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# FTIR Imaging of the Microplastics Found in the Water Collected from Malir and Thatta Rivers, Sindh, Pakistan

Muneeza Salman & Tehseen Ahmed
Department of Chemistry, University of Karachi, Karachi, Pakistan
**Corresponding Author email**: tahmed@uok.edu.pk

**Abstract**

FTIR imaging was conducted on the water of two important rivers of Sindh, Pakistan, namely Malir and Thatta. The study aims to evaluate the presence of polymer microplastics (MPs) on the surface of the water in these rivers of Sindh. The collected water was transported to the Department of Chemistry at the University of Karachi for analysis of microplastics using the oxidation method and Fourier Transform Infrared (FTIR) analysis. The results of FTIR spectroscopy, an analytical technique frequently used to detect microplastics, confirm their presence. Results showed dissimilar characteristics for both rivers, except for the 1635–1650 (amide I) and ~1530–1550 (amide II) regions, which are characteristic of polyamides (Nylon), were common. The bands at 2924 & 1460 cm$^{-1}$, which are associated with the intense aliphatic C–H stretch and $CH_2$ scissoring, are commonly observed in many plastics, including PP, PE, PA, PVC, and PVDF. Analysis revealed that PEHD and PTFE were the primary microplastics reported in the rivers, characterized by peaks at 2924 cm$^{-1}$ (PEHD) and 605 cm$^{-1}$ (PTFE). It was suggested that rivers contain MPs that require attention to prevent the dumping of various types of waste into river water.

**Keywords**: River water, FTIR, Microplastic, Nylon

## 1. Introduction

Plastic polymers are large synthetic molecules composed of repeating units of hydrocarbons, which are durable, lightweight, and resistant to degradation, making them widely used in packaging, textiles, and numerous other products [1,2]. However, their persistence leads to environmental accumulation, during which plastics break down into micro- and nanoplastics [2]. These particles can be ingested or inhaled by living organisms, causing physical harm, chemical toxicity, endocrine disruption, and bioaccumulation in food chains, ultimately threatening ecosystems and human health [3]. In 2010, an estimated 4.8 to 12.7 million metric tons (MMT) of plastic entered the world's oceans, with a commonly cited midpoint of approximately 8 MMT. The fact that polyethylene (PE) is the most widely produced and used polymer type in the world is one of the reasons why PE MPs are abundant in marine waters [4-9].

FT-IR spectroscopy uses the interaction of infrared (IR) light with materials to identify their chemical composition, making it particularly effective for characterizing the polymers found in microplastics. Microplastics are plastic particles smaller than 5 millimeters in size [9-12]. They originate either from the direct production of small plastic pellets (primary microplastics, e.g., microbeads in cosmetics) or from the breakdown of larger plastic debris through weathering, UV radiation, abrasion, and degradation (secondary microplastics). They may influence microbial communities, interfere with nutrient cycling, and contribute to long-term ecological imbalance. The detection, extraction, and identification of microplastics is essential to establish the presence and effect of MPs. For this purpose, Fourier Transform Infrared Spectroscopy (FTIR) is an influential analytical technique for detecting constituents by examining Infrared Absorption Spectra (IAS) [13-18]. The method has been used in microplastic identification since the turn of the century. Some essential properties of the marine samples were determined using FTIR and Scanning Electron Microscopy (SEM). It was discovered that FTIR is a valuable tool for identifying and characterizing microplastics and differentiating between polymers. Since then, FTIR has become one of the most commonly used techniques for detecting microplastics in environmental samples. Yang et al. [19] reported that µ-FTIR spectroscopy proved effective and reliable for detecting microplastics and can be applied to assess the removal efficiency of conventional and membrane treatment processes across different water treatment plants [19].

Shim et al. reported [20] that among the present analytical methods, micro-Fourier Transform Infrared (µ-FTIR) spectroscopy is an advanced technique for analyzing MPs, as it is a non-destructive method that can produce infrared absorption spectra for both thick and opaque materials. Generally, sample pretreatment is necessary to prevent the setup of microplastics by organic and inorganic materials and to facilitate their precise identification after digestion. The standard digestion protocols include oxidation, alkaline or acidic treatment, and enzymatic degradation [21,22]. Fenton reagent and $H_2O_2$ are the most used chemicals for oxidative digestion, which have no or very few effects on microplastic properties [23]. According to Prata et al. [24], 95% of 20 sediment studies used $H_2O_2$ and/or Fenton reagent for digestion, and more than 60% of 20 studies of water samples (mainly seawater and freshwater) used $H_2O_2$ for digestion. Enzymatic digestion is a rapid reaction for the complete degradation of organics, although it is considered an expensive, complex, and sometimes destructive method for MP extraction. The rivers in the Malir and Thatta region likely receive microplastics and other waste from various land-based sources, including urban wastewater, storm runoff carrying plastic litter, industrial discharges, and agricultural activities. The decomposition of larger plastic waste, the shedding of microfibers from synthetic textiles during washing, and waste from poorly managed landfills also contribute significantly to the pollution of these river systems. This preliminary study, conducted in the rivers of Sindh, Pakistan, aims to address the persistent problem in these river regions, which ultimately flow into the Arabian Sea. This study examines microplastics, opening the door for future studies to investigate their origin, abundance, and distribution in the region's running streams and marine food.

## 2.0. Materials and Methods

### 2.1 Sampling sites

The two sampling sites, Malir and the Thatta River (Fig. 1), were selected to investigate microplastics in these water bodies. The Malir River is a seasonal river located in Karachi, Sindh, Pakistan. It passes through the city of Karachi from the northeast, through the center, and drains into the Arabian Sea [25]. The " Thatta River" refers to the Indus River as it flows near and through the historic city of Thatta, Pakistan [26].


**Figure (1): Location of Rivers in Sindh, Pakistan Region**

### 2.1. Sampling

Three sampling areas of both rivers namely the Malir and Thatta River were selected for collecting samples of surface water in 1000 mL bottles dated May 4th to 7th, 2024 for the extraction of microplastics, The bottles were coated with PTFE, a hydrophobic, inert material, also known as Polytetrafluoroethylene, a synthetic, non-stick polymer famous for its high chemical resistance, low friction, and excellent heat resistance. The samples were transported to the Department of Chemistry at the University of Karachi for analysis (Fig. 2). Aquatic life and sediments were not analysed in the first phase of sampling to assess the impact of MPs on running streams.

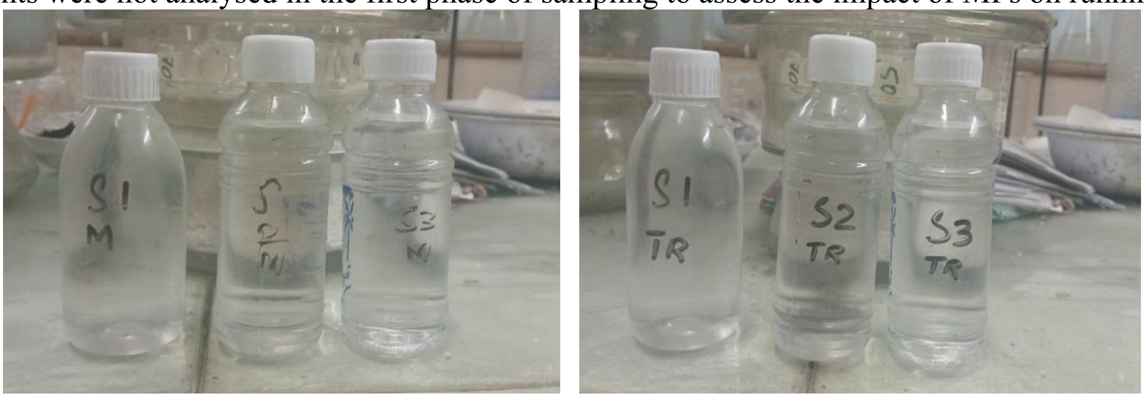


**Figure (2): The collected water sample from the rivers in Sindh, Pakistan Region**

### 2.2. Sample Preparation and FTIR analysis

All glassware was washed in triplicate with distilled water before use to analyze the samples, then covered to prevent airborne contamination. The pretreatment of the collected water was conducted by oxidation of the collected water through the use of 30% Hydrogen peroxide to remove the biological or organic contaminants, and kept in the dark for 24 hr, as they may aggregate on the surface of the water due to the hydrophobic nature of the microplastic, followed by sieving and flushing with ethanol before evaporation of the ethanol [12,27].

The final concentrated plastic particle samples were suspended in ethanol, and samples with particle sizes greater than 80 µm were deposited onto an infrared-reflective glass slide (MirrIR, Kevley Technologies) for reflection-mode FTIR imaging analysis. Particles < 80 µm were deposited onto a Calcium Fluoride ($CaF_2$) infrared-transparent window, which was then dried for subsequent analysis in transmission mode. This left the microplastic particles adhered to the slide, ready for analysis via FTIR imaging to identify and quantify microplastics in the samples. A Fourier Transform Infrared (FTIR) imaging system was used, with a spectral range of 4000–500 cm$^{-1}$, a collection time of 3 sec, and 16 co-scans per measurement in reflection mode. All obtained spectra were compared with the FTIR spectrum database to verify polymer type [28]. We considered FTIR spectra matches against spectrum standards acceptable at 70% [27].

**3.0. Results and Discussion**

The research employs Fourier Transform Infrared Spectroscopy (FTIR) as an analytical technique, providing graphical representations (Fig. 3 & 4) and a compilation of identified compounds in the water samples in the range of 3500-400 cm$^{-1}$ (Table 1-3) to ascertain the precise type of microplastic (MPs) [28-35]. The key bands identified in FTIR imaging analysis of water collected from two rivers (Malir and Thatta) indicated the presence of microplastics. The microplastics that were identified by several bends positioned at a weak band near 3460.30 cm$^{-1}$ (Thatta) 3500 cm$^{-1}$ (Malir) also correspond to N–H/O–H [26], while Nylon typically exhibits an N–H stretch in the range of 3300–3350 cm$^{-1}$, which is often weak/broadened when hydrated or at low concentration (Table 1&2). The band approximately ~3460 cm$^{-1}$ could be interpreted as broad bands of O–H stretching vibrations of carboxylic acid polymers, like polystyrene (PS) [29], while the band at 2924 cm$^{-1}$ (Thatta) & 2931 cm$^{-1}$ (Malir) showed aliphatic C–H (asymmetric) & asymmetric 1460 cm$^{-1}$, which are linked to the intense aliphatic C–H stretch and $CH_2$ scissoring, commonly found in many plastics, including polypropylene (PP), polyethene (PE), polyamide (PA), ploy vinyl chloride (PVC), and Polyvinylidene Fluoride (PVDF) [30]. Analysis revealed that Polyethylene high density (PEHD) and Polytetrafluoroethylene (PTFE) were the primary microplastics reported in the rivers, characterized by peaks at 2924 cm$^{-1}$ (PEHD) and 605 cm$^{-1}$ (PTFE). The absence of complex functional groups and a simplified $CH_2$ pattern between 2900 and 3000 cm$^{-1}$ is observed, with asymmetric stretches at 2915 cm$^{-1}$ and symmetric stretches at 2848 cm$^{-1}$, characteristic of polyvinyl chloride (PVC). The wave numbers 1535 & 1639 cm$^{-1}$ are distinguished as a pair, specifically 1635–1650 cm$^{-1}$ (amide I) and ~1530–1550 cm$^{-1}$ (amide II), which are characteristic of polyamides (Nylon) or could be interpreted as C-H bending vibrations of aromatic compounds [31]. The peak at 1111 cm$^{-1}$ is a strong band that could be a C–F stretch (suggesting a fluoropolymer such as PVDF) or an overlapping C–O or skeletal band from other polymers or additives [32]. Given the presence of aliphatic C–H at 2924 cm$^{-1}$, PTFE, which lacks C–H, is unlikely. PVDF remains a possibility, as it exhibits strong bands in the 1111.00 cm$^{-1}$ (Thatta) and 1107.14 cm$^{-1}$ (Malir) (1170–1070 cm$^{-1}$) regions. The peak at 605.7 cm$^{-1}$ (Malir), typical for C–Cl (PVC) or aromatic C–H out-of-plane bends, is not definitive on its own, but it keeps PVC in the conversation. The spectral analysis revealed a water contribution in the wastewater, which appeared at the band, and can partly include H–O–H bending (adsorbed water), if drying reduces 1639 (Malir) & 1645.28 cm$^{-1}$ (Thatta), while 1535 cm$^{-1}$ (Thatta) and 1531.48 cm$^{-1}$ stay, which favors amide (Nylon). C–F bonds typically appear in the region 1000–1400 cm$^{-1}$**.** Asymmetric stretching modes are usually found near 1100–1300 cm$^{-1}$, often giving strong, sharp peaks because the C–F bond has a significant dipole moment. Therefore, a strong absorption at 1111 cm$^{-1}$ (Malir) and 1107.14 cm$^{-1}$ (Thatta) is consistent with C–F asymmetric stretching**.** C–F bonds typically appear in the region 1000–1400 cm$^{-1}$. The spectrum most strongly suggests Nylon (polyamide)**,** with PVDF and PVC as secondary possibilities. The spectrum exhibits C-Cl bond vibrations with an intense band in the region of 605 cm$^{-1}$ (Malir) and 586 cm$^{-1}$ (Thatta ) **(**600 to 700 cm$^{-1}$), forming two peaks. The FTIR analysis of surface water from both rivers detected MPs, which may affect the survival of marine life, pose potential health risks to these organisms, and affect the use of these fish by humans.

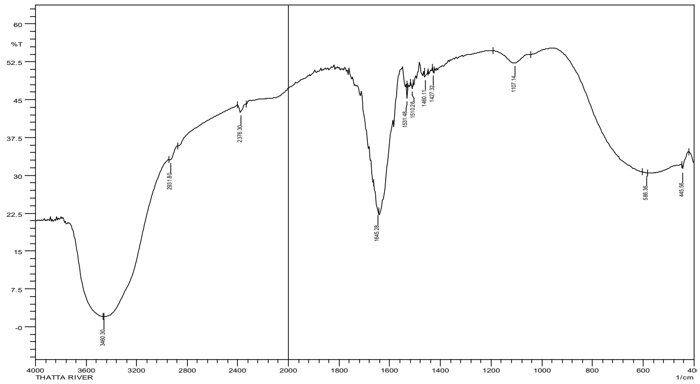


**Figure (3): FTIR Spectral Analysis of the water collected from the Thatta River**

**Table 1: Interpretation of FTIR Spectra of Thatta River**

Sample Collection Date: 04-May-2023.

Sample Description: Sample of water from the Thatta River.

Site coordinates: 24.82364 and 67.09245

| Peak | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area |
|---|---|---|---|---|---|---|
| 445.56 | 31.10 | 1.23 | 447.49 | 420.48 | 12.95 | 0.08 |
| 586.36 | 30.48 | 0.03 | 603.72 | 584.43 | 9.93 | 0.01 |
| 1107.14 | 52.23 | 2.04 | 1192.01 | 1045.42 | 39.86 | 1.02 |
| 1427.32 | 50.38 | 0.67 | 1431.18 | 1425.40 | 1.70 | 0.02 |
| 1460.11 | 49.47 | 1.12 | 1463.97 | 1450.47 | 4.07 | 0.07 |
| 1510.26 | 47.12 | 1.26 | 1517.98 | 1506.41 | 3.71 | 0.06 |
| 1531.48 | 45.21 | 2.73 | 1533.41 | 1527.62 | 1.91 | 0.06 |
| 1645.28 | 22.68 | 0.84 | 1662.64 | 1643.35 | 11.68 | 0.26 |
| 2376.30 | 42.43 | 1.62 | 2401.38 | 2335.80 | 23.77 | 0.42 |
| 2931.80 | 33.08 | 0.53 | 2943.37 | 2872.01 | 33.17 | 0.19 |
| 3460.30 | 2.01 | 0.01 | 3462.22 | 3458.37 | 6.54 | 0.00 |

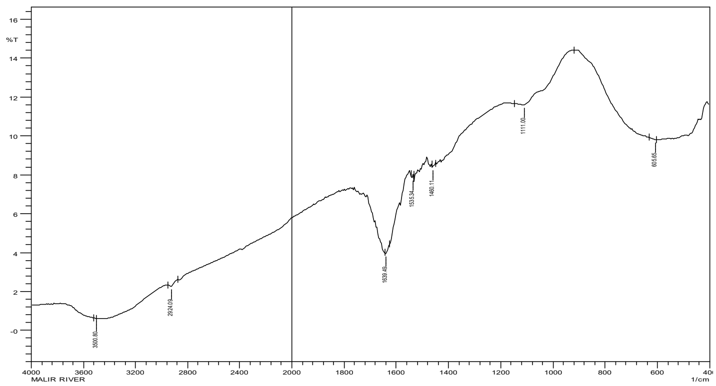


**Figure (4): FTIR Spectral Analysis of the water collected from the Malir River**

**Table 2: Interpretation of FTIR Spectra of Malir RIVER**

Sample Collection Date: 04-May-2023.

Sample Description: Wastewater-Malir River.

Sampling Site coordinates: 24.82364 and 67.09245

| Peak | Intensity | Corr..Intensity | Base (H) | Base (L) | Area | Corr.Area |
|---|---|---|---|---|---|---|
| 605.65 | 9.810 | 0.012 | 632.65 | 603.72 | 29.110 | 0.022 |
| 1111.00 | 11.605 | 0.507 | 1147.65 | 920.05 | 204.032 | 2.140 |
| 1460.11 | 8.399 | 0.173 | 1463.97 | 1450.47 | 14.470 | 0.068 |
| 1535.34 | 7.841 | 0.182 | 1543.05 | 1533.41 | 10.635 | 0.072 |
| 1639.49 | 3.950 | 0.167 | 1643.35 | 1625.99 | 24.079 | 0.226 |
| 2924.09 | 2.273 | 0.161 | 2949.16 | 2873.94 | 121.746 | 0.926 |
| 3500.80 | 0.622 | 0.003 | 3518.16 | 3498.87 | 42.422 | 0.047 |

Results revealed a particular Nylon variant that is frequently observed in both rivers, which may be due to the dumping of synthetic clothing and Nylon floating net cages in the vicinity. The degradation of nylon nets can be attributed to numerous environmental influences, including light intensity, temperature, and the presence of moss on the net [33-37]. The results of the present investigation are similar to those of previous studies, which have found that the most frequent forms of MPs in sediment and water are fibers, Nylon, polymer fragments, and films. They also reported that polyethylene (PE) and polyethylene terephthalate (PET) are the most recurrent polymer types[26,31,35] (Table 3). The following summarizes how hydrodynamics affect the retention of MPs in rivers.

**Table 3: Comparative Analysis of Microplastics Found in Malir and Thatta Rivers, Sindh, Pakistan.**

| Microplastic Polymer | Wavelengths ($cm^{-1}$) | | | Band Information |
|---|---|---|---|---|
| | Malir River | Thatta River | Reference Value ($cm^{-1}$) | |
| Polymer PE, PP, PA, PVC, PTFE, PEHD and Nylon (All Polyamide) PVC | 3500.80 | 3460 | 3500 [26] | N–H/O–H,( nylon) |
| | 2924 | 2931.80 | 2800-3000 [28] | O–H stretching/ Amine salt/Asymmetric stretching of –$CH_2$ groups |
| | 2924 | 2931.80 | ~2930 [28] | N–H stretching/ Asymmetric $CH_2$ stretching |
| | | 2376.30 | ~2200-2400 [35] | C≡N (nitrile), C≡C (alkyne), or C=N=O (isocyanate) O=C=O |
| | 1639 | | ~1635–1650 [31] | amide I polyamides (Nylon)/ C-H bending vibrations of aromatic compounds |
| | 1535.34 | 1510.26 | ~1530–1550 [31] | amide (Nylon)N-O stretching/(amide II) |
| | | 1460.11 | 1451-1492 [31] | aliphatic C–H stretch $CH_2$ bending /cellulose |
| | 1460.11 | 1427.32 | | |
| | 605.65 | 586.36 | 515-690 [33] | C–Cl (PVC) or aromatic C–H/ C–Br stretch/ (PTFE) |
| | | 445.56 | 400–500 [34] | M–O stretches |
| | 2924.09 | 2931.80 | 2932 | CH stretching/ (PEHD) |
| | 1639.49 | | 2000-1500 [35] | C=O stretching and C=C (alkene and aromatic) stretching vibrations |
| | 1460.11 | 1645.28 | 1650–1850 [35] | Aromatic rings stretching |
| | 1111.00 | 1107.14 | 1000–1400 [31] | C–F asymmetric stretching. C–F bonds |

## 4.0 Conclusion

The FTIR analysis of water collected from both rivers, Malir and Thatta, revealed the presence of microplastics, specifically Nylon, necessitating a multi-sectoral approach that involves public policies and community participation to address the entry and persistence of microplastics in the Rivers of Sindh. Based on the observed results, it is concluded that there is extensive contamination of microplastics in both river water, necessitating new research lines and further studies that examine the sources of MP emissions to accompany the present research. The observed phenomenon can be attributed to the increased diversity of plastic sources entering the river, which includes a collection of upstream debris. Ongoing monitoring and investigation into the origins of these microplastics can yield valuable insights for environmental conservation and policy development.

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**Author's Contribution:** Dr. Tehseen Ahmed wrote the article and supervised the research project, and Muneeza Salman conducted the research and helped in writing the article

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