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Induced structural changes of humic acid by exposure of polystyrene microplastics: A spectroscopic insight☆

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The occurrence of microplastics (MPs) as emerging contaminants in the environment may cause changes in water or sediment characteristics, and further affect their biogeochemical cycles. Thus, insights into the interactions between dissolved organic matter (DOM) and MPs are essential for the assessment of environmental impacts of MPs in ecosystems. Integrating spectroscopic methods with chemometric analyses, this work explored the chemical and microstructural changes of DOM-MP complex to reveal the mechanism of DOM-MP interaction at a molecular level. MPs were found to interact with the aromatic structure of DOM via π-π conjugation, then be entrapped in the DOM polymers by the carboxyl groups and C=O bonds, constituting a highly conjugated co-polymer with increased electron density. This induced the fluorescence intensity increase in DOM. The interaction affinity of DOM-MP was highly dependent on the MP size and solution pH. This work offers a new insight into the impact of MP discharge on environment and may provide an analytical framework for evaluating MP hetero-aggregation and the roles of MPs in the transportation of other contaminants. Furthermore, the integrated methods used in this work exhibit potential applications in exploring the fragmentation processes of MPs and formation of secondary MPs under natural conditions.

1. Introduction

Plastic, as a type of synthetic organic polymer, is a global environmental issue that is particularly challenging from its strongly expanded production and exposure worldwide into environment (Jambeck et al., 2015). Specifically, the occurrence and consequence of secondary plastic with a size smaller than 5 mm, the so-called microplastic (MP) that is generated from the fragmentation of plastic as an emerging contaminant, have received increasing attention recently (Browne et al., 2011; Law and Thompson, 2014; Syberg et al., 2015). Most MPs are resistant to biodegradation and usually retained in the environment for years. Compared with larger items of debris, MPs could have different environmental effects on ecosystems. MPs may provide habitats for a variety of microbial communities (Zettler et al., 2013), and can be mistakenly ingested by diverse organisms, causing not only physical harm, but also a potential risk for the food web (Setala et al., 2014), as MPs could readily accumulate toxic chemicals and pathogenic microbes (Browne et al., 2013). With concerns regarding the risks of MP exposure to ecosystems, food safety and public health, understanding the behavior of MPs in the environment, including fragmentation, transportation, accumulation and interaction with environmental species (Van Cauwenberghe et al., 2015b; Vandermeersch et al., 2015; Hüffer et al., 2017), is essential.

After entering the environment, it is possible for MPs to react with dissolved organic matter (DOM), the ubiquitously existed species in both aquatic and terrestrial ecosystems. DOM contains various functional groups, which could serve as heterogeneous sites for the binding of metals, nanoparticles and organic pollutants (Chen et al., 2014, 2017; Sun et al., 2017b). Thus, the morphology, transportation, and biotoxicity of MPs could be affected by the DOM-MP interaction. In addition, the coexistence of MPs and DOM in the environment may also have implications in the transport and transform of hydrophobic pollutants, such as polychlorinated biphenyls and perfluorooctanoic acids (Besseling et al., 2013; Bakir et al., 2014). Hence, an insight into the DOM-MP interaction is essential for understanding the environmental impacts of MPs on both marine and freshwater systems.

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Despite of a growing number of published works on the impacts of MPs on various ecosystems (Eerkes-Medrano et al., 2015; Van Cauwenberghe et al., 2015a; Green et al., 2017), the environment behaviors of MPs remain poorly understood, mainly attributed to their complex transport mechanisms and unknown interaction pathways with DOM. Therefore, there is a great need to develop effective analytical methods that are capable of revealing the structural and microstructural variations of DOM during environmental transformation and thus characterize and track its interaction with MPs at a molecular level. Spectroscopic techniques, such as fluorescence, Fourier transform infrared (FTIR), and Raman scattering, are sensitive tools for exploring the chemical structure in environmental species, and have been applied for characterizing MPs and DOM (Stedmon and Bro, 2008; Kappler et al., 2015; Song et al., 2015). However, the spectra of MP or DOM are often overlapped by coexistent interferences, and conventional spectroscopic methods fail to reveal the subtle spectral changes in the interaction process. Chemometric analyses, such as excitation-emission matrix coupled with parallel factor analysis (EEM-PARAFAC) and two dimensional correlation spectra (2DCOS), are useful to solve this problem and have been applied in elucidating environmental interactions (Wei et al., 2016; Liu et al., 2017; Sun et al., 2017a). However, there is no report about the DOM-MP interactions so far.

Therefore, the predominant aim of this work is to explore the interaction mechanism between MP and DOM at a molecular level. Fluorescence EEM-PARAFAC and infrared 2DCOS analyses were used to track the structural changes of DOM in its interaction process with MP. Experiments were conducted using polystyrene (PS) and humic acid (HA) as the representative MP and DOM, respectively. Spherical PS microplastics with four different diameters were used to explore the impact of DOM-MP on the structural change of HA as well as the surface morphological change of MPs. Also, the effects of MP concentration and solution pH on the interaction process were investigated.

2. Experimental section

2.1. Reagents and sample preparation

PS microplastics (5 wt% water suspension) with 4 different diameters (20 μm, 6 μm, 500 nm and 80 nm) were purchased from Nanking Janus Co., China. Commercial HA was purchased from Sigma-Aldrich Co., USA, and was purified prior to use following a previous work (Chen et al., 2014). In short, raw HA was initially dissolved in 0.1 mol/L NaOH solution with subsequent filtration, and the filtrate was then acidified by 0.1 mol/L HCl. Afterwards, the precipitate was collected by a second filtration (0.45 μm PVDF membrane), washed extensively with 0.1 M HCl and freeze-dried. The total organic carbon content of purified HA was 49.8 wt%.

PS stock solution was prepared by diluting the PS suspension with deionized water to a final concentration of 200 mg/L, in which the number of MPs was approximately 4.55×10^7 items L^{-1} for PS microplastics with 20 μm diameter. It should be noted that in environments the number of MP particles increases significantly when the size decreases. Thus, the concentration range of MP for the subsequent experiments (0–100 mg/L) was close to the level in natural environments (Duis and Coors, 2016). The purified HA was dissolved to a concentration of 50.0 mg/L as a stock solution. A series of samples containing 25 mg/L HA and PS in a concentration range of 0–100 mg/L were prepared by mixing appropriate volumes of PS stock solution with 10-mL aliquot of HA stock solution, and deionized water was added into the mixture solution to generate a final volume of 20 mL. The pH was maintained constant by adjusting both HA and PS stock solutions to the target value, i.e., pH 5.0, 7.0, or 9.0, and the mixed solution was fine tuned with 0.1 M NaOH or HCl solution. Details on sample series are shown in Table S1 in the supplementary information,. All samples were shaken on a horizontal shaker for 1 week at ambient temperature to ensure interaction equilibrium (Bakir et al., 2014). Then, the samples were centrifuged for 15 min at 10000 rpm to separate the residual PS particles from solution. Five mL aliquot of each supernatant sample was used for fluorescence spectroscopy analysis and 8 mL aliquot was mixed with 60 mg of KBr powders (IR grade) and freeze-dried for further FTIR spectroscopy analysis. Background solutions containing 100 mg/L PS without HA were treated by the same procedure and their spectra were also measured as control.

2.2. Procedures and parameters of measurements

The morphology, microstructure, and elemental composition of PS microplastics before and after interacting with HA were characterized by field-emission scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX, SIRION200, FEI Co., USA). The diameter change of PS microplastics before and after HA addition was measured by dynamic light scattering (DLS) using a Malvern Zetasizer ZS instrument (Malvern Instruments Co., UK). Since the DLS instrument is able to measure particles ranging from 0.6 nm to 5 μm, only the 80 nm and 500 nm PS microplastices were tested. Three parallel tests were conducted at 25 °C, and the data are presented as the mean ± standard deviation. Fluorescence EEM landscape of each sample was recorded using an Aqualog spectrometer (Horiba Co., Japan). The emission range was fixed from 211 to 618 nm with a 3.2 nm step increase, and the excitation wavelength increased sequentially from 240 nm to 600 nm with a 3 nm step. Inner filter effect, first- and second-order Rayleigh scatterings were corrected by the Aqualog software.

For FTIR measurement, the freeze-dried samples were ground, homogenized and pressed with a mould for FTIR transmission spectra measurement under the irradiation of an infrared lamp. Their FTIR spectra were generated on a Vertex 70 spectrometer (Bruker Co., Germany) with a deuterated triglycine sulfate detector. The spectral range was from 4000 to 400 cm^{-1}, and each spectrum was an average of 32 scans with 4 cm^{-1} resolution. The FTIR transmission spectra were smoothed, baseline-corrected and transformed to absorbance spectra using OPUS 5.5 software for the subsequent 2DCOS analysis.

2.3. Spectroscopic analyses

To decompose the fluorescence components in HA and track its concentration changes during interaction with PS, PARAFAC was used to analyze the fluorescence EEM data. PAFAFAC modelling was carried out in MATLAB 7.10.0 (Mathworks Inc., USA) with the N-way Toolbox 3.1. The number of components in the PARAFAC solution was determined by core consistency diagnostic and validated by the split-half analysis. Details about PARAFAC could be found elsewhere (Stedmon and Bro, 2008).

To better reveal the subtle change of IR spectra and explore the structural variation of HA after its interacting with PS, 2DCOS was applied to further analyze the IR absorption spectra. PS concentration was used as the external perturbation. The IR data set was transformed into a new spectral matrix for 2DCOS analysis, and 2DCOS maps were calculated and re-plotted by 2D Shige (Kwansei-Gakuin University, Japan) and Origin 8.5 software respectively. Principles about 2DCOS analysis are detailed elsewhere (Chen et al., 2015).