Examining the Importance of Pretreatment to Capture and Analyze Microfibers from Textile Wastewater

Sinem Hazal Akyildiz[1,*], Hande Sezgin[2], Bahattin Yalcin[3] & Ipek Yalcin-Enis[2]

[1]*Faculty of Technology, Textile Engineering Department, Marmara University, Turkey*
[2]*Textile Technologies and Design Faculty, Textile Engineering Department, Istanbul Technical University, Turkey*
[3] *Faculty of Arts and Sciences, Chemistry Department, Marmara University, Turkey*

[*]*(sinem.akyildiz@marmara.edu.tr)*

Abstract – The textile industry is one of the causes of environmental problems, which have a negative effect on all organisms in the ecosystem. In addition to the textile wastes generated by the textile industry, wet processes (dyeing, rinsing, softening, mechanical/chemical finishing) release inorganic compounds, polymers, organic products, dyes, and microfibers (MFs) into the environment. Microfibers may also accumulate in marine species and be passed to higher trophic levels, including humans, through the food chain. In order to solve this problem, it is first necessary to correctly identify it. These stages are sample pretreatment, microplastic separation, and characterization/quantification. The aim of this research is to assess the significance of sample pretreatment in detecting microfibers in wastewater from various parts of a textile company. For the purpose of observing the effect of organic removal, half of the wastewater from each process was pretreated, while the other half was not. A 6-hour pretreatment at 60 °C with Fenton's reagent was performed. A microscope and FTIR were used to investigate the MFs collected on the filter. In particular, due to the rich amount of organic matter in inflow and outflow wastewater, the lack of pretreatment made the analysis very difficult. Additionally, the FTIR analysis failed to detect some of the distinctive peaks that should have been visible in the materials.

Keywords – Microplastic pollution, microfiber, wastewater pretreatment, organic removal, Fenton's reagent

I. Introduction

The textile industry is one of the industries that consume large quantities of water and therefore generates a substantial amount of wastewater [1]. There is a wide and complex combination of contaminants in textile effluent, including inorganic substances, polymers, organic products, dyes, microplastics (MPs), and microfibers (MFs) [2, 3]. MFs are fibrous microparticles consisting of both natural and synthetic fibers [4].

It is believed that wastewater effluent from wastewater treatment plants (WWTPs) is a substantial source of MPs and the most common form of MPs found in wastewater effluent is the form of fiber [5]. An evaluation of the performance of 16 urban WWTPs across the globe [6] found an overall efficiency in MPs removal ranging from 60 to 99.9% depending on the technology used. Regarding the subsequent stages of state-of-the-art WWTP, which are mostly based on active sludge processes, it has been reported [7, 8] that 35-59% of MPs are removed through preliminary treatments, 50-98% via primary settling, up to 20% via secondary settling, and that approximately 2% residual MPs can be detected in the effluent. On the other hand, the most prevalent techniques for treating textile effluents are physical-chemical and biological procedures. But in many cases, combining these conventional methods with contemporary ones might increase the efficacy of pollution removal [9]. However, according to the findings of Ramasamy et al., even after 95-99% of MPs have been removed, municipal WWTPs leak into the environment approximately 160 million microplastics per day [10].

In order to detect microplastics in WWTPs, the following steps are often utilized: sample pretreatment, microplastic separation, and characterization/quantification. Currently, however, there is no consistency in the techniques used at any level. Since samples from WWTPs may include a substantial quantity of organic matter or inorganic solids, a number of techniques are utilized to extract microplastics from the matrix in which they were first collected. These approaches should ease the quantification and identification of microplastics. Essential for the chemical identification of microplastics is the elimination of organic components [11]. Due to the inherent complexity of wastewater samples, the organic matter must be removed by pretreatment processes prior to spectroscopic examination. The most effective pretreatment approach to date for extracting microplastics from wastewater (active aerobic biological stage) includes a seven-day digesting phase in which samples were subjected to 30% (v/v) H_2O_2. As a result, there is an ongoing demand for microplastic pretreatment techniques that allow rapid analysis of huge sample volumes. These techniques should also have a negligible effect on the surface chemistry and fragment sizes of microplastics. Indeed, the accuracy of any spectroscopic approach used for the identification of microplastics is dependent on the sample preparation procedure. Due to its propensity to quickly oxidize organic molecules, Fenton's reagent (a combination of H_2O_2 and ferrous ion, Fe2+) has been successfully employed to purify wastewater [12].

Due to their small size, MPs may enter the human body in a variety of ways. Consumption of drinking water or food is the principal route of human exposure to MPs. MPs are more likely to be absorbed when marine foods are consumed. Because of their small size, aquatic creatures at lower trophic levels, such as plankton and filter feeders, might unintentionally consume MPs. Thus, these compounds may accumulate up the food chain, with the greatest amounts of MPs seen in higher trophic level species, such as crabs and mollusks. This bioaccumulation of MPs, which may include noxious chemicals, might result in extremely dangerous seafood foods that finally reach human consumers [13].

The aim of this study is to determine the importance of sample pretreatment to detect microfibers in wastewater from various parts of the textile factory. Within the scope of the study, the wastewater from each process was split in half—half was pretreated, and the other half was not—to observe the effect of organic removal. Pretreatment was carried out with Fenton's reagent for 6 hours at 60 °C in a magnetic stirrer. The MFs collected on the filter were examined both by microscope and FTIR.

II. Materials and Method

A. Materials

The wastewater that was analyzed as part of the study was derived from various stages of a textile factory where wet processes like dyeing, rinsing, softening, and mechanical/chemical finishing were carried out. The wastewater was obtained from the following processes; acrylic dyeing, rinsing, inflow, and outflow of the on-site WWTP. The wastewater from all wet processes (dyeing, rinsing, softening, mechanical/chemical finishing) carried out in the plant on the various types of textiles made up the on-site WWTP inflow sample. The design of the on-site WWTP in the factory is based on a multi-phase physical-chemical process that aims to manage pH, organic substances, and suspended particles by adding lime, iron-sulfate, and anionic polyelectrolyte in stirred reactors, followed by a settling tank. The wastewater that was cleaned after the settling process was used to create the sample for the on-site WWTP effluent sample. From each step, 1 l of water was provided.

H_2SO_4(Sigma-Aldrich), $FeSO_4.7H_2O$ (Sigma-Aldrich), and 30% H_2O_2(Sigma-Aldrich) were used for the pretreatment of Fenton's reaction. 0.7 µm pore size glass fiber (GF, Merck Millipore, 47 mm) filter was utilized for the filtration process.

B. Methods

Wastewater Supply Process

All equipment was thoroughly cleaned with distilled water and sterilized with ethanol before sampling and processing began. The bottles were manually filled with wastewater and placed in the refrigerator to inhibit the growth of bacteria prior to examination.

Pretreatment of Samples and Separation of Microfibers

The wastewater from each process was split in half—half was pretreated, and the other half was not—to observe the effect of organic removal. Pretreatment was carried out with Fenton's reagent. For the Fenton's reaction to occur, an acidic environment is required, so the samples were first processed with H_2SO_4 at a pH of 3 to 4, followed by the addition of $FeSO_4.7H_2O$ and 30% H_2O_2 and mixing for 6 hours at 60 °C in a magnetic stirrer.

After pretreatment, filtration (Figure 1) was carried out with a glass-fiber filter with a 0.7 µm pore size, and it was then dried overnight at 40 °C.

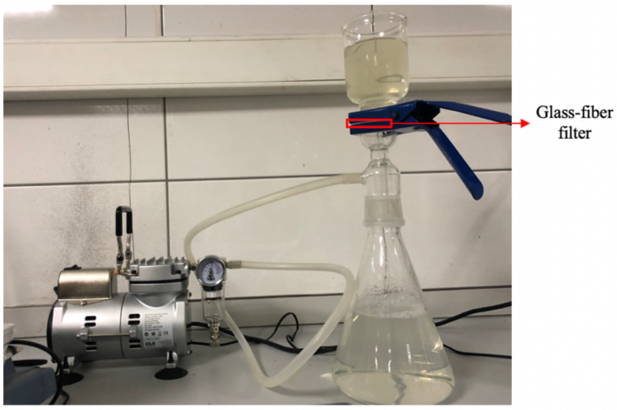

Fig. 1 Separation of microfibers with filtration process

Analysis of Microfibers

An optical microscope (Olympus SZ51) was used to detect and quantify the MFs, and a Fourier Transform Infrared Spectrophotometer (FTIR) (Perkin Elmer Spectrum 65) was used to identify the MFs.

III. RESULTS AND DISCUSSION

Figure 2 shows macro and micro images of the filters of inflow and outflow samples of on-site WWTP. It was evident that microfibers in the samples filtered without pretreatment were very difficult to identify. The structures in the inflow sample in particular rendered it nearly impossible to do the study. Wastewater samples from acrylic dyeing and rinsing exhibited a similar situation.

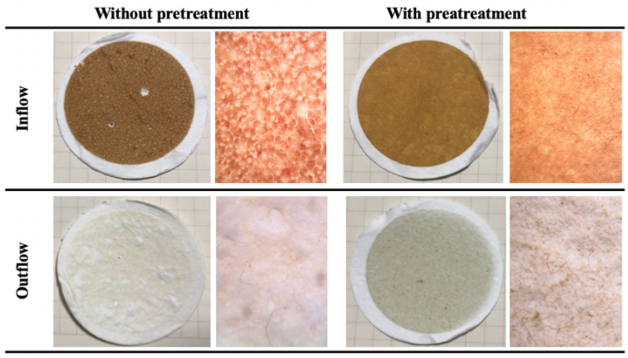

Fig. 2 Macro and micro images of inflow and outflow filters

The MFs were also characterized using FTIR in the wavelength range of 650–4000 cm^{-1}(Figure 3). The characteristic peaks of acrylic fibers(C-H stretching at 2920–2853, C=O stretching at 1734, CΞN stretching at 2242, and C–C stretch in-ring at 1464) were detected clearly in both dyeing and rinsing wastewater of acrylic with pretreatment except the peak at 2242 cm^{-1}. Figure 3(a) demonstrated that the vibration intensities of the acrylic peaks of the non-treated sample were not as high as those of the pretreated sample. In addition, there was a little shift at the peak of 1734 cm^{-1}. The peaks in Figure 3(b) appeared as predicted, given that it was acrylic rinse water and contains low organic matter. However, peak intensities were not as high as the those of pretreated sample.

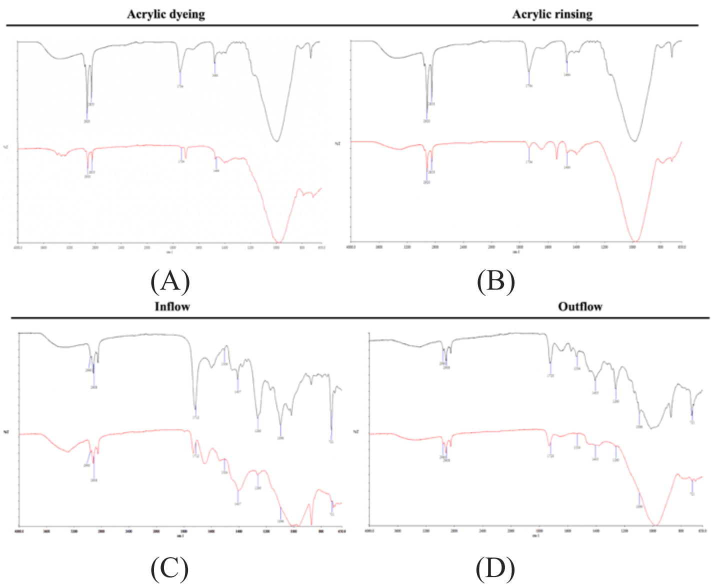

Fig. 3 Process FTIR results of (a) acrylic dyeing, (b) acrylic rinsing, (c) inflow of WWTP and (d) outflow of WWTP (black ones with pretreatment, and red ones without pretreatment)

Wastewater from various fibers that have undergone wet processing at the factory is housed in the WWTP. In the examined wastewater, characteristic peaks of polyester were discovered. The characteristic peaks of polyester fibers (C-H stretching at 2960-2908, C=O stretching at 1712/1720, aromatic ring at 1534/1504-1407/1405, the carboxylic acid (C– O) at 1260, ester (O=C–O–C) at 1096, aromatic (C–H) at 721) were detected clearly in both inflow and outflow of WWTP sample with pretreatment. In figure 3(c), the peaks at 1504,1096,721 were not observed; other peaks showed either a decrease in intensity or a slight shift. This may be due to the high amount of organic matter in the inflow water. In Figure 3(d), the peaks at 1534,1405,721 were not observed. In other peaks, either a decrease in intensity or a slight shift was detected. It's possible that this is the case because even after industrial pretreatment, there is still a significant amount of organic debris in the inflow water. This demonstrates the necessity of doing the pretreatment procedure correctly in order to accurately and delicately evaluate the microfibers in industrial effluent.

IV. CONCLUSION

The objective of this study is to evaluate the importance of sample pretreatment in identifying microfibers in wastewater from different parts of a textile factory. Half of the wastewater from each process was pretreated (Fenton's reagent), while the other half was not, for the aim of monitoring the effect of organic removal. Microscope and FTIR were used to examine the MFs captured on the filter. In particular, the high amount of organic compounds in the inflow and outflow wastewater made the analysis very difficult in the absence of pretreatment. Furthermore, it was evident from the FTIR study results that the organic components prevented the detection of a few characteristic peaks that should have been present in the materials.

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REFERENCES

[1] Serejo, M. L., Franco Morgado, M., García, D., González-Sánchez, A., Méndez-Acosta, H. O., and Toledo-Cervantes, A. Environmental resilience by Microalgae. *Microalgae Cultivation for Biofuels Production* 293–315, 2020.

[2] Sari Erkan, H., Bakaraki Turan, N., and Önkal Engin, G. Membrane bioreactors for wastewater treatment. *Fundamentals of Quorum Sensing, Analytical Methods and Applications in Membrane Bioreactors 151*–200, 2018.

[3] Belzagui, F., and Gutiérrez-Bouzán, C. Review on alternatives for the reduction of textile microfibers emission to water. *Journal of Environmental Management* 317, 115347, 2022.

[4] Zhou, H., Zhou, L., and Ma, K. Microfiber from textile dyeing and printing wastewater of a typical industrial park in China: Occurrence, removal and release. *Science of The Total Environment 739*, 140329, 2020.

[5] Xu, X., Hou, Q., Xue, Y., Jian, Y., and Wang, L. P. Pollution characteristics and fate of microfibers in the wastewater from textile dyeing wastewater treatment plant. *Water Science and Technology* 78, 2046–2054, 2018.

[6] Ngo, P. L., Pramanik, B. K., Shah, K., and Roychand, R. Pathway, classification and removal efficiency of microplastics in wastewater treatment plants. *Environmental Pollution* 255, 113326, 2019.

[7] Sun, J., Dai, X., Wang, Q., van Loosdrecht, M. C. M., and Ni, B.J. Microplastics in wastewater treatment plants: Detection, occurrence and removal. *Water Research* 152, 21–37, 2019.

[8] Gies, E. A., LeNoble, J. L., Noël, M., Etemadifar, A., Bishay, F., Hall, E. R., and Ross, P. S. Retention of microplastics in a major secondary wastewater treatment plant in Vancouver, Canada. *Marine Pollution Bulletin133,* 553–561, 2018.

[9] Barredo-Damas, S., Iborra-Clar, M. I., Bes-Pia, A., Alcaina-Miranda, M. I., Mendoza-Roca, J. A., and Iborra-Clar, A. Study of preozonation influence on the physical-chemical treatment of textile wastewater. *Desalination* 182, 267–274, 2005.

[10] Ramasamy, R., Aragaw, T. A., and Balasaraswathi Subramanian, R. Wastewater treatment plant effluent and microfiber pollution: Focus on industry-specific wastewater. *Environmental Science and Pollution Research* 29, 51211–51233, 2022.

[11] Löder, M. G., and Gerdts, G. Methodology used for the detection and identification of microplastics—a critical appraisal. *Marine Anthropogenic Litter* 201–227, 2015.

[12] Tagg, A. S., Harrison, J. P., Ju-Nam, Y., Sapp, M., Bradley, E. L., Sinclair, C. J., and Ojeda, J. J. Fenton's reagent for the rapid and efficient isolation of microplastics from wastewater. *Chemical Communications 53,* 372–375, 2017.

[13] Katyal, D., Kong, E., and Villanueva, J.Microplastics in the environment: Impact on human health and future Mitigation Strategies. *Environmental Health Review 63*, 27–31, 2020.