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# Complex interplay between formation routes and natural organic matter modification controls capabilities of $C_{60}$ nanoparticles ($nC_{60}$) to accumulate organic contaminants

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## ABSTRACT

Accumulation of organic contaminants on fullerene nanoparticles ($nC_{60}$) may significantly affect the risks of $C_{60}$ in the environment. The objective of this study was to further understand how the interplay of $nC_{60}$ formation routes and humic acid modification affects contaminant adsorption of $nC_{60}$. Specifically, adsorption of 1,2,4,5-tetrachlorobenzene (a model nonionic, hydrophobic organic contaminant) on $nC_{60}$ was greatly affected by $nC_{60}$ formation route – the formation route significantly affected the aggregation properties of $nC_{60}$, thus affecting the available surface area and the extent of adsorption *via* the pore-filling mechanism. Depending on whether $nC_{60}$ was formed *via* the “top-down” route (*i.e.*, sonicating $C_{60}$ powder in aqueous solution) or “bottom-up” route (*i.e.*, phase transfer from an organic solvent) and the type of solvent involved (toluene *versus* tetrahydrofuran), modification of $nC_{60}$ with Suwannee River humic acid (SRHA) could either enhance or inhibit the adsorption affinity of $nC_{60}$. The net effect depended on the specific way in which SRHA interacted with $C_{60}$ monomers and/or $C_{60}$ aggregates of different sizes and morphology, which determined the relative importance of enhanced adsorption from SRHA modification *via* preventing $C_{60}$ aggregation and inhibited adsorption through blocking available adsorption sites. The findings further demonstrate the complex mechanisms controlling interactions between $nC_{60}$ and organic contaminants, and may have significant implications for the life-cycle analysis and risk assessment of $C_{60}$.

## Introduction

Buckminster fullerene ($C_{60}$) is an important carbon nanomaterial that has great potential in various fields such as cancer therapeutics, drug delivery, and computer sensors (Simon et al., 2007; Campoy-Quiles et al., 2008; Li et al., 2008; Mauter and Elimelech, 2008). With the increasing production and use of this material, its environmental release is inevitable (Klaine et al., 2008). The potential risks of $C_{60}$, in particular, colloidal nano-scale $C_{60}$ aggregates (*i.e.*, $nC_{60}$), have received considerable attention, with a number of studies demonstrating $C_{60}$ toxicity (Sayes et al., 2004; Klaine et al., 2008). Further, in natural environments $C_{60}$ can accumulate organic contaminants (Yang et al., 2006; Gai et al., 2011; Zhang et al., 2011), which may further alter the risk profiles (Henry et al., 2007).

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To date, only limited studies have examined the adsorptive interactions between $C_{60}$ and common organic contaminants (including naphthalene, phenanthrene, fluoranthene, pyrene, chrysene, 1,2-dichlorobenzene, and atrazine), and the results show that the adsorption affinities of $C_{60}$ are strongly dependent on its aggregation properties (Cheng et al., 2004, 2005; Yang et al., 2006; Yang and Xing, 2007; Hu et al., 2008; Gai et al., 2011; Hüffer et al., 2013). For example, Cheng et al. (2004) reported that small $C_{60}$ aggregates with diameters of 1–3 μm (formed by magnetically stirring $C_{60}$ powder in a solution containing 0.01 mol/L NaCl and 0.01 mol/L $NaN_3$) exhibited much stronger adsorption affinity for naphthalene than did large $C_{60}$ aggregates with diameters of 20–50 μm, likely due to the increased number of adsorption sites per unit of $C_{60}$ (aggregate) mass for the smaller aggregates. Similarly, Gai et al. (2011) reported that adsorption affinities of $C_{60}$ aggregates (0.14–15.28 μm) increased with decreasing particle size. Interestingly, in another study by Cheng et al. (2005), it was found that an $nC_{60}$ sample prepared by solvent exchange from toluene had lower adsorption affinity for naphthalene than smaller aggregates formed simply through physical mixing. Gai et al. (2011) also made very similar observations using atrazine, and attributed the lower adsorption $nC_{60}$ to its lower pore volume. Thus, it appears that the formation routes/mechanisms of $nC_{60}$ (and subsequent aggregation processes) play a critical role in the adsorption affinities of the aggregates.

Chang et al. (2012) categorized the formation mechanisms of $nC_{60}$ into two general routes as (1) top-down routes whereby $nC_{60}$ is formed by breaking large aggregates into smaller ones (*e.g.*, physically mixing $C_{60}$ powder in aqueous solutions), and (2) bottom-up approaches whereby $nC_{60}$ forms from a seed-growth mechanism (solvent exchanging $C_{60}$ from organic solvent to aqueous solution). In general, $nC_{60}$ formed through top-down routes is typically larger in size and irregularly shaped (Duncan et al., 2008; Chang and Vikesland, 2009), whereas $nC_{60}$ formed *via* the bottom-up route is smaller in size with more ordered, crystalline structures (Brant et al., 2005, 2006; Fortner et al., 2005). Further, $nC_{60}$ samples formed *via* solvent exchange methods can vary significantly depending on the specific solvents used (Brant et al., 2006; Xie et al., 2008). To date, little is known about how formation routes of $nC_{60}$ fundamentally affect the adsorption affinities toward common organic contaminants.

It has been demonstrated that natural organic matter (NOM) can significantly affect the adsorption properties of $nC_{60}$ (Hu et al., 2008; Gai et al., 2011). Adsorption of NOM to $C_{60}$ aggregates can cover (or effectively block) available adsorption sites or pores of $C_{60}$ aggregates, thus inhibiting adsorption (Hu et al., 2008; Gai et al., 2011). NOM can also enhance the dispersion of $C_{60}$ (Xie et al., 2008; Li et al., 2009; Qu et al., 2010), consequently rendering more available adsorption sites. Gai et al. (2011) found that $nC_{60}$ aggregates formed by stirring $C_{60}$ powder in a humic acid (HA) solution had greater adsorption affinity for atrazine than $nC_{60}$ formed in the absence of HA, and the specific enhancement extent depended on how much enhanced dispersion due to HA modification counterbalanced the pore-blocking effect of HA. Taken together, we hypothesize that the specific effects of NOM modification on the adsorption affinities of $nC_{60}$ will also largely depend on the formation routes of $nC_{60}$.

The objective of this study was to understand how the complex interplay between formation routes and NOM modification can affect the adsorption affinity of $nC_{60}$ for organic contaminants. One physical mixing (sonication) and two solvent exchange (toluene *vs.* tetrahydrofuran (THF)) approaches were chosen to prepare $nC_{60}$ samples, and NOM modification was performed with Suwannee River humic acid (SRHA) during or after the formation of $nC_{60}$. A nonionic, hydrophobic organic molecule, 1,2,4,5-tetrachlorobenzene (TeCB), was selected as a model organic compound to avoid potential complications such as polar and electrostatic interactions. The combined effects of formation routes and SRHA modification were analyzed based on the physicochemical properties of the $nC_{60}$ samples and their adsorption affinities for TeCB.

## 1. Materials and methods

### 1.1. Materials and chemicals

Pristine fullerene powder ($C_{60}$, >99.5%) was purchased from SES Research (USA). SRHA was obtained from the International Humic Substances Society (USA), and is reported to be composed of 52.63 wt% carbon, 4.28 wt% hydrogen, 42.04 wt% oxygen, and a small amount of nitrogen, sulfur, and phosphate; the distribution of functional groups is: carboxylic (21%), aromatic (31%), aliphatic (29%), and heteroaliphatic (20%). Glass optical fibers with a 30-μm polydimethylsiloxane coating were purchased from Polymicro Technologies (USA). The fibers were cut into 3 cm lengths, and cleaned three times with 1:1 (v:v) methanol/water by shaking, then washed with deionized (DI) water to remove all the solvent, and stored in DI water until further use. 1,2,4,5-Tetrachlorobenzene (TeCB, >99%), chromatographic grade toluene and THF were purchased from Sigma Aldrich (USA).

### 1.2. Preparation and characterization of $nC_{60}$ samples

The $nC_{60}$ samples were prepared using two solvent exchange methods and a physical mixing method. The solvent exchange method using toluene was similar to that reported by Andrievsky et al. (1995). Briefly, 20 mL of a $C_{60}$ solution (1 g/L in toluene) was added to 200 mL of a 0.5 mmol/L NaCl solution and sonicated with a probe (Vibra-Cell VCX800, Sonics & Material Inc., USA) at 100 W for 3 hr in the dark. The yellow-colored suspension generated was first filtered with a 1-μm glass membrane filter and then with a 0.45-μm cellulose acetate membrane filter (Millipore Co., USA) to remove large $C_{60}$ aggregates. The $nC_{60}$ samples prepared using this method are referred to as “TOL-$nC_{60}$”.

The method developed by Fortner et al. (2005) was used to prepare $nC_{60}$ samples from $C_{60}$ in THF. Briefly, 200 mL of a $C_{60}$ solution (~9 mg/L in THF) was added to a 2-L flask and stirred rapidly. Then, 200 mL of a 0.5 mmol/L NaCl solution was added at a rate of 500 mL/min to obtain a transparent yellowish suspension. Then the suspension was heated at 75–80°C using a rotary evaporator (RE-501, Hongguan Instrument Co., CN) to remove THF. To ensure a consistent level of THF removal from solution, a stepwise evaporating procedure was used as follows (Fortner et al., 2005). Starting with 400 mL

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