The fate of microplastics during the anaerobic digestion of thermally pretreated sludge

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Abstract. The presence of microplastics (MPs) in the water environment has raised as an issue of great concern, mainly due to their persistence and potential adverse effects on biota. Municipal wastewater treatment plants have been claimed among the most important point source of MPs. Nevertheless, they act as a barrier for the spread of MPs in water, since a significant amount of these pollutants concentrates in the sludge originating from wastewater treatment. This study focuses on the presence of MPs in sewage sludge, with the main aim of assessing their fate during the mesophilic anaerobic digestion of thermally pretreated sludge. MP abundance in the digestate as well as the anaerobic biodegradability of the pretreated substrates were assessed. Experimental results addressed preliminary considerations on the effects of high temperature on the MPs as well as on their influence on anaerobic degradation processes.

Keywords: biological process, plastics, pollution, polymers, thermal pretreatment

1. Introduction

The term "microplastics" (MPs) was introduced by Thompson et al. (2004) to describe the accumulation of the smaller plastic particles in marine sediments. Later, this term was proposed to identify the "*plastic particles smaller than 5 mm*". Over time, the definition of MPs as well as the criteria for their differentiation have been refined (Frias and Nash, 2019) and various classification have been proposed.

According to the origin, it is possible to identify:

- primary MPs, made in very small size, which can be found as part of different products, such as cosmetics, medicines, textiles and dyes;
- secondary MPs, originating from the deterioration and fragmentation of primary MPs and plastic items, in general.

In the aquatic environment, the latter are more abundant than the former: according to UN records for 2017, ocean MPs are at least 51 trillion, with 15-31% of them being primary and 69-81% being secondary.

The deterioration and fragmentation of plastic items in the environment may occur as a consequence of prolonged exposure to UV light and physical abrasion (Barnes et al., 2009). Additionally, the temperature of the material and the presence of moisture have shown a considerable synergistic effect on the photodegradation of the polymeric materials (Singh and Sharma, 2008).

Polymer deterioration may occur together with degradation, which is usually referred to any change in polymer properties due to chemical, physical or biological reactions. These result in bond scissions and subsequent chemical transformations, reflecting changes in mechanical, optical or electrical properties of the material.

Depending on the average size, Barnes et al. (2009) proposed to broadly divide MPs in: mega-debris (> 100 mm), macro-debris (> 20 mm), meso-debris (5-20 mm) and micro-debris (< 5 mm). Moreover, based on the shape, they are usually recorded as beads, fragments, fibers, films, sponges, microspheres.

All these different MPs can be constituted by a variety of polymers, including chaspolyethylene (PE), polypropylene (PP), polystyrene (PS), polyethyleneterephthalate (PET), low density polyethylene (LDPE), polyether urethane, polyamide, acrylamide, polyacrylates, alkyd resin, polyvinylchloride (PVC), polyvinyl alcohol (PVA), polyether sulfone (PES) (Bui et al., 2020). The type of MPs, their size and shape are pivotal to assess their impact on the biota (Montes-Burgos et al., 2010).

The great concern posed by the presence of these tiny particles in the environment is related to the large surface that MPs offer for the sorption of pollutants and release of constituent chemicals. Additionally, the ease with which MPs could either migrate through animal tissues and enter the food chain to reacher higher trophical levels are crucial issues. Several papers have focused on the sources, distribution and fate of MPs in the environment, especially the marine one (Peng et al., 2020). Recently, the effects of

MPs in wastewater and sludge treatment has been also reviewed (Zhang and Chen, 2020). Wastewater treatment was claimed to be effective towards larger particles, which are mostly transferred and stored into the sludge produced during the wastewater treatment process (Liu et al., 2019).

During sludge treatment, MPs remain mostly stable, although different effects on the anaerobic stabilization process of sludge have been pointed out (Zhang and Chen, 2020). Mahon et al. (2017), comparing differently treated sludge samples, highlighted that the kind of treatment may play a role in degrading MPs and, more recently, the highest value ever reported for MP biodegradation after 45 days of hyperthermophilic composting were reported by Chen et al. (2020). The authors stated that high temperatures promoted the growth of bacteria particularly effective at attacking and oxidizing plastics structures, leading to effective bio-oxidation and biodegradation.

Therefore, the effects of a thermal pretreatment of sludge containing MPs and destined to anaerobic digestion is worth investigating.

The main aim of this research is in assessing the fate of different kinds of MPs during the mesophilic anaerobic digestion of thermally pretreated sludge. Pretreatment effects were assessed in terms of MP abundance in sludge samples and ultimate anaerobic biodegradability of the pretreated substrates. Experimental results were used to discuss possible research directions to promote the degradation of MPs during sludge treatment.

2. Materials and methods

2.1. Substrate preparation

Waste activated sludge (WAS) samples were collected at the municipal wastewater treatment plant of Cuma (Italy) and they were thoroughly characterized by their main chemical-physical parameters.

MPs were prepared from objects of daily-use, made of polyethylene terephthalate (PET), which were manually cut to form 5 mm tokens. These were added to WAS samples in concentration of 1 g/L. The corresponding number of tokens added to WAS samples was counted as well. In order to compare the effects of the constituting polymer of MPs, biodegradable (BD) plastic tokens were prepared as well, and added to additional sludge samples in the same concentration used for PET-based MPs.

WAS samples, either containing MPs or not, were thermally pretreated at 120°C for 30 minutes (Kumar et al., 2020).

2.1. Analytical set up

In order to assess the fate of MPs during the anaerobic digestion of thermally pretreated sludge, batch tests were set up under mesophilic conditions, for 55 days. Digested WAS, obtained from lab-scale anaerobic digestion tests, was used as inoculum. Both untreated and thermally pretreated WAS samples, either containing or not MPs, were introduced in 500 mL glass bottles and the inoculum was added to ensure a substrate to inoculum ratio of 1 g_{VS}/g_{VS} (Kumar et al., 2020).

Before and after anaerobic digestion tests, MP abundance in both untreated and thermally pretreated WAS samples was assessed by extracting (Bretas et al., 2020), weighing and counting plastic tokens. The variations in shape and average size were assessed as well by visual observation.

Moreover, thermally pretreated WAS solubilisation and methane yield after the thermal pretreatment were monitored as well, in order to identify any effect of the selected kind of MPs on the biological anaerobic process. To this end, the soluble fraction of WAS samples, obtained after centrifugation and filtration at 0,45 m, underwent both the COD and protein content analysis. The former was carried out according to the Standard Method APHA 5220B; soluble proteins were assessed by Lowry method. Biomethane production was daily monitored by a water displacement method, using an alkaline solution.

3. Results and discussion

3.1. The fate of MPs during the anaerobic digestion of thermally pretreated sludge

The high temperature reached in WAS samples after the 30 minute thermal pretreatment was expected to affect the size and shape of MPs as well as to promote the release of constituting substances in the liquid medium. Different results were expected depending on the constituting polymers.

The visual observation of the MP tokens extracted from the thermally pretreated WAS samples highlighted a variation in the shape. The deformation is the obvious effect of the pretreatment temperature, even higher than the glass transition temperature of PET, which is 70°C. This was more evident for the BD-MPs (Figure 1a). The shape variation resulted in a slight reduction of the average size of the tokens. However, any appreciable mass variation was observed.

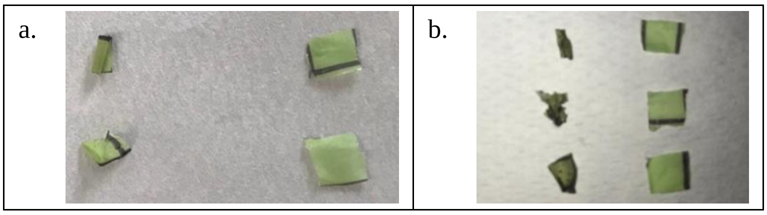

Figure 1. Shape and size of BD-MPs before and after a) WAS thermal pretreatment and b) the anaerobic digestion of thermally pretreated WAS

The comparison between the original PET-MPs and the ones extracted from thermally pretreated WAS showed minor variation in the weight, but any change in the number of tokens.

These outcomes suggest that, regardless the constituting polymers, the thermal treatment conditions did not alter the structure of MP tokens, by promoting their fragmentation. The negligible variation in the mass of the tokens extracted from the thermally pretreated WAS was found to be in the range of accuracy of the precision balance used to weight them and, thus, not significant.

Similar results were also observed when considering the MPs extracted from both untreated and thermally pretreated digested WAS samples. PET tokens seems not affected relevantly by the anaerobic digestion process, while a relevant variation in the shape and average size was observed for BD-MPs, as reported in Figure 1b. Surprisingly, any appreciable variation in the mass was found, likely due to the presence of organic matter, which could not be perfectly removed from the polymeric particles during the extraction procedure of BD-MPs.

Based on these evidences, anaerobic digestion yields in terms of methane generation were not expected to be highly variable among pretreated WAS samples containing different polymers.

3.2. Influence of MPs on anaerobic digestion

Thermal pretreatments have been widely studied to enhance the methane generation yields from sludge anaerobic digestion. Temperatures as high as 120°C were reported to effectively break the cells as well as to promote the release of proteins, polysaccharides and smaller amount of DNA/RNA into the soluble phase. This, in turn, leads to the increased availability of readily biodegradable substances that can be biochemically converted in biogas.

The degradation of the organic compounds as well as the microbial cell disintegration obtained after the thermal pretreatment contribute to the soluble fraction of the COD, whose variation is a key indicator to assess the performances of the pretreatment.

In this study, the soluble COD of pretreated WAS samples enhanced up to 5 times, regardless of the presence of MPs. Such solubilisation effect is related, indeed, to the release of soluble protein determined by the thermal hydrolysis of the sludge (Bougrier et al., 2017). This statement is confirmed by the results of the soluble protein content measured after the thermal pretreatment of WAS samples, which enhanced significantly regardless the presence of the MPs.

The effect of the thermal pretreatment in terms of WAS solubilisation suggested that higher biogas production would have been produced from pretreated WAS samples.

Experimental results show that, at the end of the digestion period, the methane produced from pretreated WAS samples was higher than that of the respective untreated samples (Figure 2). However, the samples containing BD-MPs exhibited the best performance in terms of specific methane generation. It is worth highlighting that the specific methane production of the untreated WAS samples containing BD-MPs was comparable with that of the thermally pretreated samples.

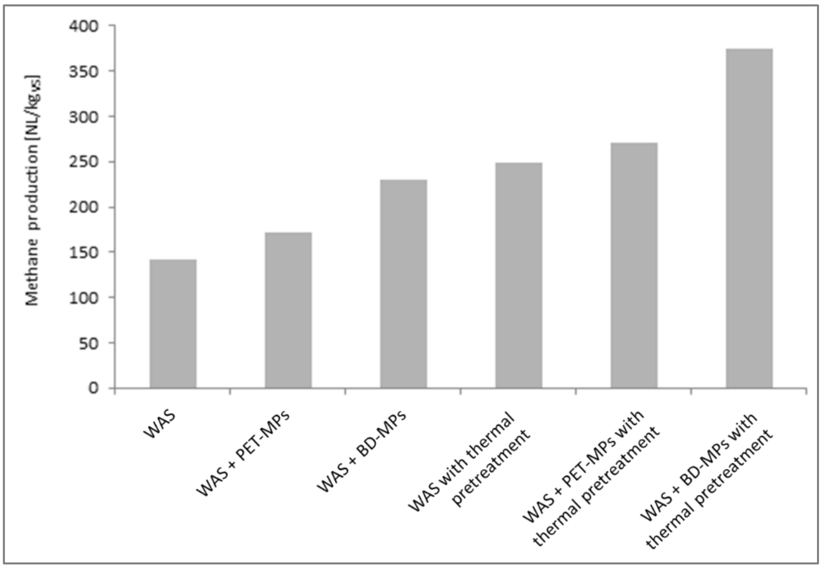

Figure 2. Cumulative methane production after 55 days anaerobic digestion

These outcomes indicate that the presence of BD-MPs plays a role in the biochemical process, promoting the generation of biomethane regardless the thermal pretreatment. This hypothesis is consistent with the apparent deformation observed for BD tokens after the anaerobic digestion of untreated WAS.

4. Conclusive remarks

WAS thermal pretreatment was studied to assess the fate of different kinds of MPs during anaerobic digestion. Experimental results showed that the thermal treatment condition did not affect the mass of MPs in WAS samples, but it altered the shape and size. This was particularly evident for BD-MPs, whose presence was found to positively influence anaerobic digestion yields. The highest specific methane production was obtained from thermally pretreated WAS samples containing BD-MPs. However, the untreated WAS samples with BD-MPs exhibited methane production comparable with that of pretreated WAS. This outcome suggests that BD-MPs can play a role in biochemical processes, paving the way for further studies. Additional research efforts should be devoted to investigate the influence of high temperature treatments on the anaerobic processing of smaller size MPs.

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