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Effect of natural organic matter on aggregation behavior of C_{60} fullerene in water

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ABSTRACT

The stability of C_{60} fullerene particles in water affects its mobility, bioavailability, and toxicity to organisms. Natural organic matters (NOMs) have pronounced effects on the aggregation behavior of C_{60} fullerene. This study was to examine the effects of NOM structural properties on the aggregation behavior of fullerene water suspension (FWS). Fulvic acid (FA), tannic acid (TA), and two structurally different humic acids (HA1 and HA7) were studied. HA1 and HA7 were sequentially extracted HAs, where HA7 was more hydrophobic than HA1 and had a higher molecular weight. Aggregation was induced by addition of varying amounts of Ca^{2+} to the FWS with 2 mg/L of each NOM. The absolute value of zeta potential $|\zeta|$ of pure FWS increased after addition of any type of NOM. Addition of Ca^{2+} to the FWS + NOM system decreased $|\zeta|$ of fullerene almost uniformly for all types of NOM. FWS critical coagulation concentration (CCC) was equal to 14.5, 6.5, 5.4, and 3.7 mM Ca^{2+} for HA7, HA1, FA, and TA, respectively. The order of increasing CCCs was positively correlated to the NOMs molecular weight and negatively to their polarity. A nearly constant ζ for FWS + NOM system at a wide range of Ca^{2+} concentrations suggested the steric stability rather than electrostatic one. This study highlighted the role of NOM in the fate of manufactured nanoparticles in the environment and linked the structural properties of NOM to their interaction with manufactured nanoparticles.

1. Introduction

C_{60} fullerene molecule has been subject of numerous research and attention since its discovery, because of its different potential applications. Consumer products containing fullerene such as lubricants and badminton racquets are already in the market [1]. Thus, it is easy to foresee the inevitability of fullerene introduction to the environment during their production, transportation, usage, and disposal. There are several concerns about the diverse effects of released fullerenes into the environment, including their toxicity and acting as a carrier and accumulator of xenobiotic compounds [2]. Several reports have shown toxicity of fullerene to various organisms and human or animal cells [3–6].

Though C_{60} fullerene molecule is extremely nonpolar and virtually insoluble in water [7], it forms stable suspensions in water at low ionic strengths [8]. Solvent exchange and extended mixing in water are different methods used in laboratory for preparing fullerene water suspension (FWS) [9]. Several studies have shown that fullerene particles in water regardless of their production routes carry negative surface charges with yet unclear origin, leading to suspension stability [10]. Pure FWS behavior perfectly follows the classic Dejaguin–Landau–Verwey–Overbeek (DLVO) theory [11].

Natural organic matter (NOM) in water greatly affects colloidal stability, thus the mobility and bioavailability of fullerene. However, different degrees or types of surface modifications of fullerenes induced by NOM can be perceived, depending upon spatial and temporal variations of NOM [12]. A few studies have been focused on the effect of NOM on the physicochemical properties of FWS. An increase in the solubilization of fullerene molecules in water was reported in the presence of 100 mg/L FA or HA [13]. Xie et al. reported a decrease in the particle size of fullerene after addition of FA, which could be due to disaggregation of fullerene aggregates after the surface sorption of NOM [12]. Espinasse et al. reported that tannic acid increased stability of FWS in the presence of Na^+ [14]. Chen et al. showed that HA could effectively increase stability of FWS [15].

However, NOM is known to be composed of materials with a wide range of structural properties and molecular weights. Structural properties of NOMs varying by their age, origin, and source greatly influence their physicochemical properties such as sorption, their dominant functional groups, surface charge, solubility, and other properties [16]. This could lead to different capabilities of HAs to stabilize fullerenes in water. In a recent study, Ghosh et al. showed that surface adsorbed, long chain humic acid molecules could provide steric stability to Al_2O_3 nanoparticles, while polar short chain HAs enhanced aggregation of Al_2O_3 nanoparticles [17]. To our knowledge, only few studies have been focused on the effect of physicochemical properties of NOM on the stability and aggregation behavior of C_{60} fullerene in water.

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The objective of this work was therefore to study the effect of different NOM structural properties on the FWS aggregation behavior, by comparing FWS stability in the presence of a series of NOMs with a wide range of structural characteristics. We utilized four different NOMs: Two structurally different humic acids sequentially extracted from an organic soil, tannic acid, and Suwannee River fulvic acid. Different concentrations of calcium chloride were used to induce aggregation of fullerene in the presence of each of NOM. Early stage aggregation kinetics of FWS was studied using dynamic light scattering (DLS) technique in the presence of each NOM. Then, several structural characteristics of NOM such as molecular weight and polarity were related to the stability of FWS with NOM.

2. Experimental

2.1. Preparation of FWS and NOM solutions

C_{60} fullerene powders were purchased from MER Corp. (Tuscan, AZ). Tannic acid was purchased from Fisher Scientific and Suwannee River Fulvic acid Standard I from International Humic Substances Society (IHSS). Humic acids (HAs) were sequentially extracted using alkali solution from an organic soil in Amherst, MA, in our previous research and were fully characterized [18,19]. HA1 was the first sequential extract while HA7 was the 7th progressive extract [18]. Characterization experiments showed that HA7 was more aliphatic with a relatively high carbohydrate content compared to HA1 [19]. Fullerene powders were dissolved in HPLC grade toluene (2 mg/mL), and then 2 mL of the purple color toluene solution was added to 150 mL of Milli-Q water and sonicated with a sonicator probe at 100 W (Fisher Scientific) for several hours until fullerene was transferred to water and all toluene was evaporated. The amber color suspension of fullerene in water (FWS) was filtered through a 0.2 μm cellulose filter, its pH was adjusted to 7 using 0.1 M NaOH or HCl solutions, and stored at room temperature in dark. Solutions of HAs, FA, and TA were made at 250 mg/L and filtered through a 0.2 μm sterile nylon filter after adjusting their pH to 7 and stored refrigerated in sterile tubes to avoid potential microbial interference.

2.2. Molecular weight measurement of NOMs

High performance size exclusion chromatography (HPSEC) was used to determine and compare the relative molecular weights of NOMs. Detailed procedure was described by Kang and Xing [20]. A TSKGEL column (Tosoh Bioscience, G3000PWXL, 7.8 mm × 30 cm, and particle size 6 μm) and TSK-GEL guard column (Tosoh Bioscience, 6.0 mm × 4 cm, and particle size 12 μm) were used with a Perkin–Elmer 200 LC diode array detector at 254 nm. Sodium polystyrene sulfonate (PSS) was used as standard molecular weight ranging from 1.8 to 35 kDa and acetone as the lowest molecular weight index. All NOMs samples and standards were injected at a concentration of 250 mg/L. The mobile phase was 0.1 M NaCl buffered with 2 mM phosphate at pH 7 and flow rate was 0.5 mL/min.

2.3. Sorption of NOMs by C_{60} fullerene

A batch sorption experiment was designed to estimate sorption of each NOM by fullerene in powder form. 10 mg of fullerene powders was transferred to 8 mL screw cap vials with Teflon liners (in duplicate) and then 8 mL of 5 mg/L solution of each NOM in 200 mg/L sodium azide at pH 7 was added. The vials were shaken for 4 days to achieve equilibrium, then centrifuged at 1000g and the supernatant was analyzed by a Total Organic Carbon Analyzer (TOC-L Shimadzu Corp., Japan) to determine initial and equilibrium concentrations of NOMs. Amount of sorbed NOM was calculated based on mass-balance with reference to blank vials (without fullerene). Adsorption coefficient (K_d) was calculated for each NOM, based on the following equation:

$$K_d = \frac{q}{C_e}$$

where q (μg/g) is the concentration of sorbed NOM on the solid phase and C_e (μg/mL) is the NOM concentration at equilibrium in the solution.

2.4. Transmission electron microscopy (TEM) and Atomic Force Microscopy (AFM) imaging

Formvar coated 400 mesh copper grids (Electron Microscopy Sciences, Hatfield, PA) were placed on the top of a drop of 5 mg/L FWS with or without different NOMs, and allowed the adsorption of particles on the formvar coating for 15 min. We chose to place grid on the top of suspension droplet to minimize possible precipitation of bigger aggregates on the grid. Then, the grids were gently rinsed with Milli-Q water and allowed to dry in a laminar flow hood to avoid airborne contaminations. A JEOL 100CX TEM (JOEL Ltd., Tokyo, Japan) at 100 kV was used to capture the images. Two samples from each treatment were prepared and at least three images at different magnifications were captured by the microscope.

In case of AFM studies, fullerene particles with or without NOMs were adsorbed on the surface of Ca saturated freshly cleaved mica and images were captured in tapping mode. A Dimension 3100 AFM instrument (Digital Instruments) in tapping mode was used to capture height and phase AFM images. The cleaved mica surface was saturated with Ca to increase adsorption of FWS by immersing mica in 1 M $CaCl_2$ solution for 30 min followed by washing with Milli-Q water to remove free $CaCl_2$. Then, Ca saturated mica was vertically placed in FWS with different NOMs and allowed adsorption for 30 min. After gently washing to remove excess particles, mica samples were dried under a laminar flow hood to avoid dust contaminations. Two slides in each treatment were prepared and at least three images (5 μm × 5 μm) per slide were captured by the AFM instrument.

2.5. Zeta potential measurements

Zeta potential (ζ) of FWS was measured using a ZetaSizer Nano ZS (Malvern Instruments, Bedford, MA) equipped with a folded capillary cell at 25 °C. This instrument employs a He–Ne laser at 633 nm and collects back-scattering data at 173°. Electrophoretic mobility was measured by a combination of laser Doppler velocimetry and phase analysis light scattering technique. Electrophoretic mobility measurements were converted to ζ using Smoluchowski's equation. Predetermined amounts of 1 M $CaCl_2$ solution were added to the FWS to get desired ionic strengths ranging from 2 to 10 mM. Concentration of all NOMs in FWS was kept at 2 mg/L. The ζ of pure HAs were measured at a concentration of 250 mg/L while that of TA and FA measured at 1000 mg/L. We had to use the high concentration of 1000 mg/L for TA and FA to get enough intensity of the back-scattered light from these smaller NOMs.

2.6. Aggregation kinetics studies

Growth rate of fullerene aggregates was also measured using the ZetaSizer Nano ZS. Three mL FWS was added to a polystyrene measurement cell and the intensity average aggregate size was recorded at 15 s intervals for 16 min at 25 °C. Predetermined amounts of NOM stock solutions were added to the FWS to get a final concentration of 2 mg NOM/L which is in range of typical concentration range