Strategies for the Quantification and Characterization of Nanoplastics in AOPs Research: A Case Study for Polystyrene Nanospheres

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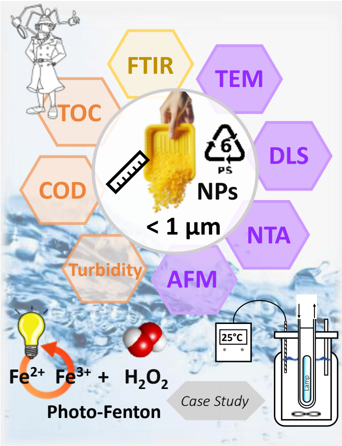

There is a growing interest in developing new degradation technologies for the removal of micro- and nanoplastics (NPs) in water. Recently, AOPs have been proposed as promising treatment alternatives for effective degradation of NPs in water. However, the selection of appropriate analytical methods for monitoring the oxidation tests remains a challenge. In this work, the feasibility of different characterization strategies for monitoring the evolution of NPs upon oxidation tests was systematically studied using polystyrene (PS) NPs of different particle sizes (D_0 = 140 − 909 nm). To quantify NPs, TOC, COD and turbidity were assessed. To characterize particle size, TEM, DLS, NTA and AFM were employed and compared. Chemical surface modifications were explored by FTIR and the carbonyl index was calculated. As a case study, PS NPs degradation upon photo-Fenton oxidation was investigated at ambient conditions and fully characterized using the mentioned techniques.

Introduction

Municipal Wastewater Treatment Plants (WWTPs) have recently been recognized as hotspots of micro- and nanoplastics (MPs and NPs) pollution in the aquatic environment. This issue has encouraged the development of novel and sustainable water treatment technologies to prevent the release of MPs and NPs from WWTPs within the scientific community. Recently has been indicated that AOPs hold great potential as tertiary treatments for the degradation of MPs and NPs in aqueous systems, with photo-oxidative treatments being the most promising alternatives [2]. However, NPs degradation has received considerably less attention than MPs, mainly due to the complexity of the analytical methods needed to monitor these tiny pollutants and the difficulty of obtaining representative NPs samples. The aim of this work was to investigate the application of different characterization techniques for following the degradation of NPs in water using AOPs. To achieve this goal, PS NPs of different particle sizes were used as model plastic pollutants, and their oxidation upon photo-Fenton treatment was fully characterized using different analytical tools.

Material and Methods

Four commercial PS nanospheres were purchased from MicroParticles GmbH (140, 252, 460, 909 nm, 5% w/v), labeled as: PS140, PS252, PS460 and PS909. Oxidation experiments were performed in an immersion-wall batch jacketed photoreactor (0.7 L) equipped with a 150 W medium pressure Hg lamp (UV-Vis Nova Light TQ-150, Peschl Ultraviolet). The experimental set-up was detailed in a previous contribution [2]. The tests were carried out under optimized operating conditions: $[PS\ NPs]_0$ = 100 mg L^{-1}; $[H_2O_2]_0$ = 1000 mg L^{-1} (H_2O_2 dosed every 30 min, 500 mg L^{-1}); pH_0 = 3 and T = 25 ºC. Turbidity measurements (HI88713, Hanna) were conducted to monitor NPs' concentration. Mineralization was followed by TOC (Shimadzu TOC VSCH) and COD. Particle size was determined by TEM (JEOL JEM 2100). Alternatively, the mean diameter was measured by DLS (Zetasizer Ultra, Malvern), NTA (NanoSight NS300, Malvern), and AFM. Surface chemistry was evaluated by FTIR (Perkin Elmer), and the carbonyl index (CI) was calculated.

Results and Discussion

Turbidity depends on the size, shape, concentration, and refractive index of suspended particles, making it a fast and simple methodology to monitor NPs concentration in clear water matrices. Fig.1A displays the dimensionless turbidity evolution of PS NPs with different particle sizes upon photo-Fenton treatment. As can be observed, the turbidity of the reaction medium decreases from its initial value until reaching completely clear solutions within 75−90 min reaction time (see insert in Fig.1A). Accordingly, when larger PS particles are being treated, the PS NPs removal rate slows down slightly, likely due to both a reduced surface-to-volume ratio and lower irradiance reaching the NPs surface. Mineralization levels can be properly followed by TOC and COD measurements (Fig.1B). These methods are inherently destructive and do not depend on particle size and nature of the pollutants but to the oxidizable matter content. It is important to highlight that the TOC instrument can be damaged due to NPs accumulation in the piping and sampling/injection systems, and consequently, it is recommended for small particles (≤150 nm) or advanced stages of the reaction. Conversely, COD analysis allows complete digestion of solid particles, making it a robust method to follow mineralization level. Under the studied conditions, a remarkable level of mineralization (> 80% TOC removal and 95% COD removal) of PS140 was achieved within 90 min reaction time (Fig.1B). Moreover, the mineralization rate appears to be slower than the plastics degradation, owing to the accumulation of leached intermediates.

TEM analysis confirmed the sphericity and monodispersity of PS NPs under study (Fig.1C). It is important to note that an accurate determination of both mean diameter and particle size distribution requires a thorough count of particles, which can be time-consuming. As photo-oxidation proceeds, the particles decrease in size, from the surface to the core, finally disappearing. For instance, after 45 min reaction time, PS NPs achieved a mean diameter of 98.3 nm and a volume reduction of 63.4%. Furthermore, PS NPs conversion could be calculated from TEM analysis considering the particle geometry, aligning closely with the results obtained from turbidity measurements (not shown). Alternatively, particle size was analyzed by DLS and NTA. It should be remarked that these techniques provide bulk measures of the hydrodynamic diameter. On one hand, DLS, owing to its intrinsic limitations, yielded mean diameters somewhat higher than those obtained by TEM. On the other, NTA was suitable to tracking smaller particles (≤ 300 nm). However, oxidized samples may form aggregates, preventing the determination of individual particle size. In addition, AFM analysis yielded mean diameters similar to those determined by TEM (Fig.1D). For PS140, fresh samples yielded sizes of 137.4 and 137.7 nm for TEM and AFM analysis, respectively. After 45 min reaction time, the size of PS NPs decreased to 98.3 and 96.8 nm for TEM and AFM analysis, respectively.

Typically, FTIR analysis of MPs/NPs involves the determination of the CI. For PS909, the CI values increased from 0.12 (0 min) up to 1.9 (60 min), corroborating the incorporation of oxygen atoms upon photo-Fenton treatment.

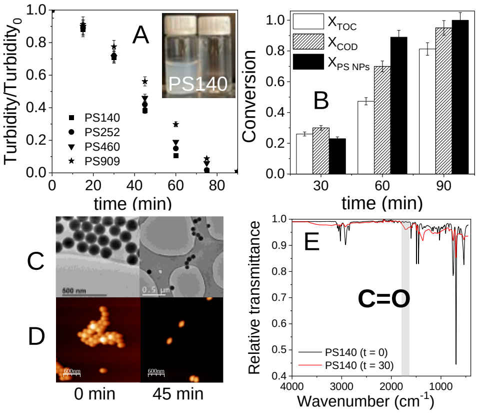

Figure 1. Characterization of photo-Fenton oxidation of PS NPs: A) Turbidity evolution, B) Conversion and mineralization levels for PS140, C) TEM images of PS140 at 0 and 45 min reaction time, D) AFM results for PS140, and E) FTIR spectra at 0 and 30 min reaction time.

Conclusions

To summarize, turbidity, TOC, and COD measurements clearly provide representative conversion values for monitoring the advanced oxidation of PS NPs in water. Morphology and particle size can be accurately determined by TEM and AFM, while DLS and NTA did not perform well in characterizing these samples. The incorporation of oxygen atoms upon oxidation treatment can be assessed by FTIR, by calculating the CI.

Acknowledgments

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