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Aggregation kinetics of microplastics in aquatic environment: Complex roles of electrolytes, pH, and natural organic matter[☆]

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ABSTRACT

Microplastics are an emerging contaminants of concern in aquatic environments. The aggregation behaviors of microplastics governing their fate and ecological risks in aquatic environments is in need of evaluation. In this study, the aggregation behavior of polystyrene microspheres (micro-PS) in aquatic environments was systematically investigated over a range of monovalent and divalent electrolytes with and without natural organic matter (i.e., Suwannee River humic acid (HA)), at pH 6.0, respectively. The zeta potentials and hydrodynamic diameters of micro-PS were measured and the subsequent aggregation kinetics and attachment efficiencies (α) were calculated. The aggregation kinetics of micro-PS exhibited reaction- and diffusion-limited regimes in the presence of monovalent or divalent electrolytes with distinct critical coagulation concentration (CCC) values, followed the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The CCC values of micro-PS were14.9, 13.7, 14.8, 2.95 and 3.20 mM for NaCl, $NaNO_3$, KNO_3, $CaCl_2$ and $BaCl_2$, respectively. As expected, divalent electrolytes (i.e., $CaCl_2$ and $BaCl_2$) had stronger influence on the aggregation behaviors of micro-PS as compared to monovalent electrolytes (i.e., NaCl, $NaNO_3$ and KNO_3). HA enhanced micro-PS stability and shifted the CCC values to higher electrolyte concentrations for all types of electrolytes. The CCC values of micro-PS were lower than reported carbonaceous nanoparticles CCC values. The CCC[Ca^{2+}]/CCC [Na^{+}] ratios in the absence and presence of HA at pH 6.0 were proportional to $Z^{-2.34}$ and $Z^{-2.30}$, respectively. These ratios were in accordance with the theoretical Schulze–Hardy rule, which considers that the CCC is proportional to z^{-6} $-z^{-2}$. These results indicate that the stability of micro-PS in the natural aquatic environment and the possibility of significant aqueous transport of micro-PS.

1. Introduction

Plastic products are extensively used in the modern world (Zhang et al., 2017). The accumulation of discarded plastics in aquatic environments is escalating due to increased production and imperfect waste management, (McDevitt et al., 2017). Plastic debris would continuously fragments into smaller plastic particles in aquatic environments, as a result of physical, chemical and biological processes (Browne et al., 2007; Halle et al., 2016; Kooi et al., 2017). Nowadays, small plastic particles, defined as microplastics with a size range of <5 mm, has been ubiquitously detected in aquatic environments (Browne et al., 2011; Cole et al., 2011; Cauwenberghe et al., 2013; Wright et al., 2013; Rochman et al., 2015; Hüffer et al., 2017; Zhang et al., 2017). Microplastics may also come from primary plastics, which are intentionally used as resin pellets or as ingredients of personal care products (Hu et al., 2016; Hernandez et al., 2017). Microplastics in aquatic environments can be mistakenly ingested by organisms, which can lead to potential adverse effects, including growth inhibition, behavioral disorders, reproductive dysfunction, feeding disorders, reduced viability, and even mortality (Cole et al., 2013; Lee et al., 2013; Mattsson et al., 2015; Lu et al., 2016; Watts et al., 2016). Furthermore, microplastics can influence the ecosystem by releasing plastic additives, such as plasticizers and flame retardants (Browne et al., 2007; Cole et al., 2011; Cauwenberghe et al., 2013; McDevitt et al., 2017), and by acting as a vector for transport of hydrophobic

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organic contaminants and heavy metals (Mato et al., 2001; Ogata et al., 2009; Hirai et al., 2011; Bakir et al., 2012; Holmes et al., 2012; Lee et al., 2014; Rochman et al., 2014; Brennecke et al., 2016; Zhan et al., 2016; Wardrop et al., 2017). Microplastics have been identified as contaminants of emerging concern in aquatic environments (Cole et al., 2011; Lu et al., 2016; Hüffer et al., 2017).

Microplastics will undergo aggregation upon release to the aquatic environments, which is one of the critical factors that ultimately controls their environmental fate and ecological risks (Carr et al., 2016; Costa et al., 2016; Besseling et al., 2017). However, to date, the underlying mechanisms of the aggregation behavior of microplastics in aquatic environments has yet to be investigated.

Several studies have been conducted to investigate the stability and aggregation kinetics of carbonaceous nanoparticles, such as fullerenes (Bouchard et al., 2009; Chen et al., 2010; Mashayekhi et al., 2012; Yang et al., 2013; Zhang et al., 2013; Choi et al., 2015; Shen et al., 2015; Aich et al., 2016), carbon nanotubes (Hyung et al., 2007; Saleh et al., 2008; Lin et al., 2012; Khan et al., 2013; Hwang et al., 2013; Chang et al., 2015; Li et al., 2016; Jiang et al., 2017a,b; Park et al., 2017; Yang et al., 2017) and graphene oxide (Zhao et al., 2014; Chowdhury et al., 2015; Hua et al., 2016; Jiang et al., 2016, 2017a,b; Feng et al., 2017; Gao et al., 2017; Li et al., 2017; Yang et al., 2017) in aquatic environments based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. According to this theory, the stability of the carbonaceous nanoparticles in aquatic environments can be determined by their potential energy curve, which strongly depends on the solution chemistry (i.e., pH, electrolytes, and natural organic matter (NOM)) (Bouchard et al., 2009; Hwang et al., 2013; Zhang et al., 2013; Chang et al., 2015; Chowdhury et al., 2015; Aich et al., 2016; Hua et al., 2016; Gao et al., 2017; Jiang et al., 2017a,b; Li et al., 2017; Yang et al., 2017). Quantitative assessment of the stability of carbonaceous nanoparticles in aquatic environments were to measure the attachment efficiency (α), the inverse of the stability ratio (W) and the critical coagulation concentration (CCC), which were the minimum concentration of electrolytes required to completely destabilize the carbonaceous nanoparticle suspension (Tadros, 2007). Attachment efficiency (α) has been recently a focus of discussion due to its importance in modeling the environmental fate of carbonaceous nanoparticle (Chowdhury et al., 2015; Aich et al., 2016; Jiang et al., 2016, 2017a,b; Afshinnia et al., 2017; Li et al., 2017; Yang et al., 2017).

Given the particulate nature of both carbonaceous nanoparticles and microplastics, this study aims to investigate the influence of solution chemistry on the aggregation behavior of polystyrene microspheres (micro-PS), as model microplastics (Lu et al., 2016), in aquatic environments. The aggregation kinetics of micro-PS were analyzed over a wide range of monovalent (i.e., NaCl, $NaNO_3$ and KNO_3) and divalent (i.e., $CaCl_2$ and $BaCl_2$) electrolytes with and without NOM (i.e., Suwannee River humic acid (HA)), at pH 6.0, respectively. The CCC values for the aggregation and interaction energy among micro-PSs were determined by combining experimental measurements and theoretical calculations. The results offered thorough information to understand the influences of solution chemistry on the aggregation behavior of micro-PS, which would be useful for assessing the environmental fate and ecological risks of microplastics in aquatic environments.

2. Materials and methods

2.1. Materials

Micro-PSs were purchased from Sigma-Aldrich, USA. The Suwannee River humic acids (HA) (Standard II, 2S101H) was obtained from the International Humic Substances Society, USA. Other chemicals including $CaCl_2$, $BaCl_2$, NaCl, $NaNO_3$, KNO_3, HNO_3, HCl and NaOH were obtained from Guangzhou Chemical Reagent Co., Ltd., China. All the chemicals used in the experiments were analytical reagent grade if not specified, and were used without further purification. Ultrapure water ($18.2\ M\Omega\cdot\ cm^{-1}$) used in this study was double distilled and deionized using a Milli-Q water purification system (Millipore, USA). The glassware was immersed in a 5% HNO_3 solution for 24 h, washed with tap water and ultrapure water, and baked at 300 °C for 12 h.

2.2. Sample preparation

Micro-PSs were weighted into ultrapure water and stirred for 30 min. Multiple 20 mL aliquots were collected from 1 to 2 cm below the suspended micro-PS surface, and combined to form the suspended micro-PS samples. The electrolytes and HA were dissolved in ultrapure water, stirred for 30 min, and then filtrated through 0.22-μm cellulose acetate filter paper (Whatman, Sanford, ME, USA). Total organic carbon (TOC) was measured before and after the filtration using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). Aliquots of the suspended micro-PSs were diluted with the electrolyte and/or HA solutions. All the suspended micro-PS samples were used only once.

2.3. Aggregation experiments and theoretical analysis

The aggregation experiments were conducted either over a wide range of pH or at pH6.0 and 20 °C for different concentration of electrolytes and HA concentrations, in which the suspended micro-PS concentrations were controlled at 20.0 mg/L. The pH of the suspended micro-PS samples was adjusted using 0.10 M HCl and 0.10 M NaOH. The electrolytes and/or HA solutions were added into the suspended micro-PS samples. The tested suspended micro-PS samples were vortexed for 1.0 s. immediately. The hydrodynamic diameters of micro-PS were determined by laser particle size analyzer (LPSA, Mastersizer, 2000, Malvern, UK). The zeta-potential of micro-PS was measured by ZetaPlus zeta potential analyzer (Brookhaven, USA). The morphological images of micro-PSs were captured using field emission scanning electron microscopy (SEM, JSM-6700, JEOL, Japan) or confocal laser scanning microscopy (CLSM, Leica TCS SP5, Wetzlar, Germany). The experiments were triplicated and results in average were reported. Data were graphed using Origin 8.5 software (OriginLab Corporation, Massachusetts, USA). Standard deviation values (represented in error bars) were calculated using Microsoft Excel Software (version 2013, Microsoft Corporation, Washington, USA).

Theoretical analysis of the aggregation of micro-PS are given in the Supplementary data.

3. Results and discussion

3.1. Characteristics of micro-PS

The SEM image of micro-PS particles is presented in Fig. 1a. The micro-PSs are close to microspheres in shape. The average diameters of micro-PS were calculated to be 12.1 ± 3.4 μm, based on the SEM analysis of 200 micro-PS particles. The hydrodynamic diameters of micro-PS measured by LPSA exhibited a narrow distribution with the peak width at half-maximum of 10.6 μm (Fig. 1b). The average diameters of micro-PS were determined to be 17.9 ± 0.2 μm ($n = 30$) with a range of 3.31–138 μm. The average diameters of micro-PS determined by LPSA were slightly greater than these obtained by SEM, which were consistent with the observations for carbonaceous nanoparticles such as fullerenes (Mashayekhi et al., 2012; Yang et al., 2013; Choi et al., 2015), carbon