Preliminary assessment of microfibres amount in textile wastewater

# PRELIMINARY ASSESSMENT OF MICROFIBERS AMOUNT IN TEXTILE WASTEWATER

Sinem Hazal Akyildiz[1], Rossana Bellopede[2], Silvia Fiore[2], Bahattin Yalcin[4], Hande Sezgin[5] and Ipek Yalcin-Enis[5]

[1] *Department of Textile, Marmara University, Turkey*
[2] *Department of Engineering for Environmet, Land and Infrastructures, Politecnico di Torino, Italy*
[4] *Department of Anorganic Chemistry, Marmara University, Turkey*
[5] *Department of Textile Engineering, Istanbul Technical University, Turkey*

ABSTRACT: Textile wastewater is a complex mixture of inorganic compounds, polymers, organic products, dyes, and microfibers (MFs), including microplastics (MPs) and natural fibers. The treatment of textile wastewater, which contains a significant share of MFs, is of great importance to prevent the release of MPs in the environment. MPs analysis requires multiple phases of pretreatment (to eliminate the organic compounds), separation of the MFs from the water, and identification of the MPs among the MFs. This work presents the preliminary results of a research aimed at exploring two issues. Firstly, the pretreatment (through Fenton, $H_2O_2$, HCl, KOH and NaOH, applied at 25 °C for 5 days and 60 °C for 6 hours) of artificial textile wastewater, evaluating the effect of the different conditions on the MFs and the MPs. Secondly, the separation of MFs from a real textile wastewater sample through different processes (centrifugation, sink-float & filtration, filtration). The results of the pretreatment tests revealed Fenton, HCl, and $H_2O_2$ at 25 °C for 5 days as the best performing chemicals and conditions. Considering the results of the separation tests, filtration gave back the best removal of the MFs from wastewater compared to centrifugation and sink-float and filtration, which left some MFs in the supernatant/float and in the sediment/sink. In conclusion, these preliminary results may be useful to further explore the detection of MFs and MPs in textile wastewater.

*Keywords: centrifugation, filtration, microfibers, microplastics, pretreatment, separation, textile wastewater*

## 1. INTRODUCTION

Since the 1930s, plastics have been manufactured in large amounts and used in a wide variety of applications (Westphalen & Abdelrasoul, 2018). Nowadays plastic particles account for 60 to 80 percent of marine litter (Bergeron, 2016). Microfibers (MFs), which can be natural or synthetic (i.e., microplastics, MPs), are fibrous microparticles with a length of up to 5 mm. MPs can accumulate in marine organisms and be transferred through the food chain to higher trophic levels, including humans (Zhang et al., 2020; Issac and Kandasubramanian, 2021). According to the International Union for Conservation of Nature (IUCN, 2017), MPs discharged into the environment during the washing of synthetic textiles may account for up to 35 % of the primary sources of MPs polluting the oceans. MPs are biologically resistant and may be responsible for adverse biological reactions in humans, such as inflammation, genotoxicity, oxidative stress, be localized cell and lead to tissue damage, fibrosis, and potential carcinogenicity (Esmeray and Armutcu, 2020).

Textile industry, which has very large production volume at global level, leaves behind solid and liquid

waste flows (Šajn, 2019). The textile industry is highly plastic-intensive; by 2020, synthetic fibers accounted for 62 % of global fibers production (Fernández, 2021), and the textile industry is a significant source of MFs (Zhou et al., 2020). Textile wastewater contains dyes and finishing chemicals that could pollute surface water and groundwater (Islam & Islam, 2021), and MFs can be released during dyeing and washing processes (Liu et al., 2021). Up-to-date industrial wastewater treatment technologies can remove about 85 % of MFs from textile wastewater, however the amount of MFs in textile wastewater is much higher than in municipal wastewater treatment plants (Zhou et al., 2020).

MPs detection is based on a multi-phase process, usually involving: a pretreatment of the water sample with a chemical reagent able to destroy organic compounds; separation of the MFs; and detection of the MPs within the MFs. While MFs may be detected through optical microscopy, MPs identification within MFs is based on microscopy coupled to Fourier Transform Infrared (micro-FTIR) spectroscopy. Several methods are available to separate MFs from water, as sink-float separation, centrifugation, digestion and filtration (Nguyen et al., 2019). Sink-float separation is a reliable approach because the polymers often differ in density, and water-dense components sink. The digestion procedure, based on the use of strong oxidizing acids (e.g., sulfuric and nitric) should be carefully applied, as it damages MPs (Liu et. al, 2020).

This study was aimed at investigating two specific phases of MFs and MPs detection in textile wastewater, e.g., the pretreatment of the water sample, and the separation of the MFs. In details, the pretreatment (through Fenton, $H_2O_2$, HCl, KOH and NaOH, applied at 25°C for 5 days and 60°C for 6 hours) of an artificial textile wastewater was explored, evaluating the effect of the different conditions on the MFs and the MPs. Secondly, the separation of MFs from a real textile wastewater sample through different processes (centrifugation, sink-float & filtration, filtration) was studied, comparing the efficiencies of the considered processes towards the separation of MFs from the aqueous phase. The MFs have been identified and measured through optical microscopy.

## 2. MATERIALS & METHODS

### 2.1. Samples origin

A synthetic textile wastewater was prepared in a laboratory high-temperature dyeing machine by dyeing 5 g of acrylic yarn with 0.2 L distilled water, a cationic dye (Maxilon blue, CIBA-GEIGY) dosed to obtain 1 % color intensity, and 10 %-wt $Na_2SO_4$ (Kent Kimya) to allow the dye to thoroughly permeate the fabric.

A real wastewater sample was provided by Kadifeteks (www.kadifeteks.com), a Turkish textile company. A 1.5 L sample was collected from the inflow of the internal wastewater treatment facility, which applies a physic-chemical process.

### 2.2. Samples pretreatment

Various chemicals in different concentrations (15 % $H_2O_2$, Fenton, 20 % HCl, 10 % KOH and 20 % NaOH, Sigma-Aldrich) have been tested to remove organic substances from the synthetic wastewater sample adopting two process conditions: 25 °C for 5 days and 60 °C for 6 hours. The real wastewater sample was pretreated with 15 % $H_2O_2$ at 25 °C for 5 days.

### 2.3. Analyses of microplastics

The pretreated synthetic water samples underwent centrifugation (6000 rpm for 30 min), and the sediments have been dried at 50 °C overnight (Figure 1). The dried residues have been analyzed with an Olympus SZ51 optical microscope to detect and measure the MFs, and then the MPs have been identified through a Perkin Elmer Spectrum 65 Fourier Transform Infrared (FTIR) spectroscope.

### 2.4. Separation of microfibers

The pretreated real wastewater sample was divided into three 0.5L aliquotes, each subjected to a different separation method and then filtered on 0.7 µm pore size glass fiber (GF) (Whatman, Ø 47 mm). Centrifugation was performed at 6000 rpm for 20 minutes, producing two phases: the sediments and the supernatant, both filtered on GF and dried at 40 °C overnight. In the sink-float method, 150 g of NaCl was added to the pretreated sample, then left to settle for 1 day. After that, the supernatant was filtered on GF and the residue was dried at 40 °C overnight. Filtration was performed on GF using three filters in sequence, then dried at 40 °C overnight.

### *2.5. Analyses of microfibers*

The MFs collected on the GF filters residues deriving from the separation tests have been identified and measured through an ORTHOLUX II POL-MK optical microscope using normal and UV light, which enables the detection of fibers containing UV stabilizers.

## 3. RESULTS AND DISCUSSION

The FTIR analysis of the acrylic MFs extracted from the synthetic wastewater after the different pretreatments (Figure 1) revealed that the peaks obtained from water treated with HCl, $H_2O_2$ and Fenton reagent are consistent with the acrylic peaks obtained from the literature (C-H stretching at 2920-2860, CΞN stretching at 2242, C=O stretching at 1733, and C–C stretch in-ring at 1452) (Sigma Aldrich, 2022). Some of these typical peaks haven't been observed in the MFs obtained from with KOH and NaOH, probably because the alkali damaged the chemical structure of the acrylic fibers. In overall, there is no significant difference comparing the two different pretreatment conditions (25 °C for 5 days, and 60 °C for 6 hours).

The microscopic images (Figure 2) of the MFs isolated from the pretreated synthetic wastewater showed that the acrylic fibers can be clearly detected in all samples except those treated with NaOH, accordingly with the results of the FTIR analyses.

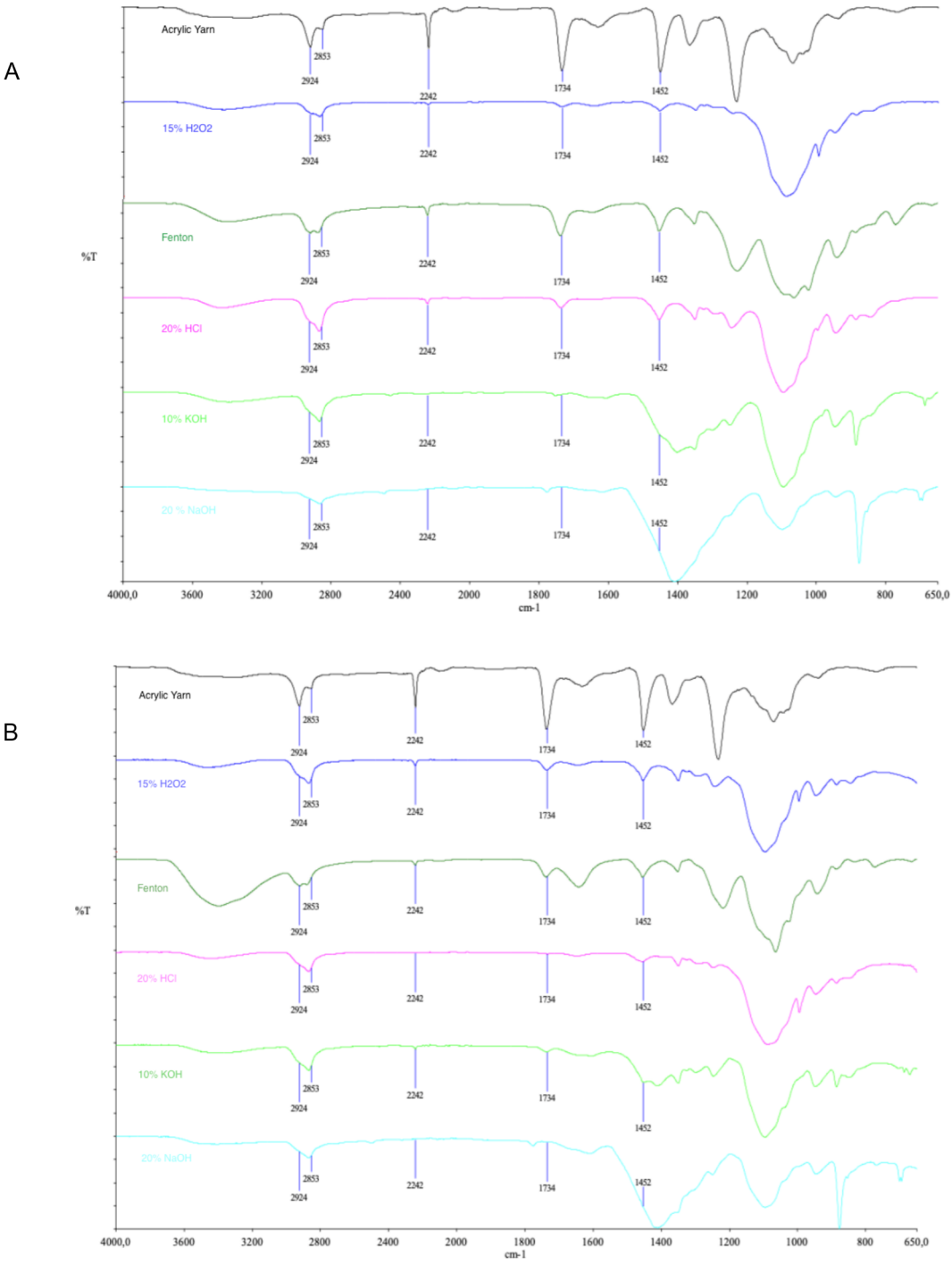


Figure 1. FTIR spectra of the MPs separated from the samples treated (A) at 25°C for 5 days, and (B) at 60°C for 6 hours

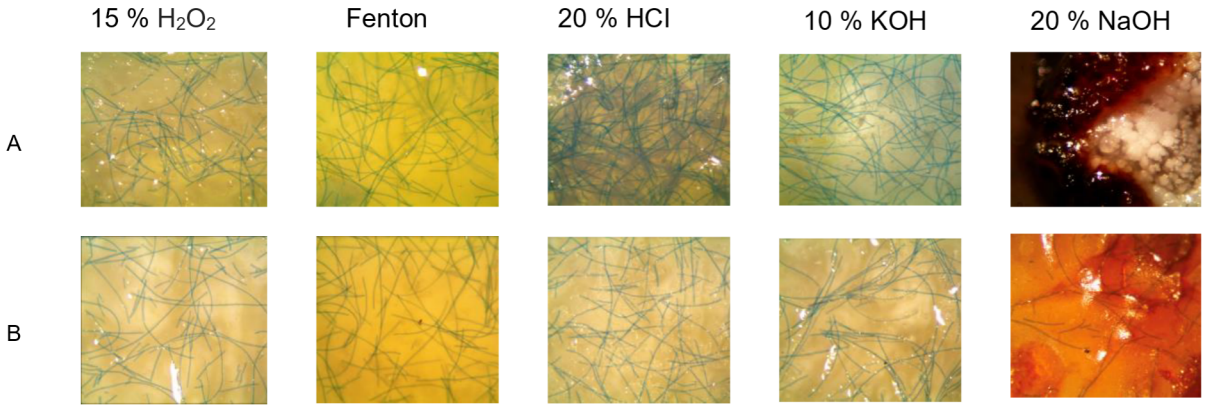


Figure 2. Microscopic images of the MFs deriving from the pretreatment tests at (A) 25 °C for 5 days, and (B) 60 °C for 6 hours

The microscopic images of the MFs obtained from three separation processes (Figures 3 and 4) allowed to measure the fiber lengths, which in all samples were in the range 10 μm – 5 mm. According to the MFs obtained from centrifugation (Figure 3), although their accumulation can be clearly seen in the sediment, some were still detected in the supernatant, indicating that the efficiency of this separation method is low. The images obtained from the sink-float showed that MFs have been detected in both products. The MFs less dense than water were located in the float, while the denser in the sink. Although this seems meaningful, it is a negative situation for the capture of MFs. In details, Kadifeteks wastewater may contain synthetic fibers such as polyester, acrylic and polypropylene, as well as cellulosic fibers such as cotton and ramie. Considering the different densities of these fibers in the range of 0.90-1.55 g/cm$^3$ (Unterweger et al., 2013), the presence of MFs in both products of the sink-float separation process was expected. The microscopic images obtained from filtration (Figure 4) showed that MFs were easily separated in all three GF filters. Although effective filtration required three GF filters due to the high turbidity of the real wastewater sample, filtration has been identified as the most efficient separation method because it was based on a single phase, while the other separation processes involved two phases each.

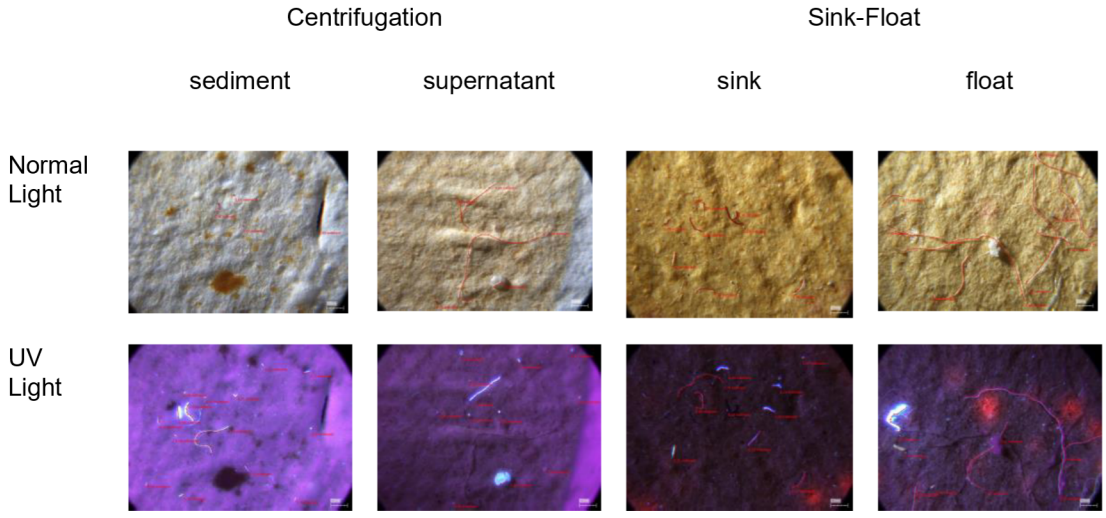


Figure 3. Microscopic images of the MFs deriving from centrifugation and sink-float separation tests

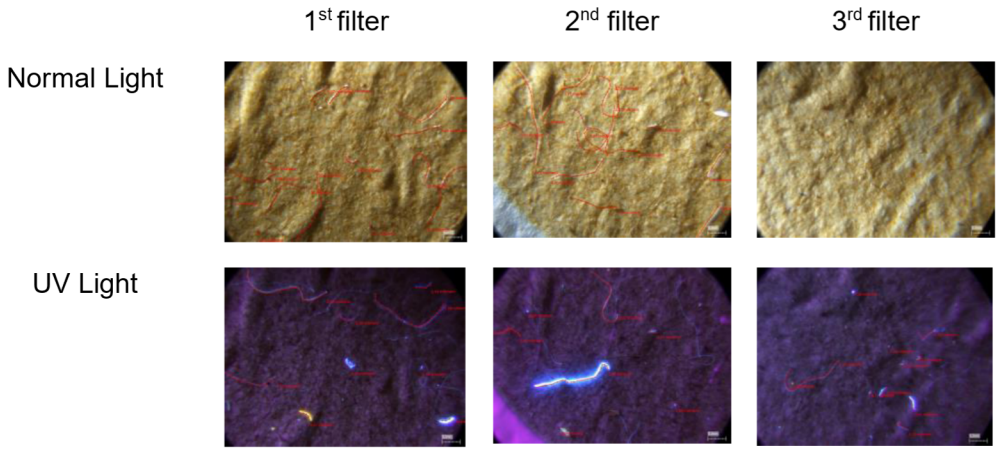


Figure 4. Microscopic images of the MFs deriving from filtration test

## 4. CONCLUSIONS

This study was aimed at investigating two specific phases (pretreatment and separation) of MFs detection in textile wastewater. The pretreatment tests (based on Fenton, $H_2O_2$, HCl, KOH and NaOH, applied at 25°C for 5 days and 60°C for 6 hours) showed that Fenton, HCl, and $H_2O_2$ were the most suitable chemicals to separate the organic components from a synthetic wastewater, while the heat applied during the pretreatment only shortened the required time. However, it could be preferable a method that doesn't apply extra heat to lower its cost. Considering the results of the separation tests, filtration gave back the best performance in concentrating the MFs in the retained phase compared to centrifugation and sink-float, which exhibited some MFs in the supernatant/float. In conclusion, these preliminary results may be useful to further explore the detection of MFs and MPs in textile wastewater.

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