FROM MICROFIBERS TO NANODIAMONDS: THE UPCYCLING AND REUSE OF WASHING MACHINE WASTEWATER

Luciana Migliore [1], Annamaria Alabiso [1], Andrea Appolloni [2], Renato Baciocchi [3], Roberto Braglia [1], Antonella Canini [1], Valerio Cantelmo [1], Roberta Congestri [1], Fiammetta Costa [4], Giulia Costa [3], Sophia de Assis Bombardelli Miranda [2], Natalia Marzia Gusmerotti [2], Massimo Longo [5], Claudia Mazzuca [5], Matteo Meraviglia [4], Laura Micheli [5], Attilio Nebuloni [4], Francesco Scuderi [1], Jacopo Valeri [3], Silvia Orlanducci [5]

[1] Dept. Biology, Tor Vergata University of Rome - Via della Ricerca Scientifica snc, 00133 Rome, Italy
[2] Dept. Management and Law Tor Vergata University of Rome, Italy
[3] Dept. Civil and Computer Science Engineering - Tor Vergata University of Rome, Italy
[4] Dept. Design, Polytechnic of Milan, Italy
[5] Dept. Chemical Science and Technologies - Tor Vergata University of Rome, Italy

ABSTRACT: Microfibers released from washing synthetic textiles pose a significant environmental challenge, polluting water sources and harming ecosystems. This project proposes an innovative approach to address this issue by developing a comprehensive solution for microfiber waste management. The key point of the project is to turn a harmful and non-served waste into a valuable resource: nanodiamonds.

Keywords: microplastic fibres conversion; hydrogen plasma pyrolysis; autotrophic/heterotrophic biofilter; microbial consortium for bioremediation; washing machine wastewater for plant watering

1. INTRODUCTION

Microplastic pollution in the oceans is largely driven by plastic microfibers released through domestic and industrial washing processes. This project, supported by the Italian Ministry of Environment and Energy Security, proposes an innovative approach to manage washing machine wastewater (WMW) that is applicable at the household level, while being scalable for industrial use.

The strategy revolves around a first two-stage mechanical filtration, employing a dual-mesh setup (and 80 μm) to trap and collect micro- and nano-plastics.

The captured plastic fibres will undergo thermal pyrolysis in a hydrogen plasma environment, breaking them down into radical, more simple compounds (-CH_3 and C_2H_2) and H_2. These radicals will then serve as precursors for nanodiamond synthesis through radical addition. This method eliminates the need for sorting plastic fibres by composition, as all materials could directly be converted into CH_3 radicals (depending on polymer source) - the fundamental building blocks for CVD diamond formation. The process is enabled by an operational pilot facility for diamond synthesis at the Department of Chemical Science and Technologies at Tor Vergata University of Rome.

Additionally, a dedicated bioremediation system has been designed, by using an *ad hoc* engineered microbial consortium, integrating a phototrophic cyanobacterium (*Trichormus variabilis*) alongside three heterotrophic bacteria, as already designed for the dishwasher wastewater bioremediation, the Zero Mile system (Congestri et al., 2020; Alabiso et al., 2023, 2024). In that system the consortium works synergistically to remove the excess of nitrogen and phosphorus. The WMW bioremediation could repurpose wastewater for irrigation, homegrown vegetable cultivation.

In this framework the double-treatment may accomplish the upcycling of both plastic fibres and organic contaminants into high-value nanodiamonds and good quality plant food.

Incorporating an eco-design perspective, the project prioritizes resource efficiency, extended product lifespan, and easy maintenance through modular component replacement. Moreover, a life cycle assessment (LCA) study is being conducted to evaluate the potential environmental benefits, alongside a baseline scenario analysis to assess social and economic impacts. This methodology aims to define the existing environment in which the project operates by identifying future risks and opportunities before developing and designing practical solutions for implementation. The results will indicate which business models are best suited to the future market and regulatory context. The methodologies and preliminary findings related to these two aspects are presented in separate contributions that will be shared at the symposium.

2 MATERIALS AND METHODS

2.1 Filtration System Development

The key point is to develop an intelligent filter capable of capturing microplastics ranging from 5 to 80 μm. To this purpose existing microfiber filters will be compared and prototypes will be developed to test filtering performance and ease of microfiber extraction. The filter will be equipped with a sensor designed to assess the quantity of retained fibres and to signal its saturation level indicating when it needs to be replaced or cleaned. The sensor is based on screen-printed electrodes (SPE) strategically placed in the system

The estimation of saturation level of this sensor is performed by the electrodes through impedance measurements, specifically by analysing changes in charge transfer resistance at the electrode interface when a small alternating current (AC) signal is applied with a constant direct current (DC) offset (Electrochemical Impedance Spectroscopy - EIS). The optimal AC voltage frequency will be identified to ensure that, when applied, it quantifies the adhered microplastics proportionally to the increase in charge transfer resistance on the SPE surface.

Moreover, this type of measurement is performed differentially, comparing a baseline condition (no microplastics) with the state in which microplastics interact with the electrodes. This approach allows for the determination of the filter's maximum load capacity and saturation threshold, indicating when replacement is required as explained before.

The biofiltering system will be developed integrating the requirements defined in the Zero Mile system for the treatment of dishwasher wastewater with the results of the experiments on WMW bioremediation, Mechanical and biological filtering alternatives will be evaluated in terms of resource efficiency, extended product lifespan, and easy maintenance through disassembly facilitation.

2.2 Upcycling of filtered fibres via Hydrogen Plasma Pyrolysis (nanodiamond production)

As mentioned, one of the main goals of the project is to evaluate the yield and quality of the produced nanodiamonds, as well as the scalability of the synthesis process, starting from the different microfiber fractions recovered from the washing machine wastewater filtration system.

Another goal has been the setting up of a database, to identify the composition of unknown samples or samples containing a mixture of polymers.

Textile microfibers can be classified based on their polymer composition and are divided into five categories:

- Polyester: Trevira Finesse, Diolen® Soft, Fortrel Microspun, DuPont Micromattique, Primabelle, Shingosen
- Nylon: Timbrelle®, Supplex Microfiber, Tactel® Micro, Silky Touch
- Acrylic: Microsupreme
- Cellulose: Lyocell
- Blended fibres: Composed of multiple polymers such as polyester, polyamide, and polypropylene.

The carbon yield of the carbonization processes for each of these polymers varies significantly although always remaining quite high: 17-22% for polyester (PET), 40% for nylon, up to 50-55% for polyacrylonitrile (PAN). Also the carbonization conditions can vary, depending on several parameters such as process temperature and pressure, the presence of additives and catalysts, as well as the purity, shape, and origin of the starting material.

The proposed high-temperature plasma-assisted pyrolysis offers several advantages over conventional carbonization techniques: it does not require prior separation of microfibers based on their composition or any pretreatment. Preliminary results indicated that carbon precursors (microfibers) undergo both pyrolysis and gasification leading to the formation of simple hydrocarbons and carbon materials. The hydrocarbons are converted by the hydrogen plasma into radicals (CH_3), which are the primary agents responsible for diamond synthesis via Chemical Vapor Deposition (CVD). The resulting materials are a nanocomposite made of carbon fibers and nanodiamond stuck together. During the synthesis process fiber morphology can be partially retained and the carbon yield can be increased compared to conventional carbonization processes.

The diamond yield will be evaluated for each individual microfiber polymer retained by the two mechanical filters, assessing the yield from real samples obtained by the filtration of washing machine wastewater.

The quality of the produced diamond and carbon nanostructured material will be evaluated by morphological analyses, performed by Scanning Electron Microscopy (SEM), while the structural characterization will be conducted through Raman spectroscopy, a key technique in investigating Carbon-Based Materials (May et al. 2008; Malard et al. 2009).

2.3 Biodegradative consortia assemblage

For the wastewater treatment experiments, we chose to use washing machine wastewater (WMW) from a household environment (Whirlpool FreshCare). The washing machine operated with Everdrop detergent for white (WMW-W) or coloured clothes (WMW-C), using eco-friendly washing cycles. Both detergents were selected based on their chemical composition, consisting of salts, engineered enzymes and surfactants (sodium sulfate, laureth-7 and sodium palmitate). This formulation is designed to minimize or completely avoid hazard to the environment.

The experimental procedure for WMW bioremediation/reuse included the following steps.

Chemical analysis of the WMW. 1.5 L samples of each WMW (WMW-W for white and WMW-C, for coloured washing) and 1.5 L of tap water were analysed via official methods according to the Italian regulation, art.16 R.D. n° 842/1928, art.16 and 18 law n°679/1957, D.M. 21/06/1978, art. 8 c.3 of D.M. 25/03/1986; tests were performed by Delta Aps srl.

Identification of the microbial community for the consortium assemblage. Wastewater samples (100 mL) were plated on three sets of Petri dishes each containing three different growth media (Tryptic Soy Agar, McConkey Agar, and Pseudomonas Agar Base), to allow the growth of the widest spectrum of bacteria. Then, one colony for each observed morphology was picked up, checked for purity, and taxonomically identified by Sanger sequencing. All the isolated were stored at -80 °C in glycerol 20%.

Microbial association tests. Before the start of consortia assemblage, the survival of *T. variabilis* in 100% WMW was evaluated: the cyanobacterium has been inoculated at an OD=0.150 (detection wavelength, λ 665 nm) in 50 mL of WMW, and its growth measured spectrophotometrically every two days as in vivo chlorophyll *a* (λ 665 nm) and culture turbidity (λ 730 nm). Tests were performed in three replicates, the control grown in BG11.0. For the 1:1 association test each bacterial isolate was challenged with *T. variabilis*, in triplicate, their growth curves monitored every 2 days for 12 days, to identify those strains guaranteeing the best performance. Then, For the 1:3 association test, the survival of consortia assembled as *T. variabilis* + 3 heterotroph isolates was monitored.

3 RESULTS AND DISCUSSION

3.1 Filtration System Development

The mechanical filtration system currently under development for microfibers exhibits high filtration efficiency for fibre fractions ranging from 5 to 80 μm. Three sensors based on screen-printed electrodes (SPE) adhere to the filter mesh on the side opposite to the collected plastic fibres, to evaluate the saturation level. The possibility to foresee the saturation in advance is a considerable advantage in comparison to existing microfiber filters.

3.1 Upcycling via Hydrogen Plasma Pyrolysis (nanodiamond production)

Fig. 1a) reports an optical image of a sample of Silicon (100) substrate coated by PP fiber dispersion and subjected to 60 minutes of Hot Filament H plasma. As can be seen, a partial morphology of fiber was conserved; the Raman map analysis, in false color on the picture, indicated the formation of C materials based both on sp^3/sp^2 C. In particular, the yellow region is due to the sp^3-rich signal, whereas the pink region is the sp^2 carbon. At a closed look, it is possible to identify the typical fingerprint of nanodiamonds (signal at about 1340 cm^{-1}); in Fig 1b), two spectra are reported. A typical SEM image of the sample is reported in Fig. 2. All the samples appear inhomogeneous with regions of carbonized fiber and others with aggregates of nanocrystalline particles. In some cases, the crystals grow on filament structures acting as templates.

a) **b)**

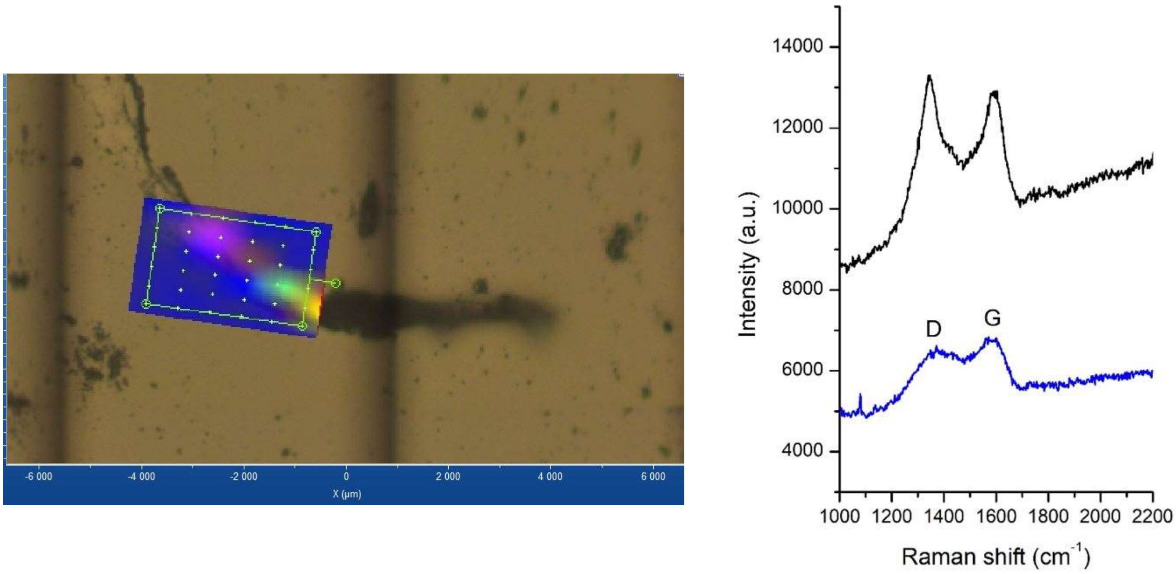

Figure 1. a) Optical images and Raman map of a PP sample after H plasma treatment. The Raman map was recorded using a 785 nm laser source, and a 50 x optical magnification. b) Two Raman spectra from the map, black line is the spectrum of a rich nanodiamond region, blue line of an amorphous region, D and G are the typical band of sp^2 carbon materials

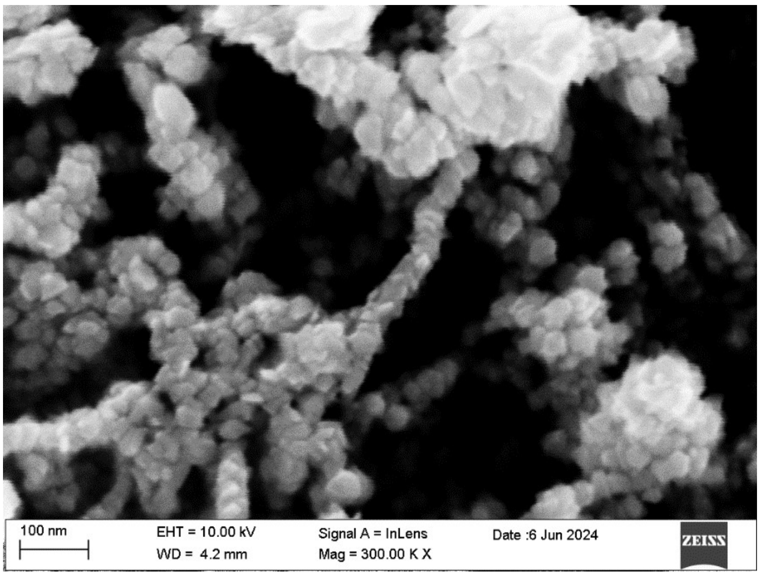

Figure 2. SEM image of a PP fibre sample after 60 min plasma treatment.

3.3 Biodegradative consortium assemblage

The chemical analysis of the WMW, highlighted a considerable concentration of surfactants, COD and BOD_5 compared to the typical composition of raw domestic wastewater. Also nitrogen exhibits slightly high values, while phosphorus is nearly absent (Tab. 1). It is worth to note that the BOD_5-COD ratio in wastewaters showed a value of 0.5, which means that is fairly biodegradable and could be treated efficiently through biological treatment (Bader et al. 2022).

Table 1. Concentration values of selected parameters in the WMW samples considered compared to tap-water

Source	Total surfactants (mg/L)	COD (mg/L O_2)	BOD_5 (mg/L O_2)	Total Nitrogen (mg/L)	Total Phosphorous (mg/L)
Tap-Water	<0.25	<15	<0.5	<1	<0.5
WMW Coloured	32.84	1828.00	914.00	62.2	<0.5
WMW White	45.31	376	188	14.2	<0.5

The morphological isolation and Sanger sequencing allowed to identify 16 isolates from WMW (Tab. 2). Few genera were found, indicating that the WMW is a quite hostile medium, and only a few are able to thrive in it. Probably, the high concentration of surfactants may inhibit the growth of microorganisms (Aloui et al. 2009) and lead to foam formation, which interfere with the formation of EPS (Zhang et al. 2023).

Table 2 . Taxonomic identification of the bacterial isolates from washing machine wastewater, performed by Sanger sequencing.

ID	*Genus*	ID	*Genus*
C1	*Priestia*	W1	*Enterobacter*
C2	*Aeromonas*	W2	*Klebsiella*
C3	*Terribacillus*	W3	*Micrococcus*
C4	*Aeromonas*	W4	*Enterobacter*
C5	*Aeromonas*	W5	*Enterobacter*
C6	*Pseudomonas*	W6	*Enterobacter*
C7	*Enterobacter*	W7	*Enterobacter*
C8	*Aeromonas*	W8	*Klebsiella*

T. variabilis showed to be unable to thrive in WMW (100% mortality in all survival tests), and this can be imputed to the high concentrations of surfactants. The same result was already observed in dishwasher wastewater (Alabiso et al. 2024), but contrary to what we observed in dishwasher wastewater also the 1:1 association test (*T. variabilis* and 1 heterotrophic isolate) did not gave promising results: only a slight increase in the consortium growth was found for the association *T. variabilis* and *Terribacillus* sp. isolate (C3), no differences were found in the other associations (Fig. 1). The two *Klebsiella* strains were excluded from these tests as, without species identification, they could be potential pathogens.

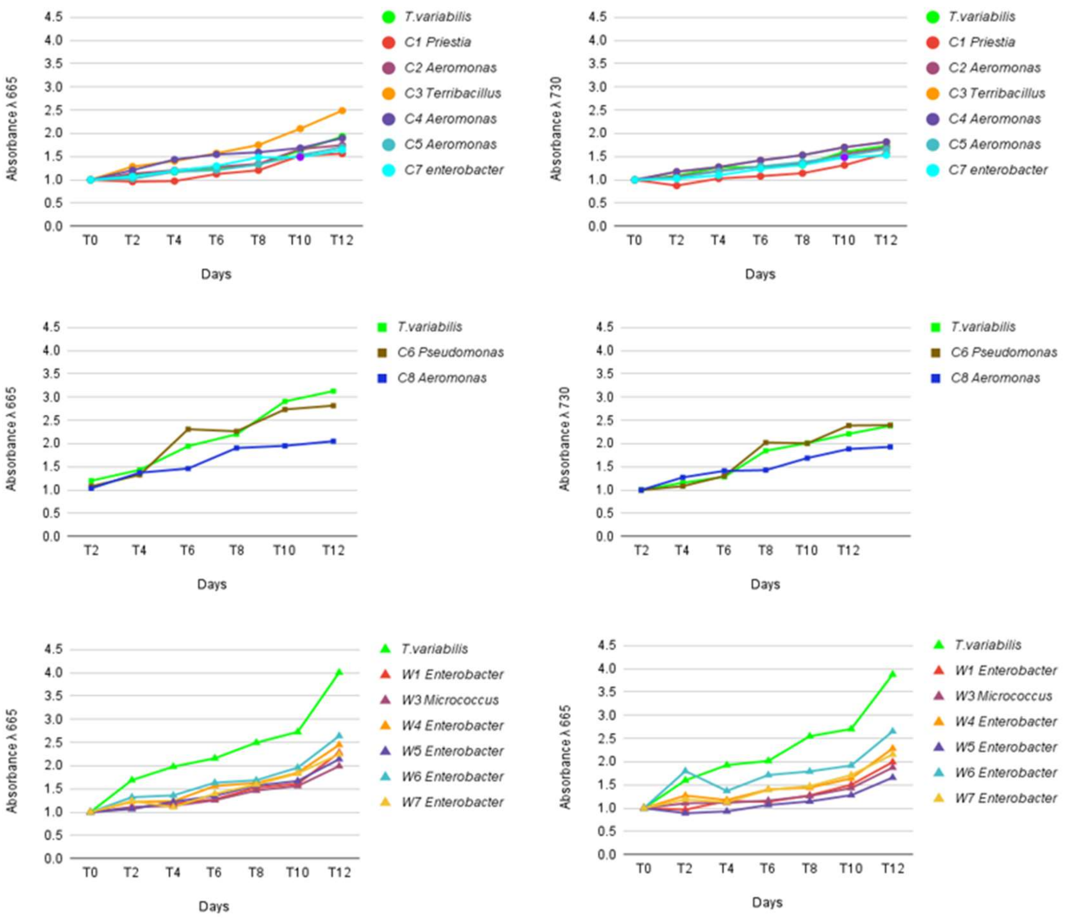

Figure 1. Growth curves of the 1:1 association of *T. variabilis* with each heterotrophic isolate collected from the washing machine wastewater normalized to the lowest value; (*left*) absorbance at λ 665, measuring *in vivo* chlorophyll *a* content (proxy of the cyanobacterial growth curve), and (*right*) absorbance at λ 730, measuring culture turbidity (proxy of the overall growth of the culture).

The not promising results of associations were confirmed by the first 1:3 test (*T. variabilis* + three heterotrophic isolates), for which we selected the C2, C3 and W3 isolates, whose growth performance demonstrated to be better or equal to the growth of *T. variabilis* alone in the 1:1 test. Unfortunately, the one-to-three co-cultures after 6 days were clearly dead (3:1 WMW-C) or highly degraded (3:1 WMW-W; Fig. 2), not showing the bright green 3D aggregates of the control consortia but a brownish/olive green discolouration of the medium, symptom of bad health of the microbial coculture (Alabiso et al. 2024).

CONTROL 3:1 WMW-W 3:1 WMW-C

Figure 2. 1:3 association test, *i.e. T. variabilis* and three heterotrophic isolates, specifically *Aeromonas* sp. (C2), *Terribacillus* sp. (C3) and *Micrococcus* sp. (W3) strains, after 6 days in washing machine wastewater.

4 CONCLUSIONS

The implementation of a mechanical filtration system to remove micro- and nano-fibres from WMW is a necessary step to reduce their environmental impact. The addition of a smart-like feature (such as a saturation sensor) enhance the system's efficiency by providing real-time information to the end user and enabling timely maintenance and replacement.

The collected micro- and nano-fibres represent a significant portion of unmanaged WMW, their conversion into nanodiamonds offers an important upcycling opportunity but also an environmental friendly and energy-efficient alternative compared to other approaches for nanodiamonds production, as detonation.

As regard wastewater bioremediation, the use of a microbial consortium does not seem promising, but the experimentation is still ongoing. However, the BOD_5/COD ratio indicate good biodegradability of the wastewater, and this may allow its direct use for irrigating plants. Furthermore, the residual presence of micro- and nano-fibres deserve further analyses to avoid possible soil contamination.

These results foster the possible future use of WMW in home gardening. This will facilitate the spreading of the urban greening to increase the energy efficiency of buildings, but also will open new scenarios for biophilic living, to re-establish positive connections between people and nature in the built environment

ACKNOWLEDGEMENTS

Work supported by the Ministry of the Environment and Energy Security (Directorial Decree EC-DEC-86, dated 07/09/23), call for circular economy projects, aimed to develop technologies for the prevention, recovery, recycling and treatment of non-recyclable waste falling into categories not already served by the supply chain consortia, 2021 edition (Decree of the Ministry of Ecological Transition of 9/12/2021, n. 83). The authors M.L., S.O., L.M., and C.M., also acknowledge the Grant MUR Dipartimento di Eccellenza 2023–27 X-CHEM project ″eXpanding CHEMistry: implementing excellence in research

and teaching.

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