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IDENTIFICATION AND CHARACTERIZATION OF PLASTIC PARTICLES FOUND IN THE LOWER DANUBE RIVER

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Abstract

Excessive production and use of plastic materials, followed by the mismanagement of plastic waste have favoured the increase of plastic particles occurrence in aquatic ecosystems. Ingestion of plastic fragments (especially micro- and nanoplastics) by aquatic fauna can lead to various diseases and disorders, which is why monitoring of plastics presence in the aquatic environment is vital. To identify the presence of plastic particles in environmental samples, several methods such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, microscopy, thermal extraction desorption–gas chromatography–mass spectrometry and pyrolysis–gas chromatography–mass spectrometry have been applied in the literature. In the present paper, attenuated total reflectance - FTIR spectroscopy was used to identify and characterize plastics debris found in the Lower Danube water, near the Galati City. Plastic particles collected had different shapes (i.e fragments, films, granules) and colours (blue, red, colourless). Based on infrared spectra obtained, polyethylene (PE) and polypropylene (PP) were the main polymers identified in the collected samples.

Key words*: plastic particles, FTIR spectroscopy, Lower Danube water, polyethylene, polypropylene.*

INTRODUCTION

According to the Plastics - the Facts 2021 report, annual global plastics production increased in recent years from 335 Mt (year 2016) to 367 Mt (year 2020) (Plastics Europe, 2021).

Irrational use of plastics and inadequate waste management has led the occurrence of plastic fragments in the environment (Zhang et al., 2021).

Plastics debris were found in soil, aquatic ecosystems (ocean, sea, lakes and rivers), air and biota (Ahmed et al., 2021).

The importance of monitoring plastic fragments (especially micro- and nanoplastics) in aquatic ecosystems is due to the fact that they can have toxic effects (e.g. tumor, growth inhibition, reproductive disorder, reduced survival rate, liver damage, eating disorder, inflammation) on the biota from long-term exposure (Ha and Yeo, 2018).

To assess the presence of plastics in aquatic ecosystems it is essential to identify them and characterize their chemical composition (e.g. polymer types) in order to know their origin and other information about the production process (Campanale et al., 2020).

Thermoanalytical (e.g. thermal extraction desorption coupled with gas chromatography–mass spectrometry and pyrolysis–gas chromatography coupled with mass spectrometry) and spectroscopic or spectroscopic coupled with microscopy (e.g. Fourier transform infrared spectroscopy - FTIR and Raman) methods have been used in the research literature for the identification and chemical characterization of plastic particles in environmental samples (Campanale et al., 2020).

The most used methods are the spectroscopic ones due to the fact that their main advantage is that they are non-destructive and allow the comparison of the obtained results with other instruments (Xu et al., 2019). Attenuated total reflectance (ATR) - FTIR spectroscopy is usually applied for identification of visible plastic debris (meso and macroplastics), while for microplastics analysis micro- FTIR is used (Chen et al., 2020). In this context, the main objective of this paper is to apply the ATR - FTIR spectroscopy method to confirm plastics and identify the types of polymers in the composition of visible plastic fragments taken from the lower Danube water.

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MATERIALS AND METHODS

A net with 125 µm mesh was used to collect the plastic fragments from the Lower Danube water (Figure 1). The sample was taken from the sampling station located at the confluence of the Siret river with the Danube river, near Galati City - Romania (Figure 2). The sampling area was chosen strategically because this sector of the Danube represents the transport route of pollutants to the Danube Delta Biosphere Reserve (Calmuc et al., 2020).

Figure 1. Sampling of plastic particles from the Danube water

Figure 2. Location of the sampling station

In order to separate the plastic fragments from the other collected impurities (organic matter, sediments, etc.) the sample was transported to the laboratory and processed. To remove organic matter, the sample was digested with a mixture (1:1, 30 ml) of KOH 10M and H_2O_2 30% for 5 days. After digestion, the sample was neutralized with 11.67 mL formic acid (Pojar et al., 2021). Plastic debris were separated from the sediment and other impurities in a separation funnel with zinc chloride ($ZnCl_2$) 60-70% to obtain a final density of about 1.6-1.8 g/mL (Stock et al., 2019). After separation, the plastics were filtered on a quantitative filter paper with a pore size of 10 µm (Figure. 3). Plastic particles collected were analysed with ATR-FTIR spectrophotometer Bruker ALPHA (Bruker Optik GmbH, Ettlingen, Germany), (Figure 4).

Figure 3. Plastics separation

Figure 4. Analysis of plastics with ATR-FTIR

RESULTS AND DISCUSSIONS

Different types of plastic fragments were collected from the Danube water in the sampling station located near the city of Galati. Figure 5 represents a picture with plastic fragments of different shapes and colours. Based on visual observation, the collected plastics are classified according to shape into films (6 particles indicated with red arrows), fragments (3 indicated with blue arrows) and a single granule (yellow arrow). Mostly film-type plastics were sampled (60%) (Figure 6). The colours found were red, blue and colourless.

In order to confirm the plastics and identify the type of specific polymers, each particle was analysed using ATR-FTIR spectroscopy method. This method is based on the molecular vibration of the sample after IR irradiation and obtaining information on specific bonds of plastics. To identify the type of polymer, the IR spectrum obtained is compared with the reference spectra (Käppler et al., 2016).

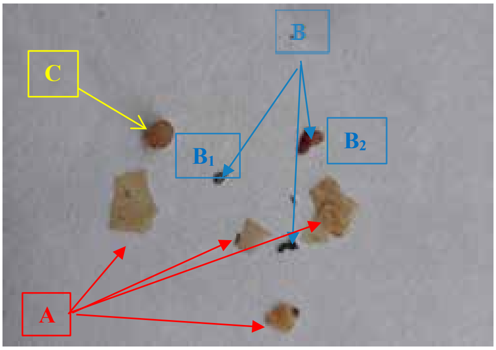

Figure 5. Visual observation of plastic particles collected from Danube water

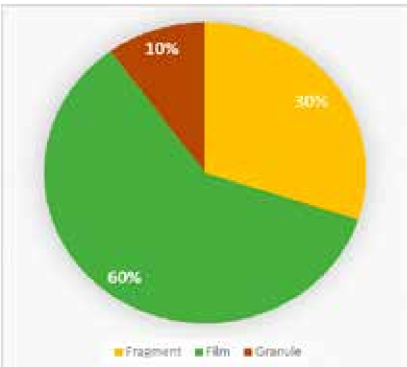

Figure 6. Types of plastic particles collected

Figures 7 and 10 show the IR reference spectra of the polyethylene and polypropylene polymers ("FTIR Polymers Spectra".). Figure 8 illustrates the IR spectrum obtained from the analysis of type A - particles (which had similar spectra). Results show significant peaks at 2915 and 2848 cm^{-1} that correspond to the C-H stretching (Syakti et al., 2018), an intense peak at 1030 cm^{-1} corresponding to -H-C-H- twisting and wagging. A medium band was observed at 717 cm^{-1} related to stretching CH_2-CH_2 network and at 1457 cm^{-1} for CH_2 bending (Suardy et al., 2020). Based on this information, the particle A were confirmed as polyethylene (PE).

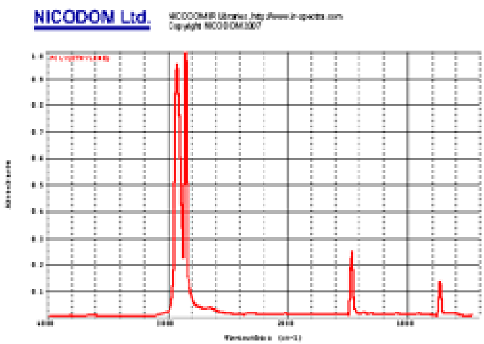

Figure 7. IR reference spectra of polyethylene

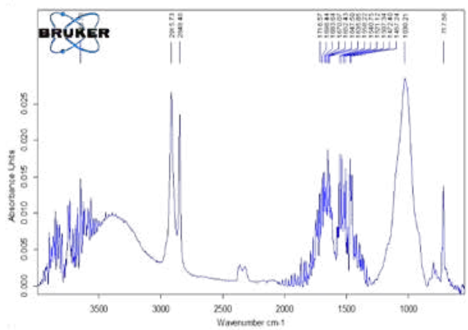

Figure 8. IR spectrum of the plastic particles A

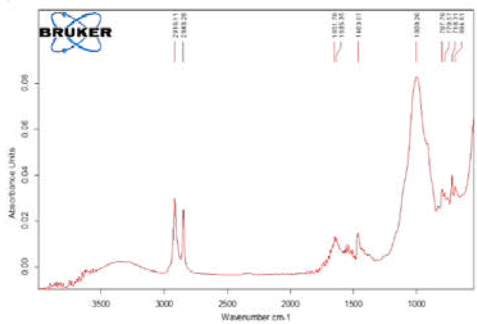

Figure 9. IR spectrum of the plastic particle C

A similar spectrum was observed for particle C (Figure 9), a medium peak in fingerprint regions at 2916 and 2848 cm^{-1} and a strong absorption band at 1000 cm^{-1} were noticed.

IR spectra for B_1 and B_2 particles represented in Figures 11 and 12 confirm the presence of the polypropylene polymer (PP) in the composition of these two analysed fragments. This result is due to the presence of CH_3 stretching peaks at 2950 cm^{-1} for B_1, respectively 2950 cm^{-1} and 2867 cm^{-1} for B_2.

Furthermore, absorption band for CH_2 stretching also was observed at 2919 cm^{-1} for B_1, respectively 2918 cm^{-1} and 2839 cm^{-1} for B_2.

Table 1 summarizes the main sources of the most common polymers in the environment (Li, 2018). Bags and bottles are the main sources of polyethylene plastic particles, while the most common sources of polypropylene are bottle caps, drinking straws, yogurt containers and. tanks.

Table 2 shows reference peaks for polyethylene & polypropylene and observed IR peaks that confirmed the type of polymer in the composition of particles A, B_1, B_2 and C.

Table 1. Origin of the plastic fragments found in the environment (Li, 2018)

Type of polymer	Origin
Polyester (PES)	Fibers and textiles
Polyethylene terephthalate (PET)	Drinks bottles, jars, plastic film, tubes, pipes, insulation
Polyethylene (PE)	Bags, plastic bottles
High-density polyethylene (HDPE)	Detergent and milk bottles, tubes, pipes, insulation
Low-density polyethylene (LDPE)	Outdoor furniture, floor tiles, films
Polypropylene (PP)	Bottle caps, drinking straws, yogurt containers, tanks
Polystyrene (PS)	Packaging foam, containers, plastic tableware, CD, cassette
Polyvinyl chloride (PVC)	Plumbing pipes, window, frames, flooring, films
High-impact polystyrene (HIPS)	Refrigerator liners, packaging, cups, electronics
Polyamides (PA) (nylons)	Fibers, toothbrush bristles, fishing line, films for food packaging
Acrylonitrile butadiene styrene (ABS)	Electronic equipment cases, pipes, bumper bars
Polycarbonate (PC)	Compact disks, eyeglasses, security windows, traffic lights, lenses, construction materials

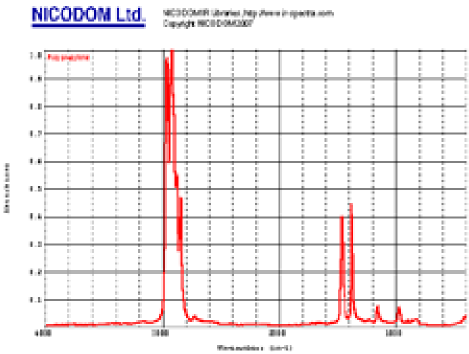

Figure 10. IR reference spectra of polypropylene

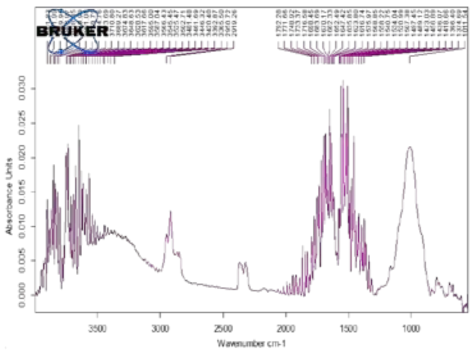

Figure 11. IR spectrum of the plastic particle B_1

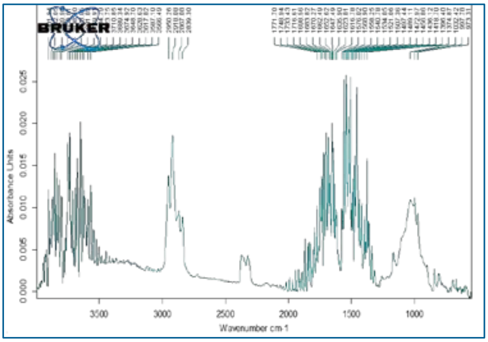

Figure 12. IR spectrum of the plastic particle B_2

Table 2. IR peaks for particles A, B1, B2, C comparison with reference peak for PE and PP

Functional group	Reference peak PE (cm^{-1}) (Suardy et al., 2020)	Reference peak PP (cm^{-1}) (Smith, 2021)	Particle A peak (cm^{-1})	Particle B_1 peak (cm^{-1})	Particle B_2 peak (cm^{-1})	Particle C peak (cm^{-1})
C-H sp^3 stretching	2911 and 2845	-	2915 and 2848	-	-	2916 and 2848
Stretching H-C-H deformation	1144	-	1030	-	-	1000
CH_2 bending	1460	-	1457	-	-	1463
Stretching CH_2 -CH_2 network	715	-	717	-	-	-
CH_3 asymmetric and symmetric stretches	-	2956 and 2875	-	2950	2950 and 2867	-
CH_2 asymmetric and symmetric stretches	-	2921 and 2840	-	2919	2918 and 2939	-

CONCLUSIONS

Plastic debris of different shapes (fragments, films, granule) and colours (blue, red, colourless) were collected from Lower Danube water. Film-type particles were mostly found (60%).

After the plastic particles were separated and isolated from the impurities, they were analysed using ATR-FTIR spectroscopy method.

Based on the obtained IR spectra, typical absorption peaks were observed that confirmed the presence of polyethylene (PE) and polypropylene (PP) polymers in the composition of the analysed plastic particles. Most of the plastic debris analysed were of the polyethylene type.

The results of this study demonstrated that the ATR-FTIR spectroscopy method is suitable for the identification and chemical characterization of visible plastics particles found in the Lower Danube water.

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