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Nanoplastics mineralization by the intensified photo-Fenton process

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Abstract
The widespread presence of microplastics (MPs) and nanoplastics (NPs) in aquatic systems has become one of the most challenging environmental issues nowadays. Although advanced oxidation processes (AOPs) have been widely studied for the treatment of persistent contaminants in water, their application for MPs and NPs removal have been scarcely addressed. In this study, the degradation of polystyrene NPs of different sizes (909 nm and 140 nm) by intensified photo-Fenton oxidation has been evaluated. The degradation experiments (6 hours) were carried out at 80ºC and pH_0=3 in a pyrex glass reactor, using an initial NPs concentration of 20 mg/L. The initial concentrations of H_2O_2 and Fe^{3+} were set at 130 mg/L and 10 mg/L, respectively, introducing additional doses of H_2O_2 to enhance the oxidation yield. Firstly, photolysis was evaluated, demonstrating that NPs are poorly degraded only by irradiation (8% mineralization). The addition of H_2O_2 (UV/H_2O_2 treatment) significantly improved the mineralization of NPs (53% mineralization regardless NP size). Finally, by the intensified photo-Fenton reaction, using Fe salts as catalyst, almost complete mineralization was achieved with both NPs (82% and 94% with NP size of 909 nm and 140 nm, respectively). These results are very promising for the elimination of plastic waste in water.

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

1. Introduction

Due to their exceptional physical and chemical properties, durability and low cost, plastics have become an indispensable material for both industry and society nowadays, increasing the worlds plastic production to almost 370 million tons in 2019 (*PlasticsEurope, 2020*). Although their benefits to the economy and the daily life are undeniable, the generation of plastic wastes represents a serious environmental problem. Microplastics (MPs) and nanoplastics (NPs), plastic materials smaller than 5 mm and 0.1 μm, respectively; are the most widespread plastic residues in the environment, detecting its presence in almost all ecosystems, whether in continental or oceanic waters, in sediments, on the ground and even in bottled water; appearing in the same way within living organisms, especially in aquatic ones (*Rezania et al., 2018*; *Cox et al., 2019*).

Although a 90-99% removal efficiency of MPs has been reported in wastewater treatment plants (WWTPs), particles of particularly small sizes (<300 μm) present greater problems for their removal (*Sol et al., 2020*). Consequently, new technologies need to be developed for the degradation of these plastic wastes.

Advanced oxidation processes (AOPs) have been widely studied for the treatment of persistent contaminants in water such as pesticides, dyes or drugs (*Malakootian et al., 2020*; *Bhat and Gogate, 2021*; *Kanakaraju et al., 2018*; *Ma et al., 2021*). Nevertheless, their use in plastic waste is currently starting to be studied.

Among these AOPs, the most studied to date is heterogeneous photocatalysis. Various authors have utilized heterogeneous nano-catalysts based on zinc oxide (ZnO) for the degradation of microplastics, reporting the appearance of cracks, holes and spots on the surface of the microplastic (*Tofa et al. 2019*) or the decrease in average particle size from 154.8 μm to 108.2 μm (*Uheida et al., 2021*) under visible light radiation. In addition, *Ariza-Tarazona et al., (2020)* have reported a maximum average mass loss of 72% using a protein-derived C,N-TiO_2 particle semiconductor as a nano-catalyst under visible light conditions. On the other hand, *Nabi et al., (2021)* has recently achieved a complete mineralization of polystyrene (PS) and polyethylene (PE) microplastics using TiO_2 films as catalysts under 24-36 hours of UV light irradiation.

Some authors have studied the effect of homogeneous Fenton-type reactions on various microplastics, showing that under ambient conditions, these processes do not cause significant changes in microplastics (*Tagg et al., 2017*; *Lang et al., 2020*; *Hurley et al., 2018*).

Photo-Fenton process presents similar chemical reactions but enhanced by irradiation of light than contribute to a faster Fe(II) specie regeneration. This photo-assistance process reduces the quantity of catalyst needed to promote the generation of HO· radicals, which quickly interact with organic compounds, and thus helps increasing the decomposition rate of the organic matter (*Silanpää et al., 2018*). These processes generally present higher rates of

degradation of organic matter than processes based on heterogeneous photocatalysis and present a more efficient consumption of hydrogen peroxide than the conventional Fenton process (*Matafonova and Batoev, 2018*). Despite these advantages over other AOPs, photo-Fenton process has hardly been used for the treatment of microplastic waste.

In this study, the degradation of polystyrene nanoparticles of two different sizes (909 nm and 140 nm) by intensified photo-Fenton treatment has been evaluated, with the aim of extending it to larger sizes of microplastic.

2. Materials and methods

2.1. Materials and chemicals

Nitric acid (65%) (CAS No.: 7697-37-2) for acidification, $TiOSO_4$ (99%) (CAS No.: 13825-74-6) for hydrogen peroxide determination and hydrogen peroxide solution (30% w/v) (CAS No.: 7722-84-1) were provided by Sigma-Aldrich. Iron (III) nitrate nonahydrate (98%) (CAS No.: 7782-61-8) was supplied by PanReac.

Two commercial NP samples of monodisperse PS, PS-R-KM248 (0.140 ± 0.005 µm, 5% w/v) and PS-R-KM123 (0.909 ± 0.027 µm, 5% w/v), were purchased from microParticles GmbH. These PS nanoparticles are prepared via free radical initiated polymerization techniques, obtaining spherical particles with high mechanical and chemical stability as well as low density (1.05 g/cm^3) (*microParticles GmbH*).

2.2. Oxidation of nanoplastics

Degradation experiments (6 hours) were performed at 80ºC and pH_0=3 in an immersion-wall batch jacketed 1 L photoreactor equipped with a 150 W medium pressure Hg lamp (TQ-150 from Heraeus) contained in a water-cooled quartz chamber provided with a temperature control unit Ministat 125 (Huber). All experiments were magnetically stirred at 500 rpm. The lamp emits in a broad spectrum between 250 and 600 nm with a UV-irradiance of 30 W/m^2 measured with a broad range photoradiometer (Delta Ohm, model HD 2102.1). The reaction volume and the initial concentration of nanoplastics were established at 700 mL and 20 mg/L, respectively. The initial concentrations of H_2O_2 (UV/H_2O_2 and photo-Fenton) and Fe^{3+} (photo-Fenton) were set at 130 mg/L and 10 mg/L, respectively. To enhance the oxidation yield, additional H_2O_2 doses (91 g/L, 1 mL) were added every 30 minutes to achieve a concentration of 130 mg/L, corresponding with the complete consumption of H_2O_2. A blank experiment in the absence of Fe^{3+} and H_2O_2 was carried out for both sizes of nanoplastics to check the possible role of NPs photolysis along the oxidation reactions.

2.3. Analytical methods

Total organic carbon (TOC) and Total Inorganic Carbon (IC) of the samples (without filtration) were measured using a TOC analyzer (Shimadzu, mod. TOC-L).

A UV 2100 Shimadzu UV–vis spectrophotometer was used to determine H_2O_2 concentration by colorimetric $TiOSO_4$ method (*Eisenberg, 1943*), and to determine the turbidity of the reaction medium at 720 nm.

3. Results and discussion

3.1. Photolytic reactions

In preliminary experiments, the possible photolysis of nanoplastics was investigated under the same operating conditions of the oxidation tests but in the absence of H_2O_2 and Fe^{3+}. The results obtained are depicted in Fig. 1. As can be seen, regardless of the nanoplastic size, the mineralization yield was approximately 8%. These results indicate that photolysis cannot promote effective degradation, requiring a large amount of energy to obtain a minimal mineralization result.

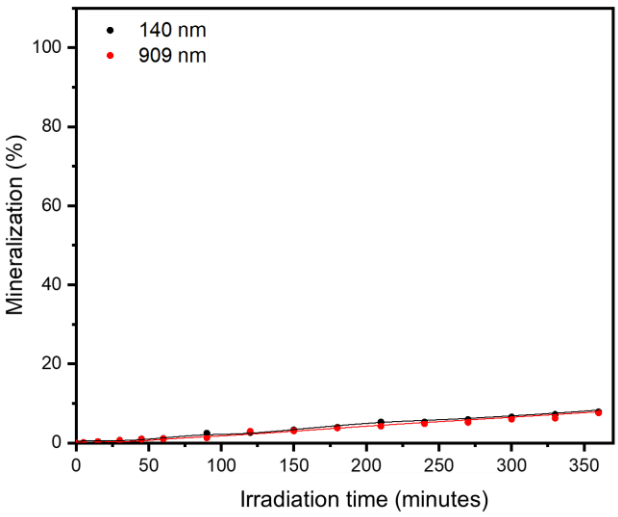

Figure 1. Mineralization plots of the NPs during photolysis

3.2. UV/H_2O_2 reactions

Fig. 2 presents the evolution of nanoplastic mineralization upon the UV/H_2O_2 treatment for both sizes of nanoplastics. Clearly, nanoplastics removal was higher than the obtained in the absence of H_2O_2. This result can be explained by the presence of hydroxyl radicals generated by the UV/thermal decomposition of H_2O_2. Quite similar results were obtained in the mineralization yield (around 53%) for both nanoplastic sizes, although the size of 140 nm showed a slightly higher initial oxidation rate. Apart from TOC evolution, the turbidity of the reaction medium was followed. A clear decrease in the turbidity of the samples was evidenced along the oxidation experiments, reaching a final decrease of 60% approximately.

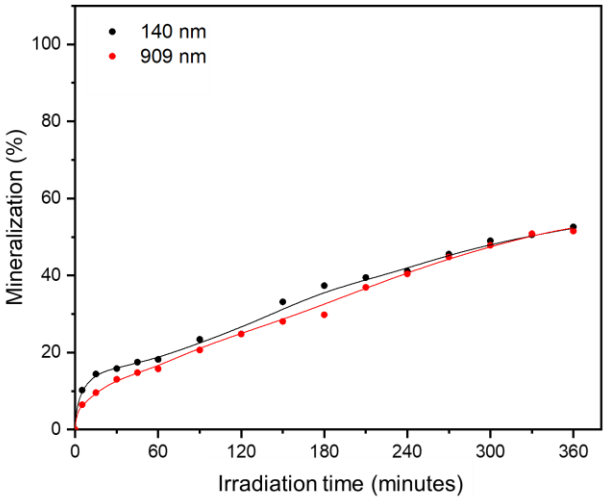

Figure 2. Mineralization plots of the NPs during UV/H_2O_2 experiments

3.2. Photo-Fenton reactions

The results obtained in the photo-Fenton oxidation of NPs are depicted in Fig. 3. The presence of iron as catalyst certainly enhanced the generation of hydroxyl radicals from H_2O_2 and thus, led to a substantial increase in the mineralization yield of NPs. It must be noted that the catalyst activity is particularly effective in the photo-Fenton system as the Fe^{2+}/Fe^{3+} redox cycle is favored by the activation of light (*Matafonova and Batoev, 2018*). In the same line, it is well-known that Fenton oxidation at high temperature increases the efficiency on the consumption of H_2O_2 (*Carbajo et al., 2021*). All in all, up to 94% mineralization was achieved with 140 nm NPs after 6 h reaction time compared to the 53% reached using the UV/H_2O_2 system.

Although a high degree of mineralization is always obtained, this is greater in the case of nanoplastic of 140 nm (94%) than in the case of the 909 nm size (82%). This may be because a smaller particle size presents a greater exposed surface, thus favoring its interaction with HO· radicals.

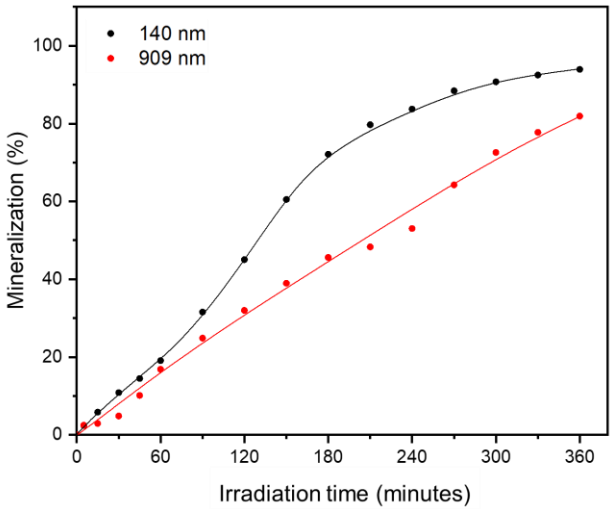

Figure 3. Mineralization plots of the NPs during photo-Fenton experiments

In this reaction, the degradation of the NPs was again evident due to a decrease in the turbidity of the aqueous suspension. However, in this case this effect was noticed after 180 minutes of reaction (after 50% mineralization) similar to the final result of the previous case.

Once the reaction was completed, a decrease in turbidity greater than 95% was reached for both particle sizes, indicating that the remaining TOC corresponds to dissolved carbon species.

Fig. 4 shows a visual comparison of the turbidity of the reaction medium before and after the different treatments studied in this work for the smaller particle size.

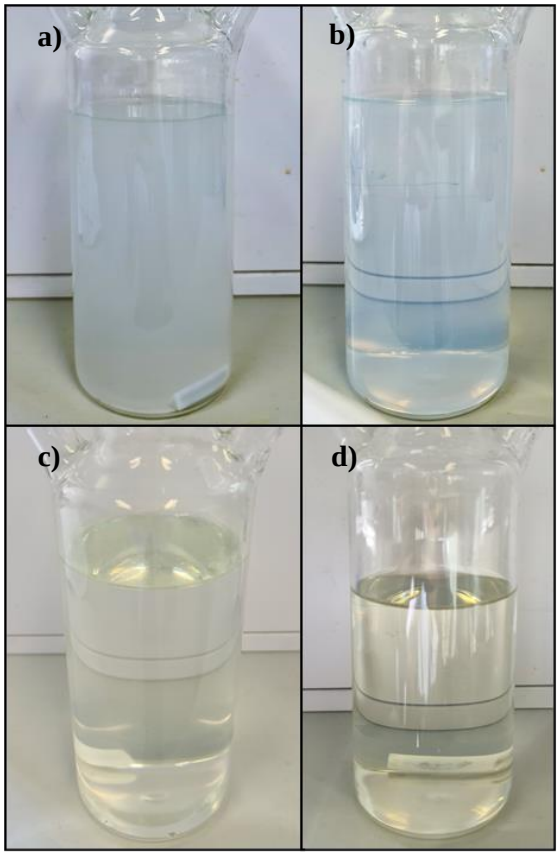

Figure 4. Visual comparison of turbidity of the reaction medium with the particle size of 140 nm **a)** before any treatment, **b)** after 6 hours with UV/H_2O_2 treatment, **c)** after 2.5 hours with intensified photo-Fenton treatment and **d)** after 6 hours with intensified photo-Fenton treatment

4. Conclusions

Intensified photo-Fenton oxidation has proved to be an effective process for the elimination of nanoplastics from water. Up to 94% mineralization was reached when 140 nm nanoparticles were treated. A slight decrease in the mineralization yield was found with 909 nm nanoparticles, where 82% mineralization was achieved. Nevertheless, in both cases, turbidity was completely eliminated from the reaction medium and thus, only dissolved TOC was present at the end of the reaction. Further research is required to deep on the effect of microplastics size on the performance of the process as well as to analyze the nature of the compounds leached from the solids. In any case, the

results obtained in this work are very promising for the elimination of plastic waste in water, overall dealing with highly polluted wastewaters.

Acknowledgments

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