ISSN 1330-3651 (Print), ISSN 1848-6339 (Online)
https://doi.org/10.17559/TV-20220121153959
Subject review

STEM Approach in Assessment of Microplastic Particles in Textile Wastewater

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Abstract: Multidisciplinary engineering approach as STEM (Science, Technology, Engineering and Mathematics) approach to characterize microplastic particles in household and industrial effluents was performed. Particles released during production, use, and disposal of plastic products now pose a significant burden on the environment. In addition to the consumption of energy, water and chemicals, the impact of the washing process is increasingly reflected in the environmental impact of microplastic particles shed from textiles. This review addresses the influences of chemistry through detergent composition, technology through the washing process, engineering aspect through hydrodynamic effects and transport phenomena, and finally the application of advanced mathematical analysis. The multivariate analysis is a selected method or proof of concept for the characterization of the washing effluents considering the particle release. The results of the cluster analysis show the importance of the temperature of 40 °C and 80 °C, the increase of the number of washing cycles and the addition of detergent as key parameters for the release of MP particles.

Keywords: hydrodynamic effect; microplastic particles; multivariate analysis; STEM; washing wastewaters

1 INTRODUCTION

The problem of pollution by microplastic particles is topical, and their impact on the environment is great. In 2017 alone, 348 million tons of plastic were produced worldwide (about 72 million tons of synthetic textiles per year). This is concerning because the plastic items, which are suitable for their high elasticity and durability, re-enter the environment after use as microplastics (MP) and accumulate in sewage, rivers, oceans, and the atmosphere. New research data show that the plastic cycle is reminiscent of the global water cycle and has atmospheric, oceanic, and terrestrial lifetimes [1]. Scientists believe that microplastics originate from plastics that are disposed of directly into environment, as well as microplastics of textile origin that are loosen during household or/and industrial washing of synthetic textiles [2].

It is known that synthetic textiles contribute to the release of microplastics during multiple interactions with the hydrosphere, but the exact amounts of microplastic release from the items of textile origin are not known, especially during washing, wearing and use of textile products. From global datasets, it was estimated that 5.6 Mt of synthetic microfibres were emitted from garment washing between 1950 and 2016. Half of this amount was emitted in the last decade, with an average annual growth rate of 12.9% [3].

There is evidence that all common household textiles release fibres and that synthetic fabrics contribute to microplastic pollution. Textile design and properties such as fibre type, yarn construction and surface treatments should also be considered as a significant potential for fibres release. Several research activities focus on the release of MP particles during washing of synthetic textiles [4-9]. However, the lack of uniform testing protocols leads to enormous variability in the results and the way they are reported [4].

The washing process inevitably involves damage, resulting in the shedding of fibres or, in the case of synthetic textiles, the release of MP particles into the environment. Despite numerous studies [4, 5], there is a lack of information on the origin of released particles from real and multicomponent textile samples. These studies [4-6, 8] show the influence of the individual parameters of the Sinner cycle, superimposed by the repetition of the washing cycles, on the number of released particles from different type of textiles (fabrics, knit wear, nonwovens, garments etc.). Many parameters make the washing process complex, so it is important to emphasize the application of modelling methodology, especially advanced statistical techniques such as multivariate analysis (MVA), that have proven successful in better defining the complexity of washing systems and the impact of parameters on particle release.

Since washing takes place in an aqueous medium and mechanics is an important parameter of the process, the influence of hydrodynamics on particle release (inorganic part of soil, pigment, undissolved ingredient of detergent, microorganisms, fibrils of different size -micro/nano) from a process chemical engineering point of view has been highlighted in this paper. In addition, an overview of methods for wastewater characterization and particle characterization MP is given. Based on the results of the quantitative gravimetric analysis [5], an MVA was carried out to demonstrate the importance of advanced process modelling techniques with the aim of influencing the interaction of parameters on MP particle release. A proof of concept was performed for the quantification of MP particles with different washing parameters. Using this methodology [10-12], similarities and differences between individual parameters that influence the number of particles released can be represented and quantified.

2 HYDRODYNAMIC EFFECTS IN WASHING PROCESS

Physical phenomena influence the mass transfer in textiles during their movement in the washing process. Thus, the movement of textiles in the washing process is ultimately determined by the velocity and deformation, which manifests itself as a hydrodynamic effect.

One aspect of the washing process involves the transport of soil from the textile to the bulk solution, which is facilitated by various mechanisms that depend primarily on the type of soil and the properties of the textile [13]. Various phases may occur in the washing of textiles: solution, dispersion, emulsion, suspension, which are specific to the interfaces involved in detergency. The mass transfer of the solution to the textile surface, the wetting of the soil and the textile surface, the penetration of the solution into the soil, the interaction with the soil and the detachment from the textile surface into the bulk solution should be considered.

For this reason, the washing process can be represented according to the principles of transport phenomena (momentum and mass transfer) in a closed mixing system, Fig. 1. It is important to define transport phenomena at three levels within the washing machine [14, 15].

- the textile micro-level
- the textile macro-level
- the machine level.

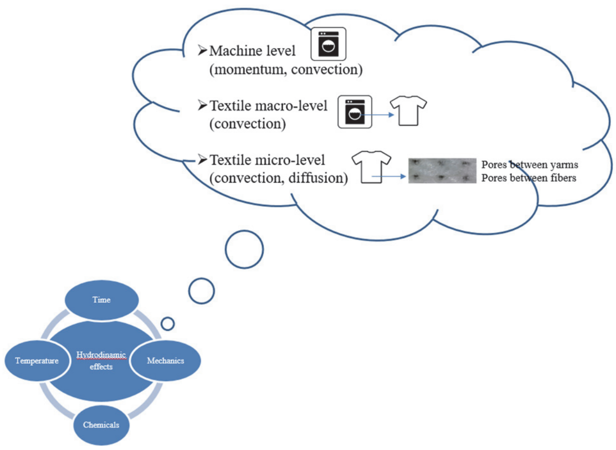

Figure 1 Sinner cycle and hydrodynamic effect [Autor own schematic view]

A typical textile is a three-dimensional bi-porous medium consisting of relatively large pores between yarns and much smaller pores between fibres. According to the principles of micro-scale transfer phenomena, mass transfer within the textile structure is governed by relatively fast convective flow through the large inter-yarn pores and rate-limiting diffusive flow through the smaller inter-fibre pores. In the pores within the yarns, mass transfer takes place by convection. There is little or no flow in the pores internal to the filaments because they contain a stagnant fluid, so mass transfer in these areas occurs by diffusion. Observation of hydrodynamic effects at this level is of particular importance for the release of particles.

At the level of the machine and at the macro level of the textiles, important mass transfer and momentum principles are involved in the movement of the textiles in the washing machine. Drum rotation increases the interaction between the washing bath and the textiles, resulting in the loosening of soil from the textiles as well as the release of fibres. The hydrodynamic effect that occurs in the aqueous medium inside the washing machine is due to the three-dimensional movement of both the textiles and the liquid, able to cause a significant deformation of the textiles as well as the release of particles.

The analysis of hydrodynamic properties in the washing machine can contribute to the understanding of particle release in the washing process. According to the dynamics of textile movement, which depends on the design of the machine, numerous differences in hydrodynamic characteristics can be observed. Since washing takes place in a closed, well-mixing solid-liquid system with physical and chemical reaction, the study of hydrodynamic effects can be carried out according to theoretical (solution of the equation Navier Stokes) and experimental (tracer experiment) approaches [16]. This has been the subject of numerous studies with the aim of better describing the motion in the washing machine in order to optimize the washing process [14, 17-23].

3 WASHING WASTEWATER

The characteristics of textile wastewater from washing are complex. The amount and composition depend on the type of textiles, soils and the parameters of the washing process (Sinner cycle). In general, they are characterized by a wide pH range, colour and turbidity, high COD and BOD, large amounts of inorganic salts, metals, surfactants, various organic substances, and waste fibrils [24, 25]. The direct discharge of wastewater with such characteristics into natural recipients has a negative impact on their flora and fauna, and causes problems in biological wastewater treatment plants and further increases the cost of purification. The discharge of synthetic microplastic particles into wastewater systems is currently not sufficiently regulated. The results of wastewater analysis are usually presented as the total amount of released fibres without distinguishing the origin of the released particles [26]. To date, there is no effective way to analyse fibres from wash effluent because the filters in the machines are not designed to fully retain particles/fibres. The release of synthetic microplastic particles into wastewater systems is currently not sufficiently regulated. Most of the studies have been carried out on the release of particles from the household washing process and only a small part from industrial washing [6, 24].

Taking all these aspects into account, there is a need for consistent and clear protocols for the quantification of particle release indicators and for standardized methods for the characterization of microplastic particles released during washing.

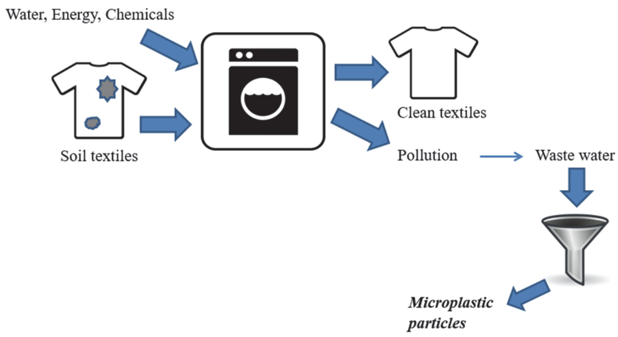

Figure 2 MP particles as output characteristics of washing process [Autor own schematic view]

Wastewater containing microplastic particles is a dispersion system, so filtration can be used as the simplest method to separate the particles, Fig. 2. Filtration involves isolating the fibres/particles from the liquid, usually under pressure with a vacuum pump. To quantify the mass remaining on the filter, the gravimetric method is useful. Depending on the need for qualitative or quantitative analysis of the particles, analysis of the filtrate and/or particles remaining on the filter can be performed using a variety of analytical methods: Physical identification, microscopy to assess microparticles by size, type (fibers, film, foam, pellets or fragments) and colour. Optical Microscopy or Scanning Electron Microscopy (SEM) can be used to determine the fibres remaining on the filter [4-6, 27].

When performing these analyses, special attention should be paid to deficiencies in order to make the results of the analyses valid. In these methods, the overlapping of the released fibres and the clogging of the filter pores with the released fibres, which occurs as a determination error, may influence the overall result (number of microfibres released).

In addition, the choice of a suitable filter, sample handling (drying, conditioning and weighing), loss of material and contamination of the sample by other substances such as undissolved ingredients of detergent, soil particles, dust, incineration residue from fabric, calcium and magnesium salts from water, can also affect the accuracy of the method for determination of microplastic particles by gravimetric analysis [6, 24, 28, 31]. Microscopic analysis of the filter cake may also show agglomerates of different shapes formed by the deposition of inorganic and organic residues during the washing process. The presence of agglomerates has been shown to decrease when the number of rinses in the washing process is increased [30].

In addition to the quantitative analysis of the total content (mass and number) of released particles, a more detailed analysis of the effluent as a dispersed system is important, focusing on the morphology, shape and dimensions of the released fibres/particles. Related to this is the analysis of the particle size distribution using laser diffraction, the result of which is the range of particle size and the proportion of the total system accounted for by each particle. This type of analysis is important for the selection of a dimension of the filter pores and the avoidance of clogging, thus contributing to the accuracy of the analysis.

Numerous methods are used for chemical characterization depending on the source of the MP particles. Existing techniques for MP chemical identification include Fourier transform infrared (FTIR) and Raman as the most commonly used. Both are vibrational spectroscopic techniques in which the sample is molecularly excited and then a characteristic spectral fingerprint is generated. With the spectra generated, it is possible to identify the substance by comparison with the spectra of known materials [31, 32].

Thermoanalytical methods, e.g. pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS), Thermogravimetric Solid-Phase Extraction and Thermal Desorption Gas Chromatography Mass Spectrometry (TGA-SPE/TDS-GC-MS) allow accurate identification of the chemical structure of the samples and not only separate between MP and non-MP particles, but also provide the polymer base and even the presence of additives. Py-GC/MS is a destructive method that uses pyrolysis to simultaneously identify microplastics and its additives by introducing the sample directly with minimal pre-treatment.

4 PROOF OF CONCEPT FOR QUANTIFICATION OF MP PARTICLES

The complexity of the washing system, the unclear methodology of wastewater characterization as well as of released particles require additional techniques.

Standard modelling and optimization techniques, which are a set of mathematical and statistical techniques, can be used to predict the desired responses. This methodology is used in various fields and can provide a significant aspect from an engineering point of view to improve the efficiency of existing washing processes and reduce the time required for process optimization [10, 33]. Conducting experiments based on a trial-and-error method is time-consuming, does not take into account parameter interactions, and causes a high error rate. For the successful application of this approach, it is necessary to determine the main task of the conducted experiment (evaluation of microplastic release). It is also necessary to select the parameters whose influence should be analysed and to define the range within which the parameter values vary. The main task is to find cause-effect relationships between input and output variables by varying the control parameters according to Sinner, with the aim of favouring the positive washing effect and reducing the release of microplastic particles.

Multivariate analysis (MVA) can be used to represent and quantify similarities and differences between individual parameters affecting the mass of released particles. In this paper, the multivariate analysis method was reviewed and performed on research results according to article obtained by gravimetric analysis (µg of fibres per g fabric) according to Hernardez et. al. [5]. The approach focused on the evaluation of MP particles in the washing process of polyester knitted fabrics and was carried out varying the temperature (25 °C, 40 °C, 60 °C, 80 °C), the composition of the bath (deionized water - DW, liquid detergent - LD, powder detergent - PD) and the number of washing cycles (1, 2, 3, 4, 5) [5]. To check the influence of washing parameters on the release of MP particles, MVA was used in this work. Cluster analysis (CA) as part of MVA distinguishes a group of objects into classes in which there are similar objects in the same class. A dendrogram as a graphical representation of the gradual combination of objects into clusters was created. Ward methods using TIBCO Statistics software was applied to the MP release. The error sum of squares (ESS) within the cluster was taken as a measure of homogeneity. Proof of concept of MVA methods based on the specified results [5] is shown as dendrograms in Figs. 3 to 5. The vertical scale shows the Euclidean distance between the two groups at the point where they were combined.

The results of the cluster analysis demonstrate a significant influence of temperature with significant differences in particle released when PES knitted fabric is washed at 40 °C. From the dendrogram shown in Fig. 3, it can be seen that the samples washed at 25 °C and 60 °C belong to the same group. The next step in the hierarchical analysis is the sample washed at 80 °C. The distribution obtained shows the importance of the temperature 40 °C and its influence on the phenomenon of particle release from PES knitted fabric.

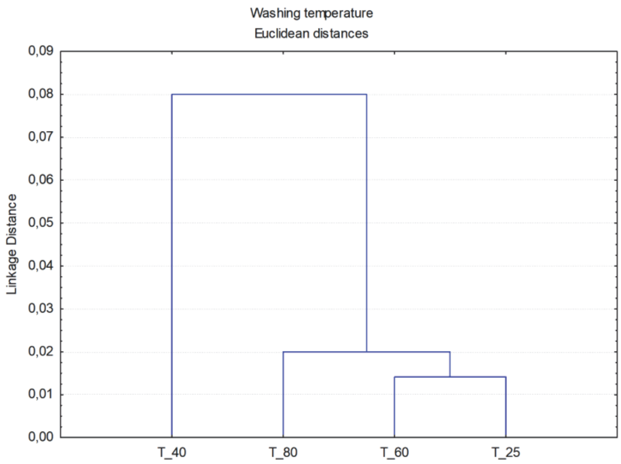

Figure 3 Dendrogram of the CA according to Ward for similarities and dissimilarities based on washing temperatures as variables

To estimate the impact of detergent type on MP release, a cluster analysis was performed. The results of the CA are shown as a dendrogram in Fig. 4, which shows a clustering of liquid and powder detergent belonging to the same group, while the deionized water is separate.

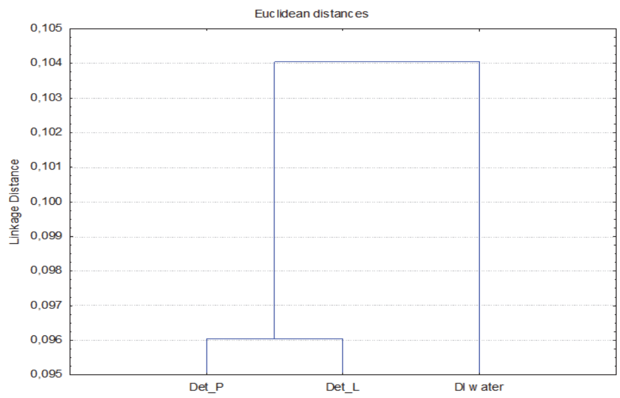

Figure 4 Dendrogram of the CA according to Ward for similarities and dissimilarities based on the composition of bath

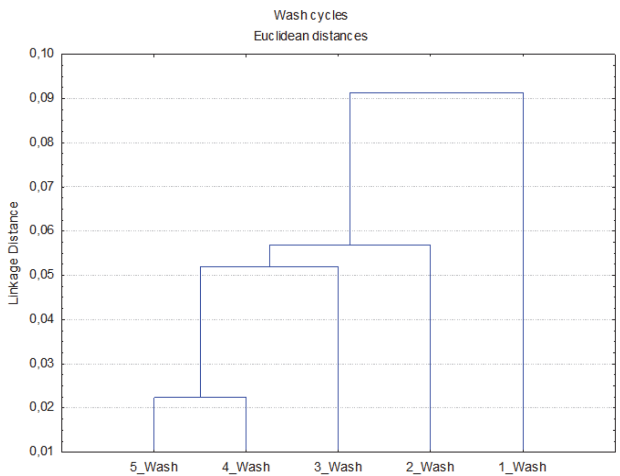

Figure 5 Dendrogram of the CA according to Ward for similarities and dissimilarities based on the repetition of washing cycles

The cluster analysis results demonstrate a significant influence of wash cycles with significant differences in particle released when textiles are washed in 4th and 5th cycle. From the dendrogram shown in Fig. 5, it can be seen that the sample washed in 4th and 5th cycle belongs to the same group. Next steps in hierarchical analysis are other cycles in between the 1st cycle have the largest distance.

5 CONCLUSION

The washing process is a multiphase and multistage system for operating a set of process parameters with distinct hydrodynamic characteristics. The interactivity and specificity of this system requires a multidisciplinary engineering approach, as the interaction of all parameters and their understanding both directly reflect the release of microplastic particles. Given the complexity of the system, there is a need for optimization of parameters, consistent and clear protocols to quantify indicators of particle release, and standardization of methods to characterize microplastic particles released in the washing process. The importance of advanced statistical techniques such as multivariate analysis has been confirmed in assessing the influence of washing process parameters, especially the importance of the temperature of 40 ºC and 80 ºC, the increase in the number of washing cycles and the addition of detergent as important parameters on MP release.

Acknowledgement

This work has been fully supported by the Croatian Science Foundation under the project IP-2020-02-7575

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