Improvement of Microplastics Separation from Synthetic Samples – A Key Step for Their Analysis

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Abstract. Identification of microplastics from the environment is a challenge mostly due to the complex nature and behavior of samples and lack of an efficient separation method. This paper approaches the issue of microplastics separation as determining step of their analysis. The separation of two types of commercial plastics from synthetic samples was investigated, namely polyethylene terephthalate (PET) and high density polyethylene (HDPE). Subsequent filtration through filters with different porosities was tested and improved by adding a surfactant in the extraction medium. For the qualitative analysis of microplastic, optical microscopy and laser-granulometry were employed. The results proved the separation of microplastics from the samples and showed a distribution between 10-100 μm for PET and 10-200 μm for HDPE. These results provide basis for the efficient microplastics separation and further quantitative analysis from more complex samples, such as environmental samples.

1. Introduction

The presence of pollutants in water is an issue of interest in the field of water management as new compounds included on the list of potentially toxic and hazardous substances are found to be present in water. A special attention was recently granted to emerging pollutants and scarce information is available regarding their effects on the environment or human health. The presence of micro- and nanoplastics in the aquatic environment raised the interest of environmental scientists due to recent reports regarding their presence and potential effects on aquatic organisms and humans [1-11].

Since the synthesis of the first plastic in the early 1900s, the production of these materials has increased significantly and millions of tons of polymers are produced every year. Plastics are versatile materials, with low weight, high durability and flexibility. They are cheaper than the traditional materials such as wood, metal, glass or paper which facilitated their wide use. The applications of such materials vary greatly from industrial (e.g. food packaging, electronics) to medicinal (drug delivery) and household purposes (e.g. grocery bags and storage flasks). However, their disposal after only one use causes the generation of significant volumes of plastic waste and a part of this waste ends up in the environment where under the influence of UV and environmental conditions degrade to microplastics and nanoplastics. These particles were shown to be present and have effects on the aquatic environment and food chain. The small size of microplastics enables their penetration in organisms and the main effect reported is physical damage. However, microplastics also have the ability to adsorb and release other toxic pollutants into the organisms which in conjunction with their size pose a greater risk to organisms after penetration [3-8, 10, 12-15].
One of the main issues related to the monitoring of microplastics in the environment is the difficulty of separating them from complex samples. The small size and the tendency to float increase the time required for their separation and limit the methods that may be used for their separation. Among these methods, density separation has been used intensely. Various solutions with density greater than the density of microplastics have been employed, such as sodium chloride, sodium iodide, zinc chloride or sodium polytungstate. This method does not ensure the complete separation of microplastics and some of the employed solutions are harmful for the environment [9, 16-20].

Sequential filtration through sieves or filters with different porosities is another method currently used for the separation of microplastics after applying the density separation method. The analysis of separated particles is firstly accomplished through a visual method followed by instrumental methods that are currently employed for the analysis of nanoparticles. The main issue of filtration is the clogging of the filters and the long time required for the passing of the aqueous medium through the filter. The addition of a surfactant, such as sodium lauryl sulphate, in the filtration medium could overcome this disadvantage and allow a better and fast separation of the microplastics [9, 16-25].

This paper presents the results obtained on the improvement of microplastics separation. The experimental procedure employed the separation of investigated microplastics by subsequent filtration of a sodium lauryl sulphate-enhanced aqueous medium followed by optical microscopy and laser-granulometry analysis. The tests were conducted on synthetic samples of widely used commercial materials, namely polyethylene terephthalate (PET) and high density polyethylene (HDPE).

### 2. Materials and methods

The plastic materials selected for testing the separation procedure were commercial polyethylene terephthalate (PET) and high density polyethylene (HDPE). Two types of PET were employed, colorless and brown.

The experimental procedure consisted of two main steps, the obtaining of the microplastic particles and their analysis. The obtaining of microplastics particles was achieved by shredding with a metallic scissor (Figure 1) followed by grinding. A specific quantity of shredded material (5-15 g) was subjected to grinding in a planetary ball mill (PM 100, Retsch) together with 50 g of sodium chloride (NaCl, density 2.165 g/cm$^3$). The grinding was performed for 10 min at 550 rpm and direction reversal every 3 min followed by a 10 s pause. Afterwards, 10 mL of distilled water were added and the grinding continued for another 50 min (Figure 2). At the end, the sample was taken using distilled water and filtered coarsely through a metallic sieve with 1 mm pores followed by filtration through polycarbonate filters with 0.4 μm porosity (Figure 3). The addition of a solution of sodium lauryl sulphate 10% and 5% (NaC$_{12}$H$_{25}$SO$_4$, density ~1 g/cm$^3$) was tested. This was added to the filtration suspension to improve the recovery of microplastics and enable the dispersion of microparticles agglomerates. Based on the results of visual identification, the use of 5% sodium lauryl sulphate proved to be more efficient and thus was used throughout the experiments.

The clogging of the filter was prevented by adding ethanol (C$_2$H$_5$OH, density 0.7894 g/cm$^3$) and the removal of potential metallic particles was achieved using hydrochloric acid solution 1:1 (HCl, density 1.08 g/cm$^3$). The final wash of the filter was with distilled water. The samples were introduced in a Petri dish and dried at 20±4°C.

The analysis of microplastics was achieved by visual identification and laser granulometry. For the visual analysis, a specific quantity (0.04 mg) of the dried microplastics was dispersed in 500 mL distilled water and 1 mL solution of sodium lauryl sulphate 5% was added. The solution was further filtered through a vacuum filtration system provided with polycarbonate filter with 0.4 μm porosity. The visual analysis was performed using an optical microscope Carl Zeiss Jena) in trinocular version, with planachromatic objectives and magnification of up to 1000x.

The size and distribution of separated microplastics were analyzed by laser diffraction. This provides indirect size measurements of spherically equivalent particles. The size and distribution of separated microplastics were determined using a laser particle sizer (ANALYSETTE 22 NanoTec, Fritsch) using wet dispersion. The material was dispersed into a liquid that circulated across a quartz
measurement cell illuminated by a laser beam. The particles with a specific size will diffract the light at a specific angle which increases logarithmically with decreasing size. This particle sizer performs measurements in the range 0.1-2100 μm. The measured data were processed and evaluated using the software provided by the manufacturer.

3. Results and discussions
Images of the shredded plastics and microplastics obtained after the milling procedure are shown in Figures 1-3.

![Figure 1. Images of shredded plastic materials: (a) colorless PET, (b) brown PET, (c) HDPE.](image)

![Figure 2. Plastic materials after grinding: a – colorless PET, b – brown PET, c – HDPE.](image)

![Figure 3. The microplastic particles resulting from the experimental procedure: (a) colorless PET, (b) brown PET, (c) HDPE.](image)

The results of the visual analysis are presented in Figure 4 and show a complex and slightly irregular shape of the particles (Figure 4 a and d). The results of filtration tests conducted using solutions of sodium lauryl sulphate at two concentrations, namely 5% and 10%, are presented. For the 10% surfactant solution, a pilling tendency was observed, as depicted in Figure 4 a for colorless PET. When a 5% surfactant solution was employed, the pilling tendency was reduced and the obtained microplastics were better separated, as shown in Figure 4 b-d for all plastics.
Figure 4. Microscopic images of the microplastics: (a) colorless PET from a solution containing 10% sodium lauryl sulphate, (b) colorless PET from a solution containing 5% sodium lauryl sulphate, (c) brown PET from a solution containing 5% sodium lauryl sulphate, (d) HDPE from a solution containing 5% sodium lauryl sulphate.

The dimensional characteristics of the obtained microplastics determined by laser-granulometry are shown in Figures 5-7 for PET and HDPE. The cumulative curve of distribution $Q_3(x)$ (left) indicating the standardized total quantity of all particles with equivalent diameters smaller than 100 μm for colorless PET and respectively 200 μm for cultured PET and HDPE together with the distribution density $dQ_3(x)$ (right) defined as the first derivative of $Q_3(x)$ are presented.

Figure 5. Granulometric distribution of colorless PET.
The results showed a monomodal distribution for both PET and HDPE, with sizes between 10-100 μm for colorless PET and between 10-200 μm for brown PET and HDPE.

4. Conclusions
This paper presented an improved separation method for microplastics from synthetic samples consisting in subsequent filtration through filters with different porosities. The method employs the addition of a surfactant in the extraction medium, to facilitate the filtration and prevent the fouling of the filters.

The improved separation method was applied on two commercial materials, PET and HDPE. To evaluate the separation of the method, the determination of microplastics was performed by visual analysis and confirmed by laser-granulometry. The results proved the presence of microplastics with size between 10 and 100 μm in the case of PET and between 10 and 200 μm in the case of HDPE.
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