

Effects of chemical pretreatment on natural fibers removal and plastic integrity for microplastics measurement in wastewater

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TEXT S1. LITERATURE REVIEW RESEARCH

((separat* OR extract* OR purif* OR digest* OR oxyd* OR isolat* OR split* OR divid* OR partition OR analys* OR identif* OR quanti* OR detect* OR analytic* OR diagnos* OR sens* OR track)wn TI) AND (microplastic* OR nanoplastic* OR micro-plastic OR micro-plastics OR nano-plastic OR nano-plastics) AND ((environment* OR complex OR *water OR water* OR influent OR biologic* OR ecologic* OR substrate)wn TI)

When multiple studies used the same protocol, the earliest published article was chosen. Preference was also given to studies comparing multiple protocols to better understand the relative performance.

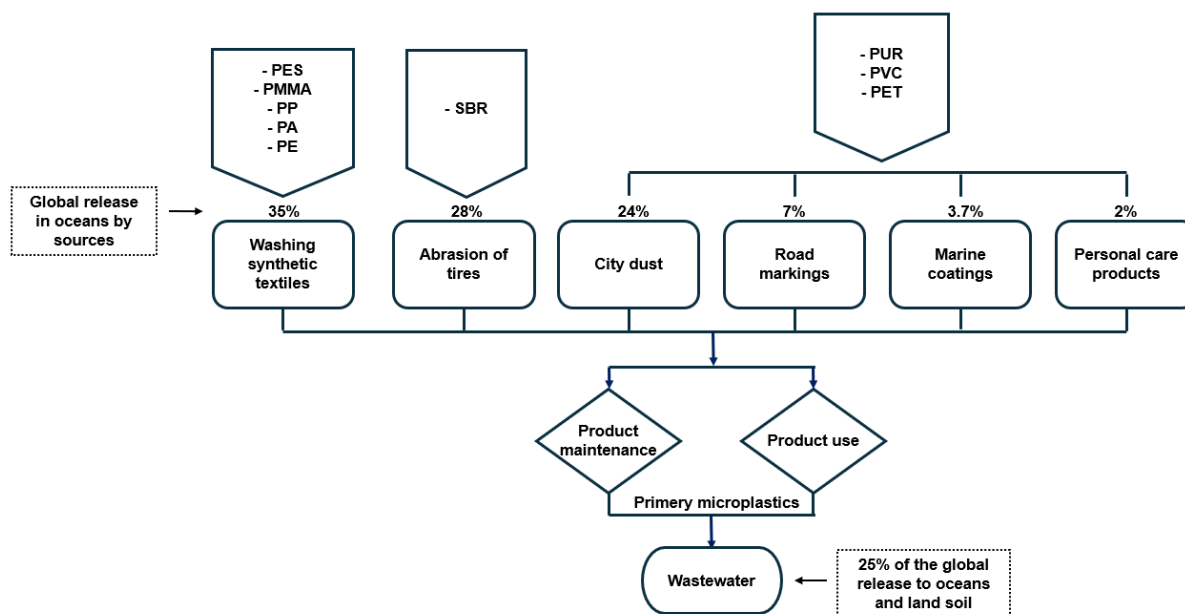


FIGURE S1 FLOWCHART OF POLYMER CONTROL CHOICE (ADAPTED FROM ^{1,2})

TEXT S2. MICROPLASTIC CONTROLS SOURCES

Synthetic fibers in consumer goods undergo a lubricating finish during the extrusion or spinning process, which is essential for making packages, bobbins or bales. The spin finish provides lubricity, thermal resistance and prevents oxidative degradation during storage. Coatings can alter microplastic resistance to pretreatment by modifying surface properties.³

TABLE S1 DIGESTION PROTOCOLS OFTEN USED IN LITERATURE SHOWED BY COMPARATIVE STUDIES

Protocol	Nature of samples	Observations	Reference
35% H ₂ O ₂ 7 d RT	Marine sediments from sand beach	92% of selected biogenic materials had dissolved completely or had lost their color Polymers >1 mm: visible changes for PA, PC, and PP (more transparent, smaller, and/or thinner). PET: brownish color. LLDPE: fragmented. Polymers <1 mm: PVC, PET, PA, PUR, PP, LDPE, LLDPE: slightly more transparent, thinner, or smaller. PC: thinner.	⁴
(6.67 g/L) Fenton reagent (30% H ₂ O ₂ + FeSO ₄)	Brown podzol soils, loamy sand with low moisture and organic content (moisture: 15.4%, OM: 5.79%) Dewatered and stabilized sludge from WWTP (moisture: 65.7%, OM: 51.5%)	No polymer size and mass changes No changes in FTIR spectra OM removal of 86.9% for sludge and 100% for soil	⁵
Proteinase K 2 h 50 °C	Sub-surface natural zooplankton and copepod tissues	No visible impact on tested polymers No changes in FTIR spectra OM degradation for both sample types >97%	⁶
Protease + lipase + cellulase + chitinase + buffer 11 days	Sea surface plankton	PP: Clear discrimination of spiked particles Sample mass reduction of 98.3 %	⁷
10% KOH 24 h 60°C	Zebrafish and <i>D. magna</i>	No changes in fluorescence intensity and surface morphology (SEM) and FTIR spectra PS: Extraction efficiency of fluorescent beads with mechanically mixed crustaceans: 99.5 %	⁸
22.5 M HNO ₃ 1 hour 60°C 1 hour 100°C	Mussel soft tissues	Degradation of 74% of OM Nylon fibers were not found PS spheres melted and clumped together	⁹
7% NaOCl 6 h 50°C	Filtered river water + Fucus algae, leaves, driftwood, fish muscles	Nylon, LDPE, PET and PS: No significant changes on physical characteristics, slight surface changes but no	¹⁰

		structural change. No FTIR spectra change except for nylon, slight rise of carbonyl index. OM mass reduction: 89%	
10M NaOH 24 h 60°C	Sub-surface natural zooplankton and capecod tissues	Nylon fibers: optimized alkaline treatment led to partial destruction. Polyethylene fragments showed signs of melting. uPVC granules exhibited yellowing. Several polyester fibers were lost during the process OM degradation for both sample types: 91.3 %	⁶

Note: RT: room temperature.

TABLE S2 PEAKS OF REFERENCE FOR INDEX CALCULATION

Polymer	Variable peak	Reference peak	Index type	Reference
PES	1713	1423-1495	Carbonyl	11, 12
PA	1643	1464	Carbonyl	11
PMMA	1721	1386-1433	Carbonyl	11
SBR	1730	1452	Carbonyl	11
PE	924-1197	2987-2866	Carbon-oxygen	11, 12
PET	1713	1423-1495	Carbonyl	11
PP	1715-1753	1460	Carbonyl	11, 12
PU	1731	1451	Carbonyl	11
PVC	1736	966	Carbonyl	11, 12

References

- (1) Julien Boucher, D. F., Primary Microplastics in the Oceans: a Global Evaluation of Sources. *International union for conservation of nature* **2017**.
- (2) PlasticsEurope *Plastics – the Facts 2022*; 2022.
- (3) Almond, J.; Sugumaar, P.; Wenzel, M. N.; Hill, G.; Wallis, C., Determination of the carbonyl index of polyethylene and polypropylene using specified area under band methodology with ATR-FTIR spectroscopy. *e-Polymers* **2020**, 20 (1), 369-381.
- (4) Nuelle, M. T.; Dekiff, J. H.; Remy, D.; Fries, E., A new analytical approach for monitoring microplastics in marine sediments. *Environ Pollut* **2014**, 184, 161-9.
- (5) Hurley, R. R.; Lusher, A. L.; Olsen, M.; Nizzetto, L., Validation of a Method for Extracting Microplastics from Complex, Organic-Rich, Environmental Matrices. *Environ Sci Technol* **2018**, 52 (13), 7409-7417.
- (6) Cole, M.; Webb, H.; Lindeque, P. K.; Fileman, E. S.; Halsband, C.; Galloway, T. S., Isolation of microplastics in biota-rich seawater samples and marine organisms. *Sci Rep* **2014**, 4, 4528.
- (7) Loder, M. G. J.; Imhof, H. K.; Ladehoff, M.; Loschel, L. A.; Lorenz, C.; Mintenig, S.; Piehl, S.; Primpke, S.; Schrank, I.; Laforsch, C.; Gerdts, G., Enzymatic Purification of Microplastics in Environmental Samples. *Environ Sci Technol* **2017**, 51 (24), 14283-14292.
- (8) Li, F.; Li, F.; Hou, X.; Luo, X.; Tu, H.; Zou, Y.; Sun, C.; Shi, M.; Zheng, H., Comparison of six digestion methods on fluorescent intensity and morphology of the fluorescent polystyrene beads. *Mar Pollut Bull* **2018**, 131 (Pt A), 515-524.

- (9) Claessens, M.; Van Cauwenberghe, L.; Vandegehuchte, M. B.; Janssen, C. R., New techniques for the detection of microplastics in sediments and field collected organisms. *Mar Pollut Bull* **2013**, 70 (1-2), 227-33.
- (10) Silvia, S. M.; Teresa, R.-S.; Joana, C. P.; Armando, C. D.; Ana Violeta, G.; Pedro, L.; Tiago, C.; João, P., A straightforward method for microplastic extraction from organic-rich freshwater samples. *Science of The Total Environment* **2022**, 815, 152941.
- (11) Veerasingam, S.; Ranjani, M.; Venkatachalapathy, R.; Bagaev, A.; Mukhanov, V.; Litvinyuk, D.; Mugilarasan, M.; Gurumoorthi, K.; Gunganathan, L.; Aboobacker, V. M.; Vethamony, P., Contributions of Fourier transform infrared spectroscopy in microplastic pollution research: A review. *Critical Reviews in Environmental Science and Technology* **2020**, 51 (22), 2681-2743.
- (12) Campanale, C.; Savino, I.; Massarelli, C.; Uricchio, V. F., Fourier Transform Infrared Spectroscopy to Assess the Degree of Alteration of Artificially Aged and Environmentally Weathered Microplastics. *Polymers (Basel)* **2023**, 15 (4).