

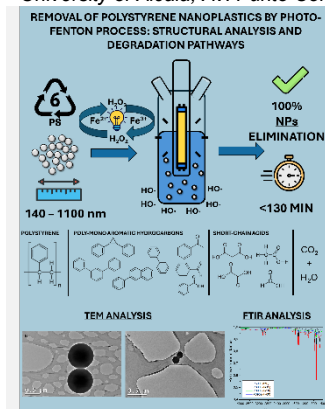
Removal of polystyrene nanoplastics by photo-Fenton oxidation: structural analysis and degradation pathways.

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WWTPs are not fully effective in removing MPs and NPs, thus the development of new technologies to mitigate the discharge of these particles into aquatic environments is currently a priority for the scientific community. AOPs, specifically the photo-Fenton process, appear as a promising technology for NPs removal, being an interesting alternative to conventional treatments. In this study, the elimination of PS NPs of various particle sizes was evaluated under optimized operating conditions, with a specific focus on analyzing structural modifications and generated degradation products. The photo-Fenton process proved effective in oxidizing the PS NPs. An increase in the carbonyl index of the samples was observed due to the addition of oxygenated functional groups on the NPs surface. Furthermore, a variety of polycyclic and monocyclic aromatic hydrocarbons were identified as reaction intermediates, along with short-chain acids. Notably, all these compounds were completely mineralized at the end of the reaction.

Introduction

Plastics have revolutionized modern society, offering versatility and convenience. However, their widespread use has led to a surge in plastic waste, resulting in the emergence of micro- and nanoplastics (MPs and NPs). These tiny particles pose significant environmental risks, particularly in aquatic ecosystems since water is the primary medium for their dispersion. Municipal Wastewater Treatment Plants (WWTPs) have recently been recognized as notable sources of MPs and NPs pollution for aquatic ecosystems [1]. Therefore, the development of clean and effective technologies for the removal of these persistent particles is imperative. Advanced oxidation processes (AOPs), specifically the photo-Fenton process, have been demonstrated to be effective in the removal of nanoplastics [2]. However, a comprehensive investigation into the modifications and by-products generated during the process is necessary to enhance understanding. The aim of this study was to assess the degradation of polystyrene (PS) NPs of varying sizes, with a particular focus on elucidating the structural modifications and degradation products arising during the process.

Material and Methods

Nitric acid (65%) and iron (III) nitrate (98%) were provided by Sigma-Aldrich. Hydrogen peroxide (33 w/w %) was sourced from Panreac. Four commercial monodisperse NPs samples were purchased from MicroParticles GmbH (140, 252, 460, 909, 1100 nm, 5% w/v). Oxidation experiments were carried out using deionized water as reaction matrix. An immersion-wall batch jacketed photoreactor (0.7 L) outfitted with a 150 W medium pressure mercury

lamp (UV-Vis Nova Light TQ-150, Pechl Ultraviolet) was used to conduct the oxidation experiments. The lamp was placed within a water-cooled quartz chamber, completed with a temperature control unit (Ministat 125, Huber). Turbidity tests (HI88713, Hanna) were conducted to monitor the oxidation assays and TEM images (JEM 2100, JEOL) were used to determine the evolution of particle size. ATR-FTIR spectroscopy analysis (Spectrum Two, Perkin Elmer) was employed for calculating the carbonyl index (CI). Pyrolysis-GC/MS (7890B, Agilent Techn.) allowed for the identification of intermediate compounds and ionic chromatography (790 IC, Metrohm) was used for the quantification of short-chain acids. Unless otherwise indicated, the NPs PS oxidation reactions were conducted under optimized operating conditions: $[NPs]_0 = 20 \text{ mg L}^{-1}$; $[Fe^{3+}]_0 = 1 \text{ mg L}^{-1}$, $[H_2O_2]_0 = 130 \text{ mg L}^{-1}$ and additional doses (130 mg L^{-1}) every 20-30 min; 25°C , $pH_0 = 3$.

Results and Discussion

The photo-Fenton process proved highly effective in removing PS NPs of different sizes (>99% reduction in turbidity). However, as can be observed in Figure 1A, turbidity evolution of PS NPs during the reaction depends on the particle size. An increase in the mean particle diameter significantly diminishes the PS NPs removal rate. Indeed, while complete removal of 140 nm particles was achieved within 40 min of reaction, particles measuring 1100 nm required longer reaction times (130 minutes). The analysis of TEM images enabled the observation of a progressive reduction in the nanoparticle diameter during the reaction. PS particle size decreased from 850 nm (initial sample, Figure 1B) to 223 nm (Figure 1C). According to these results the oxidation of PS

nanoparticles seems to occur from their outer surface towards their inner core. This observation was confirmed by TEM images for all the PS particle sizes assessed in this study (Table 1). Notably, a higher initial rate of particle volume reduction was observed with larger particle sizes, likely due to their greater exposed surface area. To gain further insights into the reaction mechanism, the evolution of the carbonyl index (CI) of the PS nanoparticles at various reaction times was investigated through analysis of the carbonyl region of FTIR spectra (Figure 2).

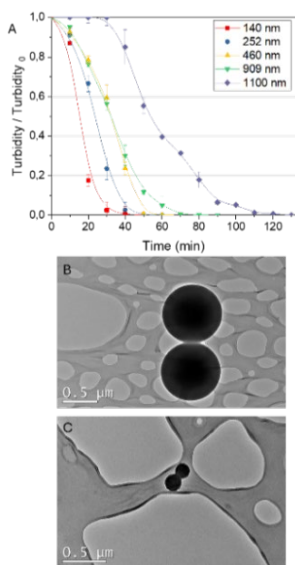


Figure 1. Evolution of turbidity in the oxidation of PS NPs (140 nm – 1100 nm) using photo-Fenton (A). TEM images of the initial sample of 909 nm NPs (B) and after 60 minutes of oxidation (C). ($[NPs]_0 = 20 \text{ mg L}^{-1}$; $[Fe^{3+}]_0 = 1 \text{ mg L}^{-1}$; $[H_2O_2]_0 = 130 \text{ mg L}^{-1}$ and dosage of 130 mg L^{-1} every 20 minutes; 25°C ; $pH_0 = 3$).

The rise in CI during the oxidation process (CI: 0.1 at 0 min, 1.0 at 15 min, and 1.9 at 60 min) indicates the incorporation of new oxygenated functional groups (carbonyl groups) onto the PS surface as the reaction progressed.

Conclusions

The photo-Fenton process proved effective in completely oxidizing a wide range of PS NPs regardless of their size. Oxidation occurred from the external surface to the inner core of the particle, resulting in the incorporation of oxygenated groups on the polymer surface, ultimately leading to the leaching of various aromatic intermediates (both polycyclic and monocyclic aromatic hydrocarbons) into the aqueous medium. The short-chain organic acids formed from the oxidation of these intermediates were subsequently mineralized to CO_2 and H_2O .

Acknowledgments

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On the other hand, the analysis using Pyr-GC/MS of the liquid fraction obtained from the samples withdrawn during the oxidation of PS NPs indicated the presence of a wide variety of aromatic intermediates formed in the early stages of the reaction. Both polycyclic (biphenyl, stilbene, chalcone, or naphthalene) and monocyclic (benzaldehyde, acetophenone and benzoic acid) aromatic compounds were identified. Additionally, at later stages of the reaction, various short chain organic acids such as acetic, formic, malonic, and oxalic acids were quantified using ion chromatography. It should be noted that these acids were completely mineralized to CO_2 and H_2O at the end of the reaction.

Table 1. Average particle size of NPs during different reaction times.

PS particle diameter (nm)	Time (min)	Measured particle diameter (nm)	Volume reduction* (%)
	0	137	0
140	20	99	61
	30	62	90
460	0	440	0
	40	216	88
	50	193	91

*Considering the reduction in size of spherical particles with the mean diameter measured by TEM.

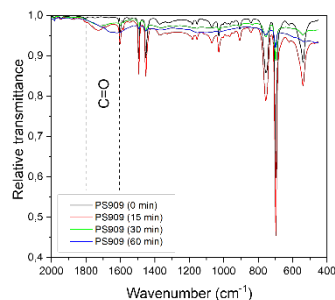


Figure 2. FTIR results for reaction times of 0, 15, 30, and 60 minutes ($D_0 = 909 \text{ nm}$, $[NPs \text{ PS}]_0 = 100 \text{ mg L}^{-1}$, $[H_2O_2] = 1000 \text{ mg L}^{-1}$ (dosing 500 mg L^{-1} every 30 minutes), $[Fe^{3+}] = 1 \text{ mg L}^{-1}$, $pH_0 = 3$, $T = 25^\circ\text{C}$).