The Effect of Photo-Fenton, Heterogeneous Fenton and UV/H_2O_2 Processes on Organic Matter and Surface of Aged/Pristine Fibres

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Microplastic microfibres (MFs) are a primary type of pollutant because they are commonly found in freshwater receiving effluents from wastewater treatment plants, indicative of inefficient treatment. This investigation addresses the impacts of Advanced Oxidation Processes (AOPs) photo-Fenton, Heterogeneous Fenton and UV/H_2O_2 on different water matrices containing fibres. The effectiveness of treatments was measured through dissolved organic carbon (DOC) and by assessing the surface of MFs using optical and scanning electron microscopies, micro-Raman spectroscopy, and FTIR analysis. Photo-Fenton applied to tap water added with pristine fibres was less effective in reducing DOC and modifying the surface of MFs compared to results obtained from washing machine wastewater containing aged MFs. Toxicity tests revealed that intermediates from AOPs were not toxic to E.coli. These findings suggest that the same AOP applied to aged and pristine fibres may have differing efficiency levels, thereby, pointing towards ways to improve treatment for fibres contaminating water within wastewater management systems.

Introduction

One of the most prevalent sub-groups of microplastics (MPs) found in aquatic environments is microfibres (MFs), particularly those made of polyester (PEST), which are significant due to their abundance in various environments, including wastewater treatment plants (WWTP) [1]. Despite the increasing number of publications focusing on the degradation of MPs, there remains a notable gap in the application of Advanced Oxidation Processes (AOPs) for the degradation of organic matter and MFs. From this perspective, the present study evaluates the application of different AOPs in water matrices containing fibres (under both pristine and aged conditions) to assess the decay of organic compounds. The novelty of this study lies in investigating the effectiveness of various AOPs in real aqueous matrices containing fibres from different sources.

Material and Methods

Water samples with markedly different matrices were collected from sources to investigate the effect of AOPs on PEST MFs. The water samples consisted of (i) washing machine wastewater containing a mixture of aged MFs, obtained by washing a 100% PEST blanket (pink colour, size 1.40 x 2.0 m) for 1.5 h at 30 ºC without detergent, and (ii) tap water supplemented with pristine PEST fibres (0.100 g. L^{-1} of 0.5 cm MF length). The photo-Fenton and photolysis tests were conducted using a photo reactor equipped with UVC light (11 W, 240 V, 254nm wavelength, 35 µmol m^{-2} s^{-1} light density, Philips) with air pumped at 6.4 L/min [2]. Hydrogen peroxide (50% w/w H_2O_2) and zero valent iron powder (pZVI, 0.45 µm) were dosed accordingly. The organic content was determinate by DOC analysis (TOC-L CPH model TOC analyser), and all experiments were conducted in triplicate. Toxicity evaluation tests on the treated water, using the filter paper disk method [3], were carried out with E.coli, including several control tests conducted in triplicate. The surfaces of MFs were characterized before and after AOP treatment using scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS), stereo microscope, Fourier-transform infrared spectroscopy (FTIR), and micro-Raman spectroscopy.

Results and Discussion

The effects of the AOPs on the DOC content in the washing machine wastewater are shown in Figure 1. The photo-Fenton process achieved a 70% removal of DOC. The synergy between p-ZVI and H_2O_2 with UVC irradiation (previous studies have reported greater MF degradation efficiency when 254 nm - UVC was applied) enhanced the formation of radicals with oxidative potential. These radicals can react with both the organic carbon structure and the surface of MFs [4].

The ORP (Oxy-Reduction Potential) in the photo-Fenton reached a peak value of 441 mV at 15 min of reaction time from an initial ORP of 29 mV, indicating a strong oxidizing environment. Subsequently, the ORP decreased, reaching 39 mV after 150 min, indicating effective consumptions of oxidative radicals [5]. This drop in ORP corresponded with the reduction in DOC values, confirming the oxidative action on the wastewater. In contrast, the ORP values in UV/H_2O_2 and heterogeneous Fenton did not decrease at similar times, suggesting a lower rate of oxidative radical consumption in these AOPs and potentially less efficient treatment. Therefore, longer AOP reaction times are considered necessary for heterogeneous Fenton and UV/H_2O_2 treatments. The variation in DOC values observed in both AOPs at certain reaction times (Fig. 1) may be related to the formation of intermediate products [4]. In the absence of AOP treatments, the PEST pink fibres from the wastewater

already exhibited an aged surface (as shown in Figure 2 (a)). Additionally, SEM micrographs revealed that after 180 min of UV/H_2O_2 treatment, the MFs appeared to have undergone a less aggressive effect on the surface (Fig. 2 (b)) compared to MFs oxidized from Fenton-based processes (Fig. 2 (c) and (d)). This indicates the different oxidative effects of AOPs on the fibres subjected to treatments.

Additional tests were conducted to examine the effect of photo-Fenton on pristine fibres (100% PEST) added to tap water, using the same experimental conditions as with the wastewater samples. However, the removal of DOC in the tap water was not as effective as observed in the wastewater samples. Instead, there was an increase in DOC values followed by their relative stability up to 180 min under the applied oxidizing conditions. To compare the extent of DOC removal, experiments with double the dosage of reagents were conducted. However, the results showed a greater concentration of DOC at certain reaction times (e.g. DOC = 53.0 mg.L^{-1} in 15 min) with no significant improvement in its removal. Furthermore, the variation in DOC values observed in these experiments suggested a possible formation of intermediates during photo-oxidative treatment. Microscope and FTIR results obtained from the surface of the fibres revealed no substantial differences on their surface before and after treatment, although SEM provided highly localised analysis.

Toxicity test with E.Coli conducted at different reaction times for Fenton-based processes and UV/H_2O_2 indicated no inhibition zones in the filtrates, suggesting that the intermediates are not toxic to E.coli.

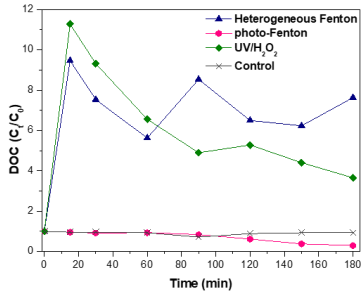

Figure 1. DOC in wastewater machine with mixed fibres during 180 min of (a) photo-Fenton, (b) heterogeneous Fenton, (c) UV/H_2O_2, and (d) control experiments (wastewater without reagents). Experimental conditions: pZVI = 1 g.L^{-1} (<0.45 µm), H_2O_2 = 2 g.L^{-1}; initial pH = 3. Initial DOC = 2.5–5.5 mg.L^{-1}.

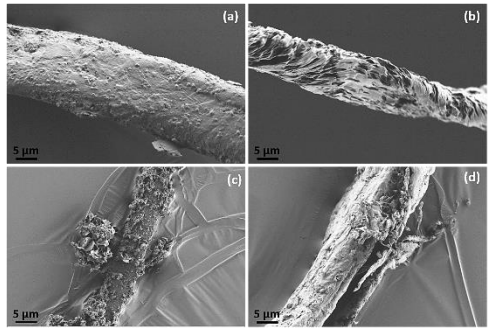

Figure 2. SEM micrographs of the PEST MFs from wastewater machine (a) before AOPs, (b) after UV/H_2O_2, (c) after heterogeneous Fenton, and (d) after photo-Fenton process.

Conclusions

Photo-Fenton (pZVI = 1 g.L^{-1}, H_2O_2 = 2 g.L^{-1}; adjusted pH = 3) achieved a reduction in DOC of up to 70% in washing machine wastewater. However, the same AOP demonstrated low effectiveness in tap water containing pristine fibres. This highlights the variable effectiveness of AOPs across diverse water matrices and the enhanced resistance to degradation of newer fibres. Results from the oxidation of fibres revealed that water with intermediates resulting of the AOPs did not exhibit toxicity to E. coli under the conditions tested. However, the formation of intermediates and their potential toxicity to other organisms during the studied AOPs must be considered, especially for other composition of MPs that could release toxic components.

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