

Production and study of model nanoplastics by top-down and bottom-up methods for environmentally relevant studies

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Résumé :

Although nanoplastic pollution is today a threat, most toxicological studies published so far use commercial polymer latexes i.e. perfect cross-linked polystyrene nanospheres modified by surface moieties, e.g. carboxylate groups. In fact, PS-NPs have little to do with real nanoplastics found in environment, of irregular sizes and shapes due to physical wearing, bearing UV-oxidized surface, coated by organic and biological layer (humic acids, "plastisphere"...). The latest literature reports two types of reference materials for environmentally relevant nanoplastics for collaborative research with (eco)toxicology laboratories:

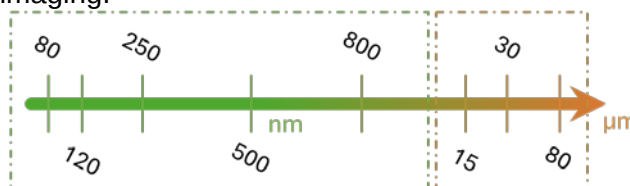
Type A NPs suspensions produced by top-down method initially described by El Hadri et al. (1), i.e. by crushing plastics litter collected by citizen associations from seashore or riverbanks. Such type A NPs are considered as "environmental nanoplastics" more representative of naturally occurring NPs (Env-NPs) produced by plastic weathering (by sun light, abrasion...) than PS-NPs.

Type B NPs prepared in the lab by bottom-up assembly of polymer chains: Briefly, virgin plastic pellets first dissolved in an organic solvent miscible with water are mixed with an excess of water acting as bad solvent. Using either this "nanoprecipitation" or an emulsion-solvent evaporation method one can reach high solid content (up to 1 wt%) and tune particle shape and size range from 80 nm to 80 µm.

First results of ecotoxicological assays on aquatic organisms (algae, clams and oysters) show that Type A NPs exert stronger impacts than Type B NPs, made from either petro- or bio-sourced polymers: even sublethal concentrations (10-100 µg/L) lead to inflammation in the organisms (2), which might arise because synthetic Type B NPs are chemically pure compared to Type A Env-NPs made from plastics weathered for decades, containing various dopants or contaminants.

The main pitfall to introduce a regulatory framework in assessment of nanoplastics is the lower limit of detection of the analytical methods, for their quantification and identification. Progress has made it possible to detect NPs in pure water (using for example pyrolysis-GC/MS technique) or in aerosols, but the next steps would be to identify and quantify them in complex matrices (soils, sea or fresh water, living tissues...). Like any colloids, dynamic light scattering (DLS) is recommended to follow the dispersion state of NPs in water. The hydrodynamic size measured by DLS generally ranges from 80-200 for true NPs to 500-800 nm (sub-micron microplastics). The size distributions can be monitored and, to some extent, controlled by physicochemical means (e.g. size fractionation by cold ultra-centrifugation).

In true ecological samples (at high dilutions), it is recommended to choose a DLS instrument with variable scattering angle (goniometer) rather than a fixed angle (usually 90° or 173°) to benefit from the angular form factor of particles, as explained in reference (3). The authors mention a LOD of 1 µg/L using a very low scattering angle (below 20°) but in practice, the detection limit that we found with such small angle DLS is more likely around 10 µg/L. This technique enables us to study the colloidal stability of Type A or Type B model NPs when exposed to high ionic strength sea water, through a microfluidic mixing chamber that mimics the slow mixing conditions in natural river estuaries like in Arcachon basin (4). One way to decrease the LOD of nanoplastics could be to label them with metals (Fe, Au...) that can be traced at very low concentration (nM) thanks to their either magnetic (Fe) or optical (Au) "fingerprints": Au-labelled NPs would be possible to detect in complex media and to differentiate from other organic matter by SERS spectroscopy or imaging.



Tunable size ranges of model particles for microplastics and nanoplastics studies

Références :

- [1] (A. Arini et al *Environmental Science: Nano* 2023 **10**, 1352 ; [2] H. El Hadri et al *NanoImpact* 2020 **17**, 100206 ; [3] G. Balakrishnan et al *Microplastics* 2023 **2**, 202 ; [4] Z. Venel, et al, *Environ. Sci. Technol.* 2021 **55**, 3001.