Perspectives on micro-plastics detection in biowaste *via* ATR-FTIR spectroscopy

V. M. Vana[1], C. Panagiotopoulos[1], D. Christianides[2], A. Mytara[1], E.M. Barampouti[2], S. Mai[2], S. Vouyiouka[1]*

[1]Laboratory of Polymer Technology, School of Chemical Engineering, Zographou Campus, National Technical University of Athens, 15772 Athens, Greece
[2]Unit of Environmental Science & Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, 9 Heroon Polytechniou Street, 15780 Athens, Greece

Corresponding author: mvuyiuka@central.ntua.gr

Keywords: micro-plastics, ATR-FTIR spectroscopy, bio-waste

Introduction

Plastic production and usage has reported a considerable expansion in recent years, especially regarding food packaging. For the most part, plastic waste is incinerated or subjected to landfilling, but huge production rates and inadequate waste management have caused a high accumulation of their fragments. These polymeric contaminants, commonly in the form of macro-, micro- (MPs) and nano-particles (NPs), are present in all environmental compartments including water, atmosphere, soil and foodstuff. In recent years, many studies have examined their presence, distribution and impact in marine environments, however, up to now, there is insufficient research for land-based sources of MPs and the lack of evaluation methods.

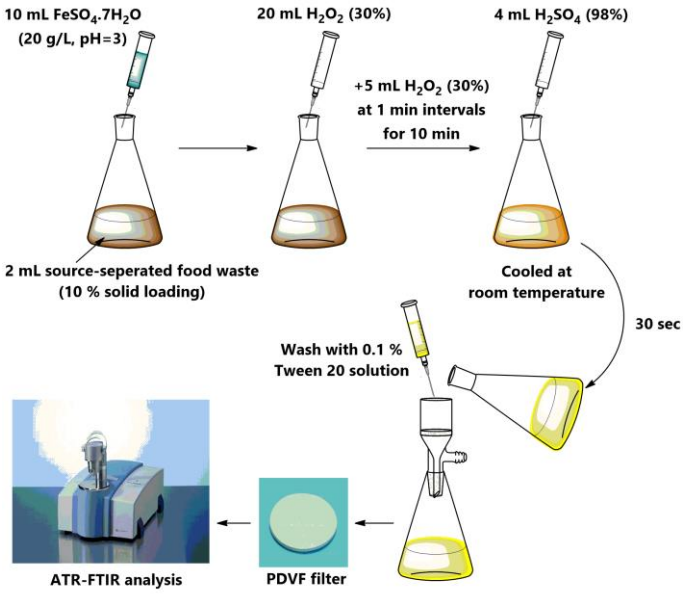
Food waste constitutes the largest part of municipal solid waste and is rather under-utilized; yet, it holds an increased energy potential, but its exploitation is rather challenging given its heterogeneous and complex nature. Nevertheless, there are concerns about the levels of plastic contaminants in food waste streams. Small plastic particles, deriving mainly from polypropylene (PP), high- and low-density polyethylene (LDPE, HDPE) and poly(butylene adipate-co-terephthalate) (PBAT) are expected to appear in source-separated biowaste. This is usually attributed to unaware disposal of plastic waste in specially designated composting bins; common residues such as stickers from fruits and packaging plastic bags are blended with the waste, whereas some composting programs in the US and Canada allow residents to include plastic-coated paper products in their compost collection bins. Often, separation from the organic part may not be efficient and consequently, their presence in residual amounts might jeopardize the application of contaminated compost or digestate (two common ways to valorise food waste) to land as a soil amendment or organic fertiliser.

The current study aimed to develop protocols for the identification and possible quantification of polymeric contaminants in source-separated food waste streams and contribute to establishing the respective compost specifications in terms of their (micro)plastics content. To the best of our knowledge, the percentage of polymeric contaminants is rarely cited in compost labels. For this purpose, solid biomass, intended for composting, was collected from a compost facility and contaminated with 5 % wt. of each type of micro-particles of PP, LDPE and PBAT with respect to the biowaste dry mass. The source-separated biowaste was initially characterized in terms of its composition, and subsequently subjected to chemical digestion. The residue was subjected to Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (ATR-FTIR) in order to identify and possibly quantify the specific polymeric contaminants. ATR-FTIR is a rapid, easily applicable and cost-effective technique that allows fast detection of contaminants after chemical digestion, with detection limits as low as 500 μm.

Experimental

Materials. The analyzed waste corresponds to a real source-separated biowaste stream that was collected from the municipality of Vari-Voula-Vouliagmeni, Attika, Greece. Virgin PP, LDPE and PBAT in the form of pellets were cryomilled into flakes using a Pulverisette grinding mill (Fritsch GmbH, Idar-Oberstein, Germany). The flakes' size was measured by running a granulometry test using sieves with different mesh and the size range was from 63 to 500 μm.

Chemical digestion (Fenton process). Neat and contaminated biowaste (5% wt. of each polymer with respect to the biowaste mass) were subjected to chemical digestion according to standard protocol [2]. At first, 10 mL of ferrous sulfate solution ($FeSO_4$) (20g/L, pH = 3) and 2 mL of biowaste sludge (25:75 dry source-separated food waste:distilled water) were added and mixed well in a 1 L glass beaker under fume hood. Then, 20 mL of H_2O_2 30% were added to initiate the reaction and at 1-minute intervals, stepwise addition of 5 mL of H_2O_2 was performed for the 10 next minutes. After the last addition, the mixture was left to cool for approximately 10 minutes. Then 4 mL of H_2SO_4 98% were added and stirred until the iron particles were fully dissolved (change of mixture color from orange to light yellow). The content was subsequently filtered under vacuum with a 0.45 μm PDVF filter. Finally, the beaker was washed with a 0.1% Tween 20 solution (with ultrapure water) to prevent micro-plastics from adhering to the glass walls. The filtered residue was oven-dried at 50°C, removed from the filter, submitted to optical microscopy in order to check for plastic presence and finally measured *via* ATR-FTIR spectroscopy.



Scheme 1. Chemical digestion of organic matter (Fenton process)

ATR-FTIR spectroscopy. The virgin polymers in the form of micro-particles (after cryomilling), biowaste before and after chemical digestion were analyzed *via* ATR-FTIR in an Alpha II (Alpha II, Bruker, Germany) at room temperature in the absorbance mode. The dried samples were placed on the aperture and 32 scans were performed over the spectral range of 400-4000 cm^{-1} at 4 cm^{-1} resolution and averaged across the spectral range to improve the signal-to-noise ratio. Also, OPUS Software® delivers atmospheric compensation for CO_2 (in the 2282-2399 cm^{-1} region) and H_2O (in the 1400-1800 and 3667-3996 cm^{-1} regions) for all samples and the spectra presented in the following sections were taken from an average of ten random spectra from each material.

Results and discussion

Initially, the findings after the chemical digestion of organic matter (Fenton process) were interpreted. Fenton process was successful and the organic matter was removed by 86.5 to 92.0 % in all cases. The neat dried source-separated food waste displayed 7.3 % of undigested mass at the end of the digestion, which can be attributed to inorganic substances (salts, minerals, metals, etc.) or even plastics initially present in the food waste, which remained unaffected by the Fenton reagents. Their presence can also be corroborated by the 11.5 % of ash left after a heating treatment of the food waste up to 600 °C, in order to determine its composition (**Table 1**).

Table 1. Composition of the neat dried source-separated biowaste.

Composition	% dry base
Oils	12.0
Water soluble solids	30.8
Volatile solids	88.5
Ash	11.5
Cellulose	12.7
Hemicellulose	9.3
Starch	7.1
Acid soluble lignin	1.8
Acid insoluble residue	12.4

The contaminated food waste samples exhibited higher levels of undigested mass, ranging from 10.7 to 12.5 % (Table 2). This increase of the undigested part corresponds to the presence of the plastic contaminants, and the respective difference from the neat food waste is in good agreement with the nominal amount of polymer initially added, except in the case of LDPE. In this case, the Fenton reagents may have affected somehow the polymeric chains and further study (even on other methods of chemical digestion) should be carried out to exclude polymeric decomposition.

Table 2. Undigested residues after the Fenton process of the neat dried source-separated food waste and of contaminated biowaste.

Sample	Undigested part (%)
Neat food waste	7.3
5% LDPE	10.7
5% PP	12.5
5% PBAT	12.1

In **Figure 1** the different FTIR spectra are depicted, i.e. for the neat biowaste, neat polymer (after cryomilling) and food waste with 5% wt. polymeric contamination before and after chemical digestion. Initially, the neat polymeric micro-particles were properly paired with the reference PP, LDPE and PBAT spectra by using the database of OPUS Software®. Chemical digestion was then found necessary in order to obtain clearer peaks and identify the characteristic absorption bands for the MPs contaminants; prior to Fenton process these characteristic peaks for each polymer type were overshadowed by the biowaste ones. More specifically, regarding biowaste contaminated with PP (Fig.1a), its characteristic bands were clearly pinpointed after chemical digestion at 1456 and 1376 cm^{-1} attributed to the symmetrical $-CH_3$ stretching and bending vibrations, respectively. For the LDPE contaminated samples (Fig.1b), the typical PE bands at 1464 and 718 cm^{-1} which refer to $-CH_2$ bending and asymmetric rocking, became evident and used for its identification. In the case of the sample contaminated with PBAT (Fig.1c), the most characteristic absorption bands that appeared more clearly were at 1710 cm^{-1} associated with the C–O stretching vibration, at 1504 cm^{-1} ascribed to the skeleton vibration of the benzene ring, and finally at 726 cm^{-1} attributed to the bending vibration of –CH in-plane of the benzene ring. Our next aim is to create a calibration curve based on the integrated absorbance area of the aforementioned peaks per polymer type, in order to quantify the microplastic content in the foodwaste stream.

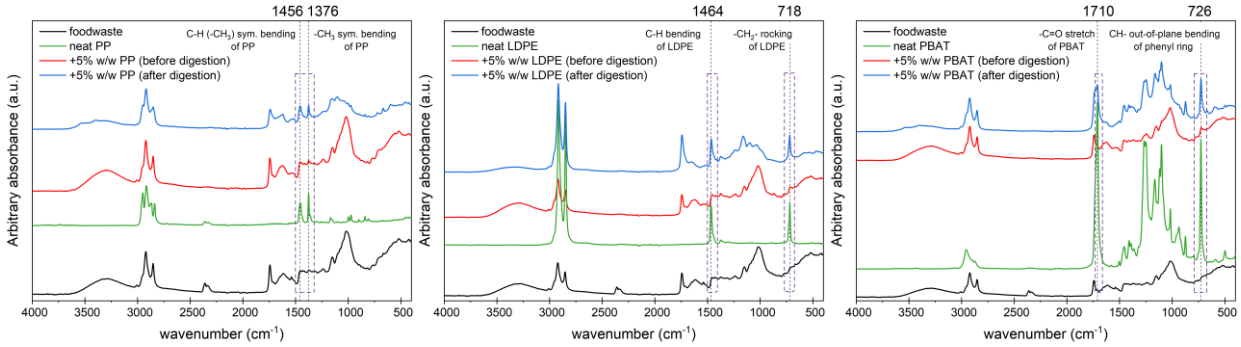


Figure 1. ATR-FTIR spectra of neat food waste, neat polymer micro-particles and food waste with 5% wt. polymeric contamination before and after chemical digestion for **a)** PP, **b)** LDPE and **c)** PBAT

References

[1] Al-Azzawi, M.S.M., Kefer, S., Weißer, J., Reichel, J., Schwaller, C., Glas, K., Knoop, O. & Drewes, J.E. (2020). Validation of Sample Preparation Methods for Microplastic Analysis in Wastewater Matrices - Reproducibility and Standardization. *Water*. *12*(9):2445.

[2] Thompson, R.., Swan, S., Moore, C. & vom Saal, F. (2009). Our plastic age. *Philosophical Transactions Of The Royal Society B: Biological Sciences*. *364*(1526), 1973-1976.

[3] Lievens, S., Slegers, T., Mees, A.M., Thielemans, W., Poma, G., Covaci, A. & Van Der Borght, M. (2022). A simple, rapid and accurate method for the sample preparation and quantification of meso- and microplastics in food and food waste streams. *Environmental Pollution*. *307*(119511).