Complex interplay between formation routes and natural organic matter modification controls capabilities of C\textsubscript{60} nanoparticles (nC\textsubscript{60}) to accumulate organic contaminants

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**A B S T R A C T**

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

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**Introduction**

Buckminster fullerene (C\textsubscript{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\textsubscript{60}, in particular, colloidal nano-scale C\textsubscript{60} aggregates (i.e., nC\textsubscript{60}), have received considerable attention, with a number of studies demonstrating C\textsubscript{60} toxicity (Sayes et al., 2004; Klaine et al., 2008). Further, in natural environments C\textsubscript{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 C₆₀ and common organic contaminants (including naphthalene, phenanthrene, fluoranthene, pyrene, chrysene, 1,2-dichlorobenzene, and atrazine), and the results show that the adsorption affinities of C₆₀ 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 C₆₀ aggregates with diameters of 1–3 μm (formed by magnetically stirring C₆₀ powder in a solution containing 0.01 mol/L NaCl and 0.01 mol/L NaN₃) exhibited much stronger adsorption affinity for naphthalene than did large C₆₀ aggregates with diameters of 20–50 μm, likely due to the increased number of adsorption sites per unit of C₆₀ aggregate mass for the smaller aggregates. Similarly, Gai et al. (2011) reported that adsorption affinities of C₆₀ 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 nC₆₀ sample prepared by solvent exchange from toluene had lower adsorption affinity for naphthalene than small aggregates formed simply through physical mixing. Gai et al. (2011) also made very similar observations using atrazine, and attributed the lower adsorption nC₆₀ to its lower pore volume. Thus, it appears that the formation routes/mechanisms of nC₆₀ (and subsequent aggregation processes) play a critical role in the adsorption affinities of the aggregates.

Chang et al. (2012) categorized the formation mechanisms of nC₆₀ into two general routes as (1) top-down routes whereby nC₆₀ is formed by breaking large aggregates into smaller ones (e.g., physically mixing C₆₀ powder in aqueous solutions), and (2) bottom-up approaches whereby nC₆₀ forms from a seed-growth mechanism (solvent exchanging C₆₀ from organic solvent to aqueous solution). In general, nC₆₀ formed through top-down routes is typically larger in size and irregularly shaped (Duncan et al., 2008; Chang and Vikesland, 2009), whereas nC₆₀ 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, nC₆₀ 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 nC₆₀ 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 nC₆₀ (Hu et al., 2008; Gai et al., 2011). Adsorption of NOM to C₆₀ aggregates can cover (or effectively block) available adsorption sites or pores of C₆₀ aggregates, thus inhibiting adsorption (Hu et al., 2008; Gai et al., 2011). NOM can also enhance the dispersion of C₆₀ (Xie et al., 2008; Li et al., 2009; Qu et al., 2010), consequently rendering more available adsorption sites. Gai et al. (2011) found that nC₆₀ aggregates formed by stirring C₆₀ powder in a humic acid (HA) solution had greater adsorption affinity for atrazine than nC₆₀ 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 nC₆₀ will also largely depend on the formation routes of nC₆₀.

The objective of this study was to understand how the complex interplay between formation routes and NOM modification can affect the adsorption affinity of nC₆₀ for organic contaminants. One physical mixing (sonication) and two solvent exchange (toluene vs. tetrahydrofuran (THF)) approaches were chosen to prepare nC₆₀ samples, and NOM modification was performed with Suwannee River humic acid (SRHA) during or after the formation of nC₆₀. 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 nC₆₀ samples and their adsorption affinities for TeCB.

1. Materials and methods

1.1. Materials and chemicals

Pristine fullerene powder (C₆₀, >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 nC₆₀ samples

The nC₆₀ 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 C₆₀ 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 & Materials 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 C₆₀ aggregates. The nC₆₀ samples prepared using this method are referred to as "TOL-nC₆₀".

The method developed by Fortner et al. (2005) was used to prepare nC₆₀ samples from C₆₀ in THF. Briefly, 200 mL of a C₆₀ 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
total volume (1:1 (v:v), water:THF), 220 mL was evaporated and collected. The remaining yellow solution was diluted with 40 mL of 0.5 mmol/L NaCl solution. The solution was then evaporated again to 180 mL and then diluted with 40 mL of 0.5 mmol/L NaCl solution. Finally, the solution was evaporated again to the final volume of 200 mL. Afterward, the nC60 suspension was filtered with a 0.45 μm cellulose acetate membrane filter to remove large C60 aggregates. The nC60 samples prepared using this method are referred to as “THF-nC60”.

For the physical mixing method, which is similar to that reported by Hwang and Li (2010), a mixture of 100 mg C60 powder and 200 mL 0.5 mmol/L NaCl solution was sonicated at 100 W using the abovementioned sonication probe for 2 hr. Then, the suspension was filtered with 1-μm glass membrane filters. The nC60 samples prepared using this method are referred to as “SON-nC60”.

For each preparation method, two SRHA-modified samples were prepared. The first set of SRHA-modified samples (indicated by a suffix “/SRHA”, i.e., “TOL-nC60/SRHA”, “THF-nC60/SRHA” and “SON-nC60/ SRHA”) were obtained by replacing the 200 mL 0.5 mmol/L NaCl solution with a 5 mg/L SRHA solution. To prepare the second set of SRHA-modified samples (indicated by a suffix “+ SRHA”, i.e., “TOL-nC60 + SRHA”, “THF-nC60 + SRHA” and “SON-nC60 + SRHA”), the nC60 samples made in the absence of SRHA were equilibrated with a SRHA solution by magnetically stirring for 4 hr in the dark, to give a final concentration of SRHA of approximately 5 mg/L. All the SRHA-modified nC60 samples were diazylized using dialysis bags of 6000–8000 molecular weight cutoff to remove the freely dissolved SRHA (Li et al., 2009). All the nC60 samples were kept in the dark at 4°C and were stable during the period of this research. The concentrations of C60 in the nC60 samples were determined using an ultraviolet–visible spectrophotometer. The presence of a small amount of HA (below 5 mg/L) in the solution had negligible effect on the C60 measurement (Xie et al., 2009). The ultraviolet (UV) absorbance spectra of the nC60 samples were recorded with a UV/vis spectrophotometer (TU1810, Puxi Instruments Co., CN). The scan was performed in the wavelength range of 200–600 nm. The slit width and sample interval were set at 1 and 0.2 nm, respectively. Hydrodynamic diameters (Z$_{avg}$) and particle size distributions of the nC60 samples were measured by dynamic light scattering (DLS) and ζ potentials were measured by electrophoretic mobility at 25°C using a ZetaPALS (Brookhaven Instruments, USA). The morphology of all nC60 samples was examined with a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) operated at 80 kV. The samples were prepared by air-drying a drop of each nC60 sample onto a copper TEM grid (Electron Microscopy Sciences, USA).

1.3. Adsorption experiments

Prior to initiating an adsorption experiment, a series of brown glass vials each containing 20 mL nC60 suspension were prepared. Then, different amounts of TeCB stock solution (in methanol) was added to the vials. The vials were capped and tumbled end-over-end at 1 r/min for 5 days to reach adsorption equilibrium. Afterward, fibers were exposed to the nC60 suspensions and were allowed to equilibrate for another 5 days (see the sorption kinetics in Appendix A, Fig. S1). Then, the fibers were taken out, wiped with a wet tissue, and extracted with hexane to analyze the concentrations of TeCB on the fibers. The concentrations of freely dissolved TeCB were calculated based on the concentrations on the fibers and the distribution coefficient of TeCB to the fiber (the procedures used to determine the fiber–water distribution coefficient are given in Appendix A). The concentrations of TeCB on nC60 were calculated based on mass balance. All the samples were run in duplicate. The blank control samples of TeCB showed no degradation during the adsorption experiments, and pH remained constant during all the experiments. The adsorption affinity of TeCB on SRHA was also tested using the procedures mentioned above, and the only difference was that the nC60 suspension was replaced with 5 mg/L SRHA solution.

The concentrations of TeCB were determined using a gas chromatograph equipped with an electron capture detector (6890N, Agilent, USA) and an HP-5 capillary column. No peaks for potential degradation or transformation products were detected in the spectra.

2. Results and discussion

2.1. Characteristics of nC60 samples

Physicochemical properties of the nine nC60 samples are summarized in Table 1. The results indicate that the aggregation properties and surface charge of nC60 are greatly dependent on the synthesis route by which nC60 was formed. The nC60 samples prepared through solvent exchange methods were considerably smaller in size compared with the nC60 samples prepared via physical mixing (Fig. 1): the Z$_{avg}$ values of the three nC60 samples prepared by sonication ranged from 303.5 to 350.2 nm, whereas the Z$_{avg}$ values of the six samples prepared by solvent exchange were only 124.2 to 173.8 nm. Furthermore, nC60 samples made using the two different solvent exchange methods also differed considerably in size and uniformity — samples made through THF exchange were more orderly and tightly packed, whereas the samples made through toluene exchange were irregular in shape. In comparison, the samples made by solvent exchange from toluene were generally spherical, which was in contrast to the samples synthesized through physical mixing which were irregular in shape. In comparison, the samples made by solvent exchange from toluene were generally spherical, which was in contrast to the samples synthesized through solvent exchange via THF, which were in ordered (faceted) crystalline forms. Morphological differences shown in Fig. 2 are also consistent with the findings in the literature (Fortner et al., 2005; Brant et al., 2006; Duncan et al., 2008; Xie et al., 2008; Gai et al., 2011; Chang et al., 2012; Wang et al., 2014). Compared with the aggregates formed via “top-down” routes (e.g., sonication as used in this study), by which large C60 aggregates are broken into smaller ones, the aggregates formed via “bottom-up” routes (e.g., solvent exchange) are built from monomers or crystalline primary aggregates (Andrievsky et al., 2002; Avdeev et al., 2004; Brant et al., 2006; Chen and Elimelech, 2006). Thus, it is likely that the aggregates formed via solvent exchange are more orderly and tightly packed, especially for the case of solvent exchange with THF.
The effects of SRHA modification on the aggregation properties of the nC60 samples were also dependent on the formation route (Table 1 and Fig. 2). For the samples prepared through physical mixing, SRHA modification significantly decreased particle size (\(Z_{\text{ave}}\)) both when SRHA was present during the sonication and when added afterward. When sonicating C60 powder in SRHA solution, SRHA could stabilize the small C60 aggregates taken apart by physical forces and thus prevent them from aggregating again. The fact that when SRHA was added after sonication the sizes of C60 aggregates were still substantially decreased indicates that the packing of C60 aggregates formed by sonication was relatively loose in nature, and could be broken down into smaller pieces under appropriate energy conditions. For samples prepared by solvent exchange with toluene, significant reduction in particle size (\(Z_{\text{ave}}\)) was only observed when SRHA was present during the formation of nC60. This was expected, as C60 aggregates formed via this route were tightly packed and not easily broken down. For the samples prepared by solvent exchange with THF, SRHA modification only slightly decreased the \(Z_{\text{ave}}\), regardless of the stage in which SRHA was introduced. This was likely because the dispersing effect of SRHA was relatively small, owing to the water miscibility of THF. The preparation-method-dependent effects of SRHA modification on size distribution of nC60 are generally consistent with results in the literature (Xie et al., 2008; Wang et al., 2012, 2014). The TEM

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Physicochemical properties</th>
<th>Fitted adsorption parameters</th>
</tr>
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<tr>
<td></td>
<td>(\zeta) potential (mV)</td>
<td>(Z_{\text{ave}}) (nm)</td>
</tr>
<tr>
<td>SON- nC60</td>
<td>-26.01</td>
<td>350.2</td>
</tr>
<tr>
<td>SON-nC60/SRHA</td>
<td>-23.84</td>
<td>303.5</td>
</tr>
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<td>SON-nC60 + SRHA</td>
<td>-27.77</td>
<td>315.1</td>
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<tr>
<td>TOL- nC60</td>
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<td>160.2</td>
</tr>
<tr>
<td>TOL-nC60/SRHA</td>
<td>-23.39</td>
<td>124.2</td>
</tr>
<tr>
<td>TOL-nC60 + SRHA</td>
<td>-22.40</td>
<td>151.4</td>
</tr>
<tr>
<td>THF- nC60</td>
<td>-22.78</td>
<td>173.8</td>
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<tr>
<td>THF-nC60/SRHA</td>
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<td>164.8</td>
</tr>
<tr>
<td>THF-nC60 + SRHA</td>
<td>-24.28</td>
<td>167.7</td>
</tr>
</tbody>
</table>

PDI: polydispersity index.

The acronyms “SON”, “TOL” and “THF” indicate preparation methods, i.e., sonication, solvent exchange from toluene, and solvent exchange from tetrahydrofuran. The term “nC60” indicates samples prepared in the absence of Suwannee River humic acid (SRHA), and the terms “nC60/SRHA” and “nC60 + SRHA” indicate the SRHA-modified samples, for which SRHA was added during or after nC60 was formed.
micrographs in Fig. 2 further corroborate the aforementioned effects of SRHA modification, in that SRHA significantly altered the morphology of the \( nC_60 \) samples synthesized via sonication, but had smaller effects on the \( nC_60 \) samples synthesized through solvent exchange.

The UV/vis spectra of \( nC_60 \) samples (Appendix A Fig. S2) show that \( nC_60 \) samples formed via different routes had absorption maxima of markedly different shape and position. However, for a given formation route, SRHA modification had little effect on the absorption maximum. These observations were consistent with those reported by others in the literature (Chang and Vikesland, 2011; Wang et al., 2012). All \( nC_60 \) samples were negatively charged, as indicated by the \( \zeta \) potential values (Table 1). Formation routes and SRHA modification had noticeable effects on \( \zeta \) potential; however, no clear trend can be established with these data sets.

### 2.2. Effects of formation routes on adsorption affinities of \( nC_60 \)

The adsorption isotherms of TeCB to the three \( nC_60 \) samples prepared via different routes (in the absence of SRHA) are compared in Fig. 3. The isotherms are also shown in logarithm scale (Appendix A Fig. S3) so that differences for low concentration ranges can be seen clearly. Adsorption data were fitted with the Freundlich model: 

\[
q = K_F \cdot C^n,
\]

where \( q \) (mmol/kg) and \( C \) (mmol/L) are the equilibrium concentrations of TeCB on \( nC_60 \) and in the solution, respectively; \( K_F \) (mmol\(^{1-n}\)/L)/kg is the Freundlich affinity coefficient; and \( n \) (unitless) is the Freundlich
At very low adsorbate concentrations, both TOL-\(n_{C60}\) and SON-\(n_{C60}\) were stronger adsorbents than THF-\(n_{C60}\). However, the pore spaces can be filled gradually with the increasing mass of adsorbate. Accordingly, at higher TeCB concentrations the differences among the three \(n_{C60}\) samples were controlled mainly by the differences in their particle sizes (i.e., available adsorption sites).

### 2.3. Effects of SRHA modification on adsorption affinities of \(n_{C60}\)

The effects of SRHA modification on the adsorption affinities of \(n_{C60}\) samples for TeCB are shown in Fig. 4 (the fitted Freundlich model parameters and the distribution coefficients (\(K_d\)) are given in Table 1). Note that the \(q\) values of the SRHA-modified \(n_{C60}\) samples are calculated based on the mass of \(n_{C60}\) rather than the total mass of \(n_{C60}\) and SRHA. This was because TeCB adsorption to SRHA was negligible compared to that to \(n_{C60}\) (the partition coefficient, \(K_d\), of TeCB to SRHA is \(10^{2.02}\), far smaller than the \(K_d\) values to \(n_{C60}\) from \(10^{4.10}\) to \(10^{5.68}\)). Interestingly, the effects of SRHA modification varied significantly among the \(n_{C60}\) samples formed through different routes.

For the \(n_{C60}\) samples prepared by sonication, SRHA modification enhanced adsorption affinities consistently, both when present during the formation of \(n_{C60}\) and when added afterward (Fig. 4). Between the two modification approaches, introducing SRHA during sonication had a greater effect in enhancing the adsorption affinities of \(n_{C60}\) (Fig. 4). As discussed earlier (Section 2.1), sonication breaks large \(C_{60}\) aggregates into smaller ones, and the presence of SRHA in aqueous solution can prevent the re-aggregation of \(C_{60}\) aggregates by serving as a stabilizing agent (Chen and Elimelech, 2007; Xie et al., 2008); even when added after sonication, SRHA can still disperse loosely packed \(C_{60}\) aggregates. Consequently, the SRHA-modified \(C_{60}\) samples (i.e., SON-\(n_{C60}\)/SRHA and SON-\(n_{C60}\) + SRHA) were much better dispersed and smaller in size compared with the unmodified one (SON-\(n_{C60}\)), and had larger amounts of exposed adsorption sites. Since more effective dispersion was achieved when SRHA was present during the sonication, greater adsorption enhancement was observed for SON-\(n_{C60}\)/SRHA.

For \(n_{C60}\) samples prepared through solvent exchange from toluene, the two SRHA modification methods had opposite effects on the adsorption affinity of \(n_{C60}\) when SRHA was present during phase transfer (i.e., TOL-\(n_{C60}\)/SRHA), SRHA modification enhanced the adsorption affinity of \(n_{C60}\) noticeably, whereas when added after phase transfer, SRHA modification decreased the adsorption affinity of \(n_{C60}\) (Fig. 4). As a “bottom-up” process, phase transfer of \(C_{60}\) from toluene to water involved aggregate formation of \(C_{60}\) due to a sudden transition from a favorable environment (i.e., toluene, with smaller amount of energy required for cavity formation (Schwarzenbach et al., 2003)) to a highly unfavorable environment (i.e., water, with high-energy required to form cavities, due to the extremely high hydrophobicity of \(C_{60}\)). It has been proposed that because toluene is immiscible with water, \(C_{60}\) first forms crystal-like primary aggregates and then primary aggregates further form secondary aggregate structures (Martin et al., 1993; Andrievsky et al., 2002; Avdeev et al., 2004; Brant et al., 2006; Chen and Elimelech, 2006). The presence of SRHA in water can facilitate the phase transfer of \(C_{60}\) by forming a coating on the primary and secondary aggregate structures.
aggregates. As a result, TOL–nC₆₀/SRHA had smaller particle size than TOL–nC₆₀ (Table 1 and Fig. 1) and consequently, greater adsorption affinity. Further, it has been proposed that NOM may serve as a “core” to facilitate the formation of secondary aggregates (Wang et al., 2012). This can make the resulting aggregates relatively less tightly packed and thus more porous, which would favor adsorption of TeCB molecules. Note that unlike the nC₆₀ samples formed via sonication, the samples formed via solvent exchange (in the absence of NOM) are much more tightly packed and thus, adding SRHA after the formation of nC₆₀ had very little effect on the aggregation properties of nC₆₀. More importantly, when added after the formation of nC₆₀ (i.e., TOL–nC₆₀ + SRHA), SRHA likely would coat the surface of the nC₆₀ aggregates, and accordingly, would inhibit the adsorption of TeCB by occupying available adsorption sites, and possibly by blocking pore spaces (the high-energy, favorable adsorption sites).

For nC₆₀ samples prepared by solvent exchange via THF, SRHA modification decreased the adsorption affinity of nC₆₀, especially when SRHA was present during the formation of nC₆₀ (Fig. 4). The strikingly inconsistent effects of SRHA modification on the THF–nC₆₀ samples compared with the TOL–nC₆₀ samples are counter-intuitive, as both approaches involved the phase transfer of C₆₀ molecules from a favorable solvent to unfavorable solvent. Here we propose that the differential effects of SRHA were likely due to the fact that THF is a water-miscible solvent whereas toluene is a non-water-miscible solvent. When toluene (containing dissolved C₆₀ molecules) was first added to water, it likely existed as small droplets and then gradually evaporated; this was possibly the cause for the formation of primary aggregates. Thus, even when SRHA was present in the aqueous solution, it was likely that SRHA could only coat the primary aggregates, but not C₆₀ monomers. However, when THF was added to water, it would immediately mix with water, thus allowing SRHA to interact with (or coat) C₆₀ monomers. Consequently, the most prominent effects of SRHA modification on nC₆₀ samples formed by solvent exchange from THF was the coating of SRHA on C₆₀, and, a more thorough coating would occur when SRHA was present during the phase transfer. Since SRHA had little effect on particle size when THF was used (Table 1 and Fig. 1), SRHA consistently inhibited the adsorption affinity of nC₆₀ by covering adsorption sites, especially when added during the formation of aggregates.

3. Conclusions

The adsorption affinity of nC₆₀ for nonionic, hydrophobic 1,2,4,5-tetrachlorobenzene is directly affected by the formation route/processing of nC₆₀, in that the formation route significantly affects the aggregation properties of nC₆₀, which in turn affects the available surface area for adsorption and the extent of adsorption via the pore-filling mechanism. The effects of SRHA modification on the adsorption affinity of nC₆₀ also vary remarkably depending on the formation route of nC₆₀. Depending on whether nC₆₀ is formed via the “top-down” route or “bottom-up” route and what kind of solvent is involved, SRHA modification can both enhance and inhibit adsorption affinity of nC₆₀. These findings further demonstrate the complex mechanisms controlling the interactions between
nC60 and organic contaminants, and may have significant implications for the life-cycle assessment and holistic environmental risk analysis of C60.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.07.009.

REFERENCES


