On the Fenton oxidation of polystyrene microplastics

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Abstract This work aims at evaluating the fate of polystyrene (PS) microplastics along Fenton oxidation. Experiments were carried out under relatively severe operating conditions (80 ºC) given the high persistence of these solids to oxidation. Slight mass losses (up to 10%) were found after the Fenton treatment of microplastics in the micro range (100–250 μm). Nevertheless, the particles clearly suffered important changes in their surface due to the introduction of oxygen groups, which made them more acidic and hydrophilic. These surface alterations completely changed the sorption properties of microplastics. For instance, their adsorption capacity for diclofenac was sharply decreased from 102 to 28 μg g^{-1}. Apart from surface modifications, microplastics clearly decreased their size after Fenton oxidation, which was more evident in the 50–100 μm range. To further evaluate the oxidation yield of PS microplastics upon Fenton oxidation, particles in the sub-micro range (140 nm) were treated. Notably, up to 75% TOC mineralization was achieved, which proved that microplastics can be completely oxidized to CO_2 upon Fenton oxidation. Finally, the biodegradability of the dissolved compounds leached from oxidized microplastics was evaluated. Remarkably, bacterial growth efficiency was higher in the solution coming from the oxidized PS microplastics than that of the fresh one.

Keywords: Water treatment; Fenton oxidation; microplastic; nanoplastic; polystyrene.

1. Introduction

The outstanding properties of plastics have promoted their widespread use by the industry and general society. In 2019, global plastic production reached almost 370 million tons (Plastics Europe, 2020) and it is expected to double in the next 20 years (MacArthur et al., 2016). The dark side of this flourishing story is the generation and poor management of plastic wastes, which represents a critical environmental issue. Plastic debris smaller than 5 mm, the so-called microplastics, are the most expanded plastic particles in the environment. Due to their ubiquitous occurrence, high persistence, and bioavailability across trophic levels given their tiny size, they are regarded as a new class of emerging contaminants (Alimi et al., 2018; Dyachenko et al., 2017; Li et al., 2018). Furthermore, they can act as carriers of other persistent pollutants like heavy metals, pesticides, fuel aromatics or pharmaceuticals (Wu et al., 2016; Li et al., 2019; Müller et al., 2018; Wu et al., 2019).

Microplastics usually end-up in the oceans but terrestrial sources contribute with up to 80% of the microplastic load in the marine environment (Li et al., 2018). In fact, municipal wastewater treatment plants (WWTPs) have been recently identified as a major via for microplastics discharge into natural waters (Li et al., 2018). Accordingly, the development of innovative wastewater treatment technologies for the removal of such harmful particles at WWTPs is essential.

Advanced Oxidation Processes (AOPs) have emerged as promising wastewater treatment technologies for the elimination of a wide range of emerging pollutants such as pharmaceuticals, personal care products, pesticides or hormones (Oturan and Aaron, 2014; Miklos et al., 2018; Serrano et al., 2020). However, their application for the removal of microplastics has been scarcely investigated so far. The limited publications found in the literature are mainly related to the use of photocatalysis (Thomas et al., 2013; Ariza-Tarazona et al., 2019). Usually, low mass losses and subtle surface modifications have been found in the treatment of these hazardous solids. Recently, almost complete mineralization of commercial polystyrene sub-microparticles (400 nm) was achieved using a TiO_2 nanoparticle film (Nabi et al., 2020), but long reaction times (12 h) were required.

Fenton oxidation is a particularly attractive AOP given its high cost-effectiveness. So far, this process has been mainly investigated as pre-treatment method to isolate microplastics from different kinds of waters with the aim of analyzing the microplastics (Tagg et al., 2017; Hurley et al., 2018). Subtle modifications in microplastics along this treatment have been reported *viz.* small mass losses or surface micro-cracks, but there are important gaps in knowledge regarding the changes and degradation that microplastics can undergo along Fenton oxidation. This work aims to address such challenging goal by deeply evaluating the fate of microplastics upon the Fenton treatment under relatively severe conditions (80 ºC). Realistic expanded polystyrene (PS) microplastics obtained from commercial food trays were used as target pollutants given their particularly resistance towards WWTPs treatment (Bayo et al., 2020).

2. Experimental procedure

2.1. PS microplastics obtention and characterization

Microplastics were obtained by cutting-up commercial PS food trays with stainless-steel scissors. The resulting particles were further grinded using a cryogenic mill (CryoMill, Retsch) to achieve microplastics of 50 – 100 μm and 100 – 250 μm size ranges. To evaluate the oxidation of microplastics in the sub-micro range (140 nm), a commercial sample of monodisperse PS (PS-R-KM248) was purchased from microParticles GmbH.

Scanning electron microscopy (SEM) and light microscopic images of the microplastics were obtained using a JSM 6335 (JEOL) and an Eclipse Ci-S/Ci-L (Nikon) microscopes, respectively. "ImageJ" software was used for counting and measuring the microplastics in SEM images. Particle size distribution of microplastics was also measured by laser diffraction particle-size analysis using the Mastersizer 3000 (Malvern) equipment. Elemental analyses (CHNS) were performed in a LECO CHNS-932 elemental analyzer (LECO Corporation). Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a FTIR Bruker IFS66v spectrometer. Water contact angle measurements were performed in the sessile mode at room temperature using a Dataphysics OCA 15 system. Determination of the pH_{slurry} of microplastics was performed placing 0.2 g of the solid in 10 mL distilled water at pH_0 = 6. The suspensions were kept in a continuously stirred bottle at room temperature until pH of the slurry was stable (at least, 24 h).

2.2. Typical reaction procedure

Oxidation runs (5 days) were performed at 80 ºC and acidic pH (pH_0 = 3) in a glass batch reactor under constant stirring (200 rpm). A reactor volume of 75 mL and a mass of 100 mg were established. The initial concentrations of Fe^{3+} and H_2O_2 were set at 10 mg L^{-1} and 1000 mg L^{-1}, respectively. To enhance the oxidation yield, three additional H_2O_2 doses (1 mL, 75 g L^{-1}) were added per day once complete consumption of the reagent was reached. In the case of Fe^{3+}, an additional dose (1 mL, 750 mg L^{-1}) was added every 24 h.

To follow the oxidation yield along the experiment carried out with PS sub-micro particles, total organic carbon (TOC) was measured. For such goal, samples were periodically taken from the reactor and immediately analyzed. A TOC analyzer (Shimadzu, mod. TOC VSCH) was used. H_2O_2 concentration was determined by colorimetric titration following the titanium sulfate method (Eisenberg, 1943).

3. Results and discussion

Own-prepared PS microplastics were fully characterized. They showed an irregular and rough shape, as appreciated in SEM and optical microscopic images. It was also confirmed that the size of the microplastics fell within the ranges sieved (50 – 100 μm; 100 – 250 μm). The elemental analysis was consistent with the unique presence of polystyrene polymer, which was further proved by FTIR analysis. PS microplastics showed strong hydrophobic properties, with a water contact angle value of 133º. Consistent with these results, the high pH_{slurry} value of the solids (pH_{slurry} = 8.9) confirmed their basic character.

3.1. Impact of Fenton oxidation on PS microplastics properties

The general properties of PS microplastics were deeply characterized after being submitted to Fenton oxidation. As can be seen in Figure 1, relatively low mass losses were found in the microplastics (100 – 250 μm) considering the severe operating conditions tested. At the most, a 10% mass loss was obtained when 5 doses of Fe^{3+} were added during the Fenton experiment. Furthermore, it must be noted that no significant changes were found in the FTIR spectrum of the oxidized microplastics compared with the fresh ones. These results confirm the high resistance of microplastics to be oxidized by the Fenton oxidation treatment.

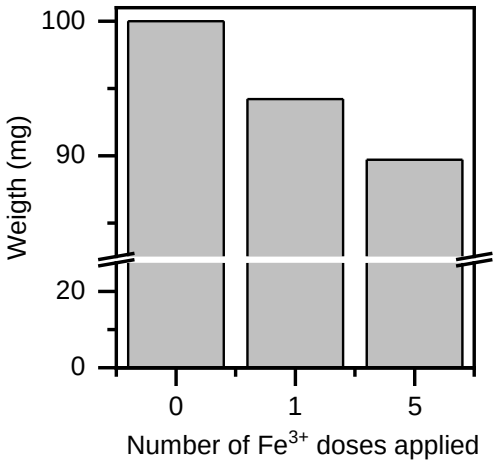

Figure 1. PS microplastics (100 – 250 μm) mass loss reached after oxidation using different Fe^{3+} doses.

Despite the low mass losses, microplastics suffered some changes in their surface along the oxidation treatment. As can be seen in the microscopic images of Figure 2, parts of the microplastics became transparent. On the other hand, it was visually evident that the hydrophilicity and wettability of microplastics was increased after the oxidation process. They were essentially floating on the water surface at the beginning of the reaction but at the end, they were well dispersed and even settled. Consistent with this observation, the water contact angle value was reduced around 10% while the pH_{slurry} was dramatically decreased up to 5.1.

The impact of the oxidation treatment on the surface chemistry of PS microplastics was further evaluated by analyzing the behavior of both fresh and oxidized solids in

the adsorption of the hydrophobic pharmaceutical diclofenac. As can be seen in Figure 3, a substantial decrease on the adsorption capacity of PS microplastics was found after their Fenton oxidation, which can be directly attributed to the presence of acid-type surface oxygen groups in their surface.

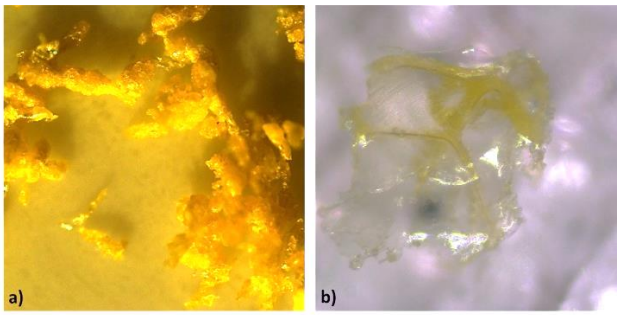

Figure 2. Optical microscopic images of PS microplastics (100 – 250 μm) before (a) and after (b) Fenton oxidation.

Another important observation found in the microplastics after Fenton oxidation is that the particles slightly reduced their size. The size distributions of fresh and oxidized PS microplastics (50 – 100 μm), measured by laser diffraction, are depicted in Figure 4. As can be seen, the percentage of microplastic particles below 50 μm clearly increased after the oxidation treatment, while those above this threshold value sharply decreased.

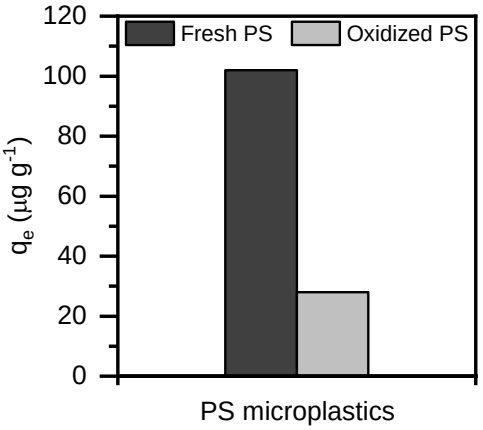

Figure 3. Impact of Fenton oxidation on the adsorption capacity of PS microplastics (100 – 250 μm) for diclofenac ($[DCF]_0$ = 15 mg L^{-1}; [microplastics] = 6.7 mg mL^{-1}; MP size = 100 – 250 μm; pH_0 = 7; T = 25 ºC).

3.2. Fenton oxidation of PS microplastics in the sub-micro range

The abovementioned results clearly confirmed that microplastics slightly reduced their size along the oxidation treatment. To get deeper insights onto the yield of the oxidation process, a new experiment was carried out using commercial PS particles in the sub-micro range (140 nm). As these microplastics were homogeneously dispersed in water, the evolution of their concentration was followed by analyzing the TOC along reaction. The obtained results are depicted in Figure 5. Remarkably, a high mineralization yield (75%) was achieved. Accordingly, microplastics undergo an oxidation process from the surface to the core of the particle, which ultimately leads to their complete oxidation to CO_2.

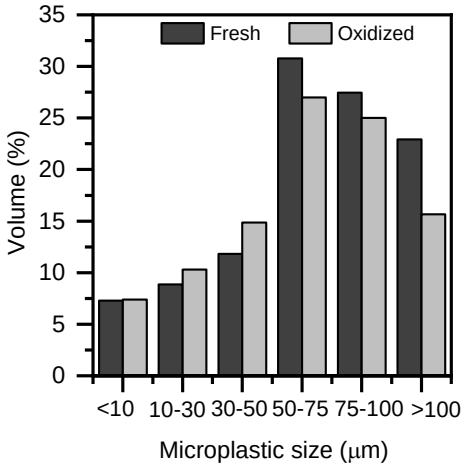

Figure 4. Impact of Fenton oxidation PS microplastics (50 – 100 μm) size distribution.

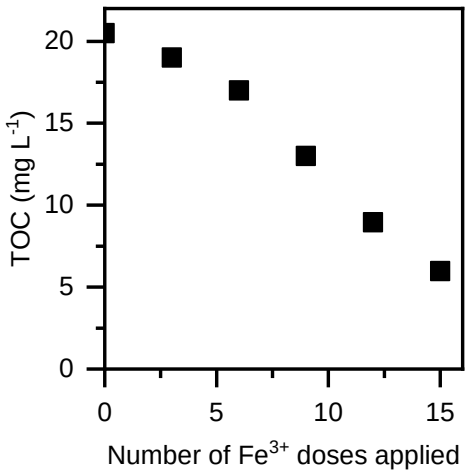

Figure 5. Evolution of PS sub-micro particles (140 nm) along Fenton oxidation.

3.3. Biodegradability of oxidized PS microplastics

Once confirmed that PS microplastics underwent a surface chemical oxidation that ultimately resulted in high mineralization yields, the leaching of both fresh and oxidized microplastics was analyzed in terms of biodegradability following the procedure described elsewhere (Romera-Castillo et al., 2018). After six days of incubation (photodegradation in aqueous saline media), fresh and oxidized PS microplastics leached 104 and 205 μM dissolved TOC. Bacterial incubation assays were carried out afterwards using those leaching solutions. Remarkably, 34 and 63 μM dissolved TOC were consumed in the fresh and oxidized PS microplastics,

respectively. In fact, bacterial growth efficiency was higher in the solution coming from the oxidized PS sample compared to the fresh one. Furthermore, it was confirmed that the leaching from oxidized PS microplastics did not inhibit bacterial growth.

4. Conclusions

The results obtained in this work have proved that PS microplastics undergo important changes along the high-temperature Fenton treatment. The oxidation process starts in their surface, leading to the formation of oxygen functional groups, which consequently increase their acidity and hydrophilicity. Furthermore, they progressively reduce their size, which ultimately results in their complete oxidation to CO_2. Remarkably, the dissolved TOC leached along the oxidation process does not inhibit bacterial growth.

Acknowledgements

This research has been supported by the Autonoma University of Madrid and Community of Madrid through the project SI1-PJI-2019-00006, and by the Spanish MINECO through the project PID2019-105079RB-I00. Munoz and J. Nieto-Sandoval thank the Spanish MINECO for the Ramón y Cajal postdoctoral contract (RYC-2016-20648) and the FPI predoctoral grant (BES-2017-081346), respectively. D. Ortiz thanks the Spanish MIU for the FPU predoctoral grant (FPU19/04816).

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