Microplastics extraction from a sandy beach: methodology development and challenges

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1. Introduction

In 2017, the world plastic production almost reached 350 million tonnes. This represents an increase of more than 233 % over the last six decades (PlasticsEurope, 2018). According to PlasticsEurope (2018), more than 50 % of plastics are produced in Asia, being China the largest producer (29.4 %), followed by Europe (18.5 %) and NAFTA (17.7 %). Among plastic litter, the increased input of microplastics on the aquatic ecosystems is a growing concern worldwide and have had a special attention by the researchers due to their negative impacts on marine biota and human health (Barboza et al., 2018).

Microplastics' size ranged from < 5 mm to 1 µm. It can occurs in different forms in the marine environment, such as spherical beads, films, irregular fragments, filaments, foam, granules and fibres (Karthik et al., 2018; Tiwari et al., 2019). Microplastics can be categorised into primary and secondary; primary microplastics are microscopic-size's materials and are mainly produced from cosmetic products' industry (e.g. micro cleansing beads) or from sandblasting (e.g. cleaning rust) (Syberg et al., 2015; Tiwari et al., 2019). While secondary microplastics are fragments resulted from the physical, chemical or biological degradation of larger plastic debris such as fishing equipment, laundry discharge, packaging material etc. (Syberg et al., 2015; Tiwari et al., 2019). In the environment, the continuing fragmentation of plastics has led to the decreasing of plastic's particle size which makes its monitoring, extraction/separation, identification and quantification a challenge. In addition, the Marine Strategy Framework Directive was amended to highlight that "the composition of microplastics has to be characterised in marine litter and the marine coastal environment". Thus standard methods are still developing.

In the literature, density flotation method has been widely used for microplastics extraction in the marine sediments. This method promotes the separation of the lesser density plastics from the sediments, which have a higher density, by using high density salt solutions. For instance, Imhof et al. (2012) developed a new Munich Plastic Sediment Separator using zinc chloride (1.6-1.7 kg L^{-1}) as separation liquid to extract microplastics from river sediments. Even though recovery rates were up to 100 % for ten types of microplastics with 1-5 mm size and 95.5 % for seven types of microplastics with < 1 mm size, this method entails the construction of an apparatus with materials that are not often available in any conventional laboratory. Nuelle et al. (2014) proposed a two-step extraction method to separating microplastics from beach sediments. This method consisted on the fluidisation of sediments in a saturated NaCl solution followed by flotation of microplastics in a sodium iodide salt solution. Using this method, the recovery rates for polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS) and polyurethane with sizes of approximately 1 mm ranged 91 % – 99 %. The current work aims to propose and test a simplification of that method by removing the first step of the extraction process. Thus, the main research question of the current work is: are the recovery rates of plastic materials using a single extraction method as good as using a two-step method? Additionally, it is also assessed the recovery rates of plastic materials with different particle sizes: i) > 2 mm; ii) 2 mm – 1 mm; iii) 1 mm – 0.5 mm; iv) 0.5 mm – 0.2 mm and v) 0.2 mm – 0.05 mm, using the proposed single extraction method.

2. Materials and methods
2.1 Chemicals and plastic materials

Saturated ZnCl$_2$ solution was prepared by dissolving 1.8 kg of ZnCl$_2$ anhydrous extra pure (labkem, labbox, Barcelona) in 1 L deionized water to obtain a solution with approximately 2.0 kg L^{-1}. Before its use, ZnCl$_2$ solution was filtered through qualitative paper to remove the undissolved salts or impurities.

Several plastic products made of PP, PS and PVC were used in the extraction experiments. Each plastic product was firstly cleaned using deionised water and 70 % ethanol and then was dried at 60 °C.

2.2. Preparation of microplastics samples

Each plastic product was firstly cut in approximately 3 cm size. Then it was grounded in a mill and sieved through a 2-, 1-, 0.5-, 0.2- and 0.05-mm stainless-steel to obtain the five fractions of different sizes. Table 1 presents the mass of each plastic material used in the extraction experiments. Before its use, the microplastics' fractions were mixed in a beaker, washed using distilled water and dried at 60 °C.

Table 1 Mass of microplastics' fractions used in the extraction experiments (*not available due to the grinding mechanism).

Size	Plastic material (g)		
	PP	PVC	PS
> 2 mm	2.5	2.5	2.5
2 mm – 1 mm	2.5	2.5	2.5
1 mm – 0.5 mm	2.5	2.5	2.5
0.5 mm – 0.2 mm	1.5	1.5	2.5
0.2 mm – 0.05 mm	0.5	–*	1.0
Total (g)	9.5	9.0	11.0

2.3 Sandy beach sampling and samples' preparation for extraction method

On April 2018, approximately 3 kg of sand were collected from a beach located on Figueira da Foz, Coimbra, Portugal (40°10'07.6"N, 8°53'15.8"W). At laboratory, sub-samples of 150 g of sand were placed in 600 mL beakers and 250 mL $ZnCl_2$ was added. This mixture was slowly manually stirred for 2 min, in order to wash out the plastics from the sand, and left to settle for 15 min. The supernatant was discarded and the procedure was repeated using 500 mL HCl 0.001 M instead. This cleaning procedure was made until no $ZnCl_2$ be detected in supernatant. The sandy beach samples were then dried at 100 °C for 48 h.

Three 600 mL beaker with cleaned sand were spiked with one type of plastic: PP or PVC or PS (Table 1) (in duplicate), to determine the recovery rates for the proposed extraction method. The overall recovery rates (%) for each plastic material was calculated as follow:

$$Overall\ recovery\ rate\ (\%) = \frac{Microplastic\ mass\ obtained\ at\ the\ end\ of\ extraction\ (g)}{Microplastic\ mass\ added\ at\ the\ beginning\ of\ extraction\ (g)} * 100$$

The same calculation was done for the five microplastics' fractions: > 2 mm, 2-1 mm, 1-0.5 mm, 0.5-0.2 and 0.2-0.05 mm.

2.4 Microplastics extraction using the flotation separation method

The microplastics were extracted using a modified flotation/density method described by Nuelle et al. (2014). The principle of the proposed method is to use a salt solution with higher density, such as $ZnCl_2$ (density ≈ 1.8 kg L^{-1}), than the microplastics in order to promote the separation of it from the sandy beach samples by flotation. Firstly, the 600 mL glass beaker containing the microplastics plus the sand was filled with 250 mL of $ZnCl_2$ and slowly manually stirred for 2 min. Then, this beaker was held using a clamp and ≈ 500 mL of $ZnCl_2$ was pumped from a glass beaker into it using a peristaltic pump, which created an overflow of the top layer, with microplastics in, into the 2 L glass beaker ("1st flotation"). Afterwards, the pump was turned off and the outside wall of 600 mL glass beaker was rinsed using $ZnCl_2$ to remove any microplastics that had stuck to. After 15 min, the supernatant of 600 mL beaker was decanted into the 2 L glass beaker. The mixture of the 2 L glass beaker was subsequently sieved through a 0.05 mm stainless-steel sieve installed on a vacuum filtration unit. The sand in the 600 mL beaker was again submitted to the extraction procedure to ensure that any remaining microplastics are extracted from sand ("2nd flotation"). The microplastics resulting from the 1st and 2nd flotation procedure and the sand left in the 600 mL beaker were rinsed several times with HCl 0.001 M to clean $ZnCl_2$ and then placed in an oven at 60 °C for 48 h. Afterwards, the dried microplastics were sieved through a 2-, 1-, 0.5-, 0.2- and 0.05-mm stainless-steel sieve and then each fraction was weighed. The sieved $ZnCl_2$ and sand were stored for reuse. The extraction procedure was done in duplicate.

3. Results and discussion
3.1 Recovery rates for different types of microplastics

The mass of microplastics obtained at the end of each flotation procedure is shown in Figure 1. A repetition of flotation for the same sample extracted a very small amount of microplastics; only about < 4 % of PP and PS and about 1 % of PVC were extracted in the 2nd flotation. These results reveal that the 2nd flotation is not necessary which makes the application of the proposed extraction procedure faster.

The overall recovery rates for PP, PS and PVC using the proposed extraction method (Figure 1) ranged from 97 % (PS) to 100 % (PVC). PS and PP, which have the lowest density, registered a slightly lower recovery rates than PVC (2-3 %). In general, no remarkable differences were noted between the different plastic materials. By applying this single extraction method, the recovery rates of microplastics with < 2 mm size can be considered good. In comparison with the two-step separation method developed in the study of Nuelle et al. (2014), which comprised the steps of fluidization of sediments followed by the flotation of the plastic materials, the global recovery rates attained in the current work were higher for PP (3 %), PS (7 %) and slightly lower for PVC (1 %).

Overall, the results above demonstrated that different types of plastic materials of < 2 mm size are efficiently extracted using the separation method proposed in the current work.
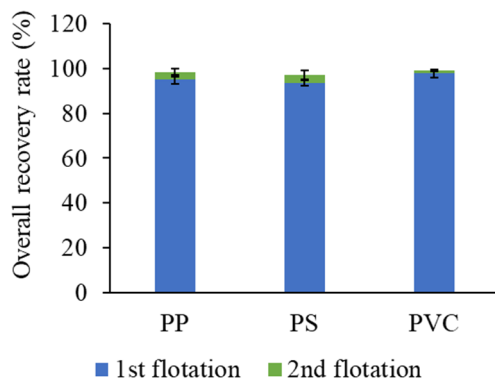

Figure 1 Overall recovery rates (%) (n=2; mean ± standard deviation; PP: polypropylene; PS: polystyrene; and PVC: polyvinyl chloride)

3.2 Recovery rates for microplastics with different size

Figure 2 presents the recovery rates for the five microplastics' fractions used in the single extraction method tested in the current work. Regardless the size and type of microplastics, the average partial recovery rates ranged between 51 % ± 8 % - 133 % ± 1 %. These data displayed a high variability with relative standard deviation ranging from 1 % to 27 %.

Microplastics with lowest size (0.05-0.2 mm) and low density (PP and PS) displayed the lowest recovery rates (51 % for PS and 60 % for PP). This may be attributed to losses occurred during the extraction method or even due to strong adherence of these types of plastics to surface of the materials used to perform the recovery experiments.

The PVCs' microplastics (higher density) exhibited the highest recovery rates: 133 %, with 0.5-1 mm size. The value of 100 % was over exceeded. According to Nuelle et al. (2014), the extraction methods for microplastics are extremely prone to contamination by fibres from the working space. To overcome the problem of fibre contamination, further works should include the performing of some blank samples to quantify the impact of it on the overestimation of recovery rates. Moreover, in the extracted microplastics were also found some particles of sand and unknown fragments. In order to assess its influence on the recovery rates, the extracted PVC with 0.5-1 mm size were submitted to a cleaning procedure. This procedure consisted on i) mixing of the extracted microplastics with 200 mL $ZnCl_2$; ii) manually slowly stirring for 2 min; iii) filtrating of microplastics followed a rinsing with HCl 0.001 M; iv) drying at 60 °C and v) weighing. Only a 3% of weigh loss of microplastics were observed after the application of this cleaning procedure. Additionally, the shape and size of the microplastics may be affected by the extraction procedure by have been in contact with $ZnCl_2$ and/or sand. This may cause the transference of the microplastics that at the beginning of experiment were included in the < 2 mm and 1-2 mm fractions into the small fraction with 0.5-1 mm size; PVC extracted with 1-2 mm size registered a recovery rate of only 72 % ± 9 %.

To the best of the author's knowledge, this is the first study in which different types of plastics with several sizes have been separated from a sandy beach using a flotation-based extraction method. This allowed not only obtain the overall efficiency but also assess the efficiency of the proposed method for microplastics with different sizes, as these usually appear in the aquatic environment.
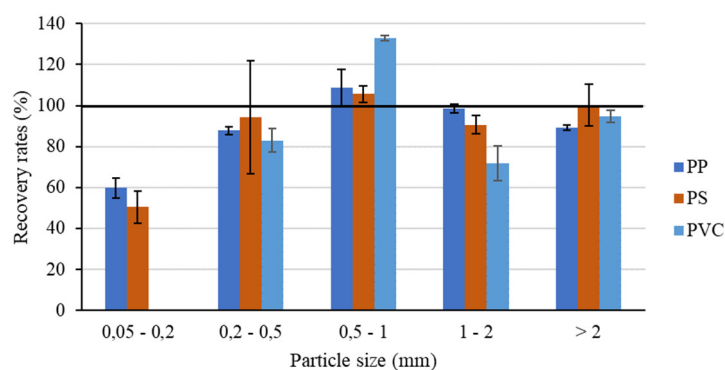
Figure 2 Recovery rates of the microplastics' fractions (%; mean ± standard deviation, n=2) of PP, PS and PVC (considering only the first flotation)

4. Conclusions

The overall recovery rates obtained in this work were considered as good, which demonstrates the potential of the proposed extraction methodology. Furthermore, the major advantage of the proposed method is that no sequential extraction steps are needed, as applied in previous studies. Finally, this analytical extraction method can contribute to boosting advancements for determining the occurrence of microplastics in the marine sediments. In order to validate the proposed methodology, further work has to be done using real beach samples.

Acknowledgments

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