol cotton blue stain and observed under the Light microscope. [12,13]

Biodegradation of PS foam and PET powder under field condition

Soil, cow dung and sewage were transferred to plastic tray and inoculated with PS and PET flakes separately for a period of 70 days. Soil, cow dung and sewage not inoculated with PS foam and PET were maintained as control simultaneously. At end of the 70th day, the PS foam and PET inoculated in soil, cow dung and sewage were collected and sonicated in MSM. Fungi in the MSM were isolated using Rose Bengal Chlormophenicol Agar by pour plate methods. Further, colonies were identified by adopting Lacto-phenol cotton blue stain and observed under the Light microscopic[12,13].

FTIR Spectrophotometer studies

Fourier transform infrared (FT-IR) measurements were carried out with a BIO-RAD spectrometer (model FTS 40A) in the range of 4000-650 cm^{-1}. The FT-IR spectra were recorded at a resolution of 2 cm^{-1} and an accumulation of 32 scans.

Result

FTIR analysis of PET and PS flakes and powder exposed to soil, cow dung and sewage

FTIR spectra of PET powder were performed from 200 cm^{-1} to 400 cm^{-1}wave number region after 70 days of incubation in soil. The absorption bands at 3430 cm^{-1} has been attributed to O-H bond stretching ,3063 cm^{-1} and 2961 cm^{-1} to C-H bond stretching (methylene groups), 2545 cm^{-1}, 2358 cm^{-1} and 1721 cm^{-1} to C=H bond stretching (carbonyl group), 2111 cm^{-1} and 866 cm^{-1} to C=C bond stretching (Benzene),1412 cm^{-1} and 1341 cm^{-1} to C-H bond stretching (Methylene group),1263 cm^{-1} and 1117 cm^{-1} to C-O bond stretching (ether group formation), 1017 cm^{-1}, 791 cm^{-1} and 723 cm^{-1} to C-H bond stretching (Methylene group)(Fig -1). It is inferred from fig -2 that PET powder on inoculation with the soil under laboratory condition exhibited appearance of three characteristic absorption peaks at 1637 cm^{-1} and 1503 cm^{-1} which has been assigned to C=C bond stretching (Benzene ring) and 1121 cm^{-1} to C-O bond stretching (formation of ester group) .On inoculation of PET powder with sewage, appearance of new absorption peaks at 1636 cm^{-1} and 1507 cm^{-1} was evident in the FTIR spectrum which has been attributed to C=C bond stretching (Benzene ring) [fig-3]. It is inferred from fig-4 that PET powder on inoculation with cow dung , elicited characteristic absorption peaks at 1639 cm^{-1} , 1507 cm^{-1} and 973 cm^{-1} which has been attributed to C=C bond stretching and C-O bond stretching (formation of ester group),respectively .

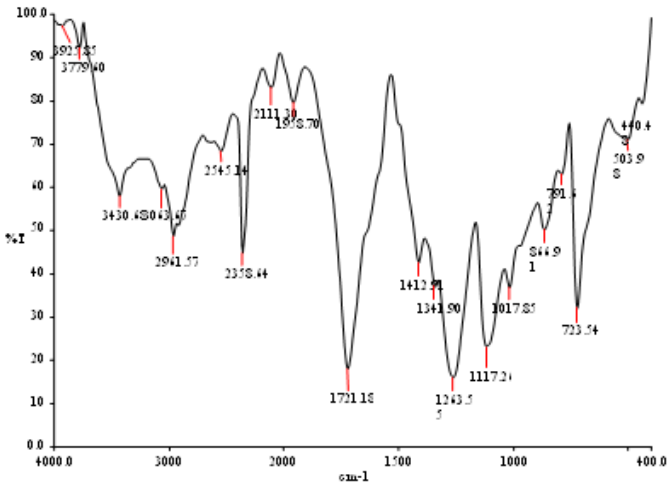

Fig 1. FTIR spectra of untreated PET powder

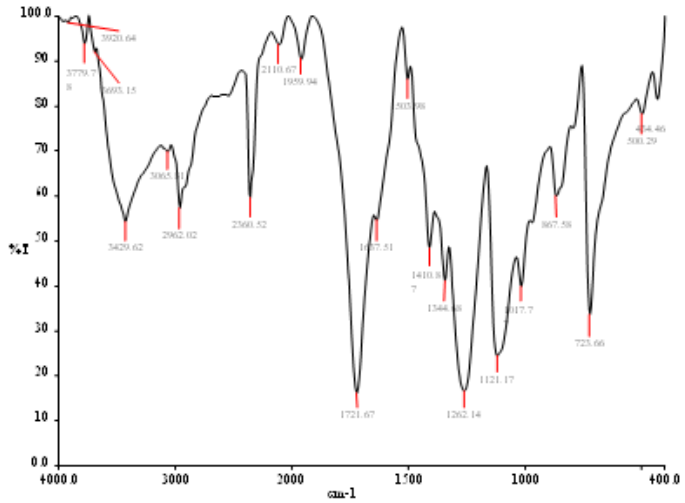

Fig 2. FTIR spectra of soil buried PET powder under laboratory conditions

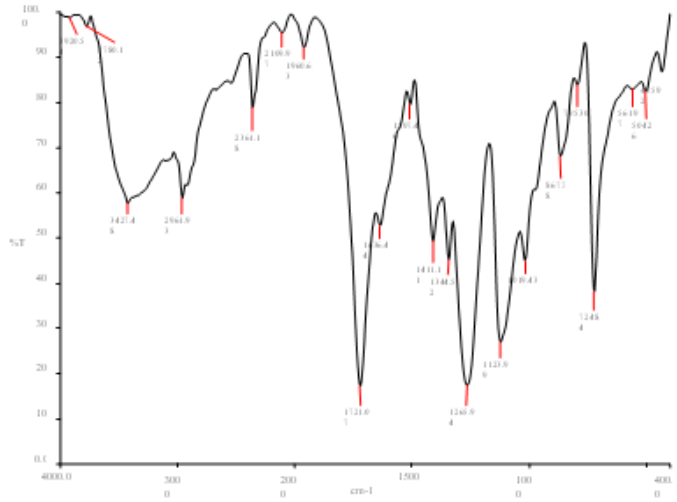

Fig 3. FTIR spectra of sewage buried PET powder under laboratory conditions

FTIR spectrum of untreated flakes is presented in fig-5. The absorption bands at 3431 cm^{-1}, 2357 cm^{-1} and 1729 cm^{-1} has been assigned to C=O bond stretching (Carbonyl group), 1631 cm^{-1} to C=C bond stretching (Benzene ring), 1459 cm^{-1} and 1379 cm^{-1}, 1073 cm^{-1} and 744 cm^{-1} to C-H bond stretching (

Methylene group),1938 cm^{-1} to C=C=C= bond stretching . On inoculation of PET flakes with soil under the field condition , appearance of new absorption peaks at 2930 cm^{-1} and 2869 cm^{-1} reveals C-H bond stretching (CH_2) ,2725 cm^{-1} and 2520 cm^{-1} has been assigned to C=O bond stretching (Carbonyl group) and 2118 cm^{-1} and 877 cm^{-1} to C=C bond stretching (Benzene ring) as evinced in the FTIR spectrum [fig-6].

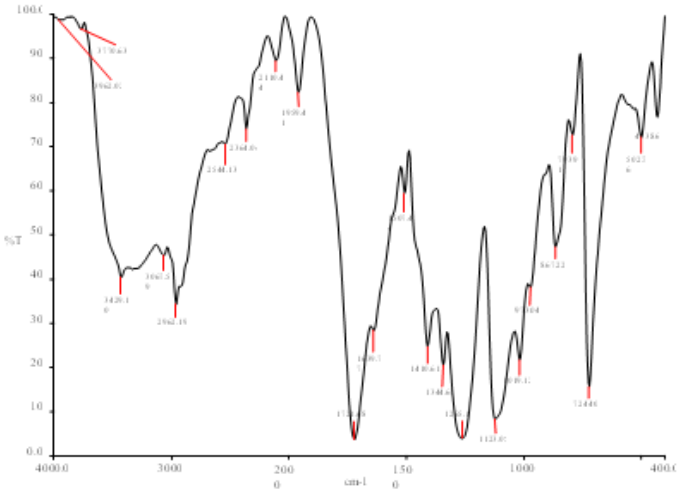

Fig 4. FTIR spectra of cowdung buried PET powder under laboratory conditions

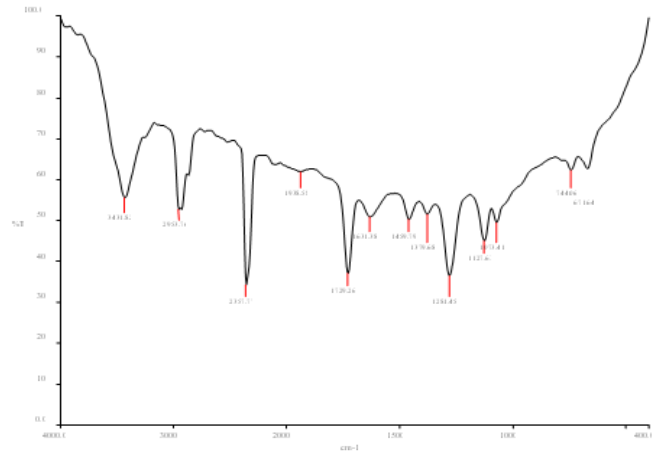

Fig 5. FTIR spectra of untreated PET flakes

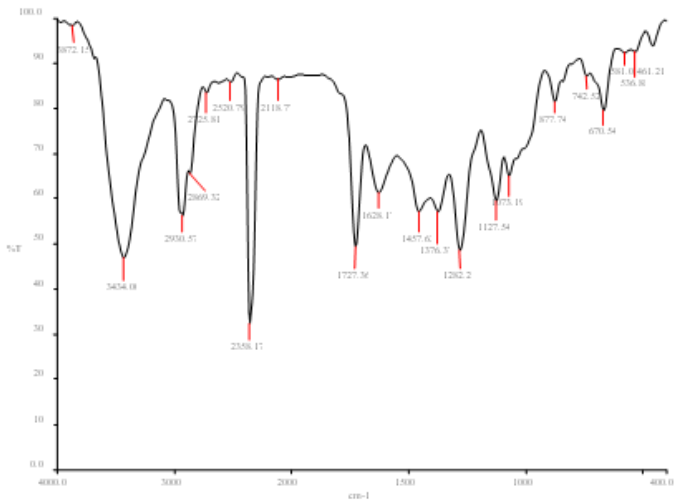

Fig 6. FTIR spectra of soil buried PET flake under field conditions

The FTIR spectrum of PET flakes on inoculation with sewage under the field condition is shown in fig -7. Absorption peaks at 2871 cm^{-1} , 966 cm^{-1} and 702 cm^{-1} has been assigned to C-H bond stretching, 2527 cm^{-1} to C=O bond stretching (carbonyl group) , 2103 cm^{-1} to C=C bond stretching (benzene ring).

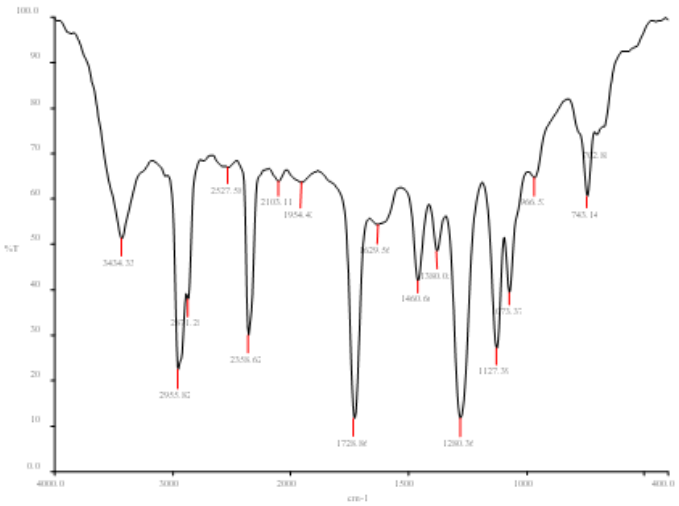

Fig 7. FTIR spectra of sewage buried PET flake under field conditions

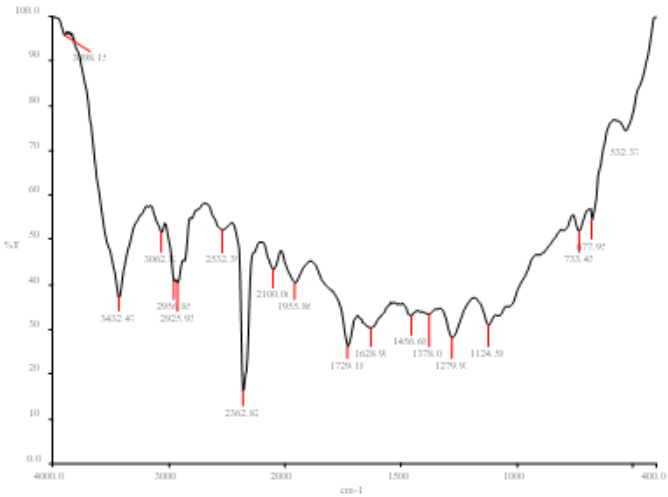

Fig 8. FTIR spectra of cow dung buried PET flake under field conditions

The FTIR spectrum of PET flakes [fig-8] after inoculation in the cow dung under the field condition shows a number of new group formation at peaks 3062 cm^{-1} and 2925 cm^{-1}, which has been attributed to C-H bond stretching (methylene group), 2532 cm^{-1} to C=C bond stretching (Benzene ring),733 cm^{-1} to C-H bond stretching. The FTIR spectrum of polystyrene foam powder is shown in fig-9. The absorption band at 3435 cm^{-1} reveals O-H bond stretching , 2919 cm^{-1} and 2854 cm^{-1} to C-H bond stretching, 2357 cm^{-1} to O-C-O bond stretching, 1873 cm^{-1} and 1804 cm^{-1} to C=O bond stretching (carbonyl group). Absorption peaks at 1668 cm^{-1} and 1596 cm^{-1} has been attributed to C=C bond stretching (Benzene ring) , 1488 cm^{-1}, 1446 cm^{-1}, 1366 cm^{-1} to C-H bond stretching (methylene group), 1064 cm^{-1} to C-O bond stretching ,1022 cm^{-1} cm^{-1},905 $cm^{-1}$and 754 cm^{-1} to C-H bond stretching (methyelene group), 844 cm^{-1} to C=C bond stretching (Benzene ring). It is inferred from fig -10 that polystyrene foam powder on inoculation with soil under laboratory condition elicited two characteristic absorption peaks at 1155 cm^{-1} which has been attributed to C-O bond stretching (formation of ester group), 689 to C=C bond stretching (Benzene ring).

FTIR spectrum of PS foam powder when buried in sewage under laboratory conditions for 30 days exhibited many different

absorption peaks at 2099 cm^{-1} and 1631 cm^{-1} which has been assigned to C=C bond stretching, 1453 cm^{-1} and 1282 cm^{-1} to C-H bond stretching, 1222 cm^{-1} to C-O bond stretching, 746 cm^{-1} to C-H bond stretching [fig- 11] .

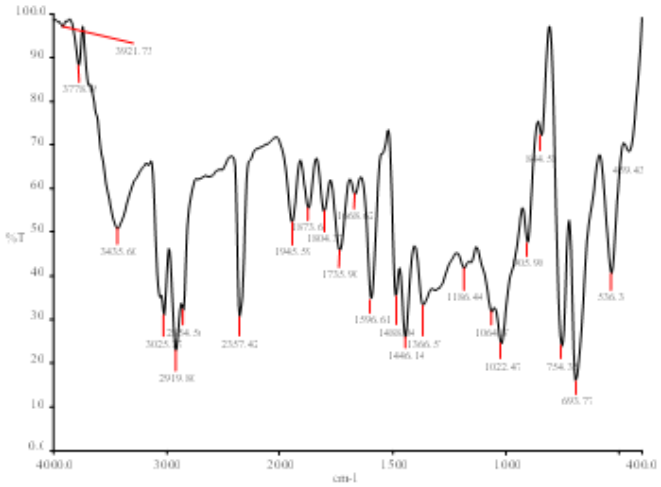

Fig 9. FTIR spectra of untreated PS foam powder

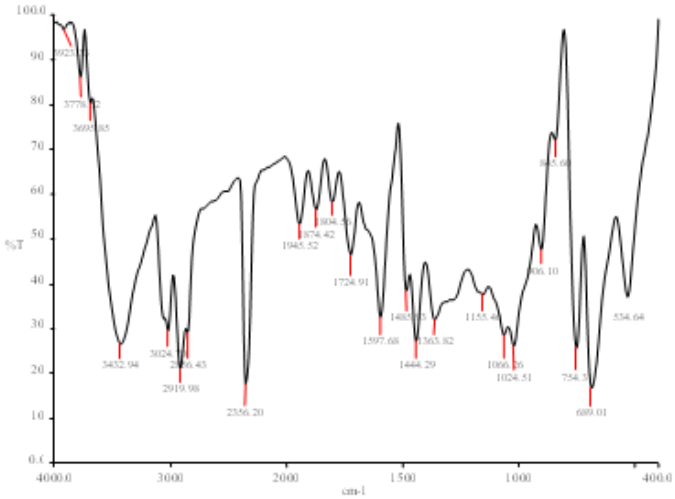

Fig 10. FTIR spectra of soil buried PS foam powder under laboratory conditions

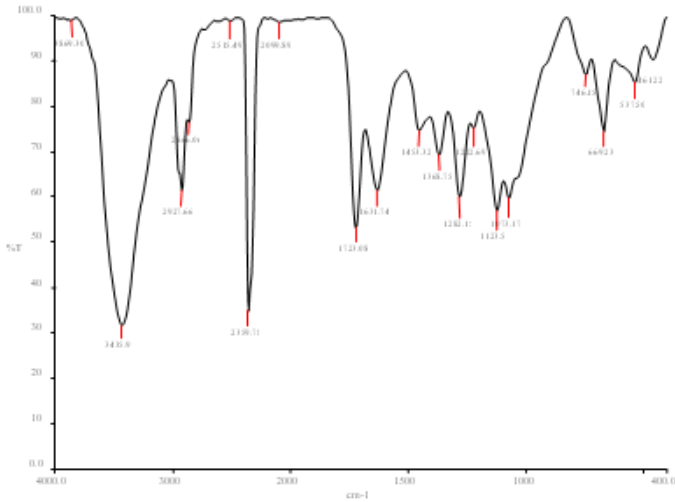

Fig 11. FTIR spectra of sewage buried PS foam powder under laboratory conditions

It is inferred from fig 12 that PS foam powder treated with cow dung under laboratory condition elicited four characteristic absorption peaks at 3698 cm^{-1}, which has been attributed to O-H bond starching, 2729 cm^{-1} to C=O bond stretching which indicates carbonyl group formation, 1597 to C=C bond stretching (Benzene ring) , 1275 cm^{-1}, to C-O bond stretching (ester group formation). The FTIR spectrum of untreated polystyrene foam flakes is shown in [fig -13]. The absorption bands at 3895 indicate O-H bond stretching, 3434 cm^{-1}, 2613 cm^{-1}, 2509 cm^{-1} and 1876 cm^{-1} has been attributed to C=O bond stretching (carbonyl group), 2351 to O-C-O bond stretching, 2095 cm^{-1} to C=C bond stretching, 2195 cm^{-1} to O-C-O bond stretching,1876 cm^{-1} to C=O bond stretching, 1800 cm^{-1}, and 1728 cm^{-1} to C=O bond stretching (carbonyl group) ,1607 cm^{-1} to C=C bond stretching (benzene ring),1447 cm^{-1},1369 cm^{-1},1023 cm^{-1},913 cm^{-1} and 756 cm^{-1}, has been assigned to C-H bond stretching. The structural differences revealed by FTIR spectrum of soil buried polystyrene foam flakes under field condition is presented in fig-14.

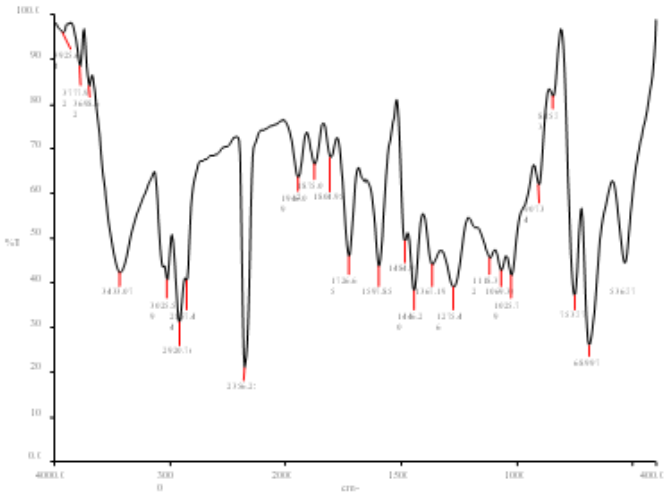

Fig 12. FTIR spectra of cow dung buried PS foam powder under laboratory

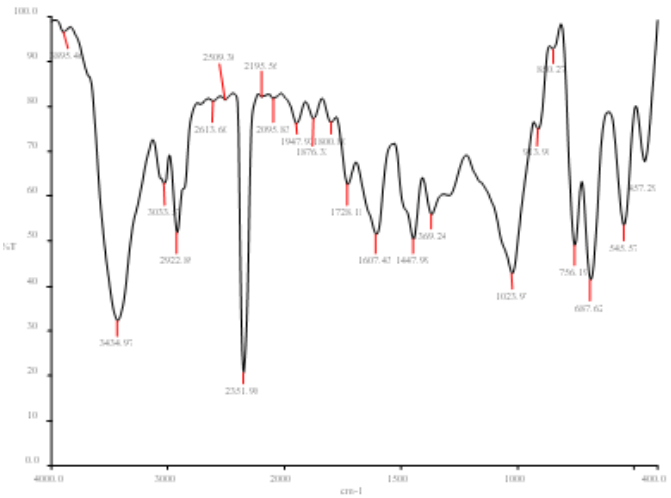

Fig 13. FTIR spectra of untreated PS foam flakes

In comparison to the FTIR spectrum of untreated polystyrene foam, appearance of new absorption peaks were evinced. Absorption intensity at 3630 cm^{-1} , 3551 cm^{-1},3433 cm^{-1},3337 cm^{-1}, and 3231 cm^{-1} has been assigned to O-H bond stretching. Absorption band at 2913 cm^{-1} has been assigned to C-H bond stretching, 2542 cm^{-1} to C=O bond stretching, 1578 cm^{-1} to C=C bond stretching ,1380 cm^{-1} to C-H bond stretching (formation of ester group), 1074 cm^{-1}, 795 cm^{-1}, and 734 cm^{-1}, to C-H bond stretching (methylene) . It can be seen from [fig-15]. that new absorption peaks appeared at 1595 cm^{-1} indicating C=C bond stretching (benzene ring). on inoculation of PS foam

flake in sewage under field condition Further, on PS foam burial with cow dung, appearance of two absorption frequencies were noticed at 2729 cm^{-1} and 1629 cm^{-1} which indicated C=C bond stretching (Benzene ring) [fig- 16].

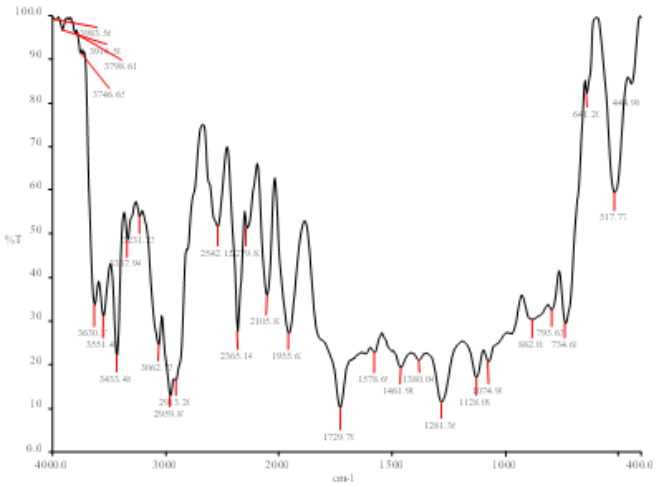

Fig 14. FTIR spectra of soil buried PS foam under field conditions

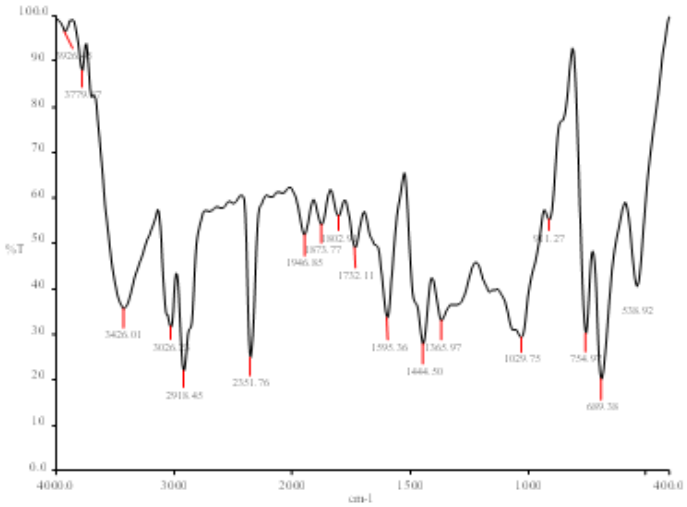

Fig 15. FTIR spectra of sewage buried PS foam flakes under field conditions

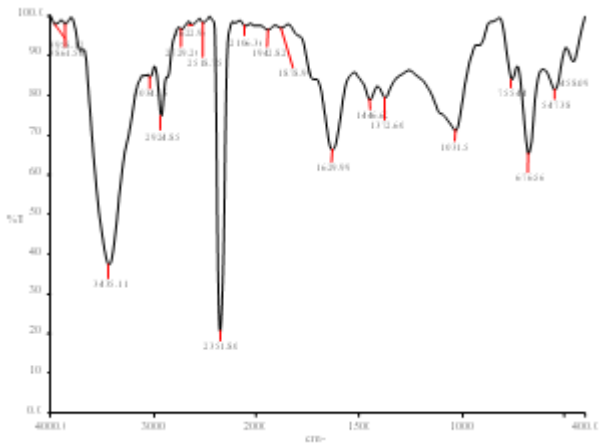

Fig 16. FTIR spectra of cow dung buried PS foam flakes under field conditions

Discussion

FTIR spectra of treated PS and PET buried in soil, cowdung and sewage indicate chemical changes. This observation coincides with Darby and Kaplan [14] who have reported that soil micro organisms can degrade polyester PU, whilst the closely related polymer polyether PU is more resistant to microbial attack. It has been shown that microbial communities are capable of utilizing diethlyene glycol terephthalate (DTP), a subunit of PET, as a sole carbon and energy source[15]. The present observation is well supported by Chonde Sonal [16] who have proved through FTIR study that fungi *Trametes versicolor* NCIM 1086 has the potential to degrade nylon 6. They have researched out *Trameters versicolor* NCIM mediated biodegradation of nylon 6 which has lead to the formation of new chemical groups such as CH_3, CHO, and COOH due to the process of hydrolysis and oxidation. Further, explained that this may be caused due to cleavage of C-C bond in H_2C-CH_2 adjacent to Nitrogen atom[22]. This observation is in parallel to the present finding that PET and PS foam degradation by fungi has occurred due to the cleavage of C-O , C-H, C=O, C=C, O-H bond stretching when buried in soil, cow dung and sewage as evident FTIR spectra[17,18].

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