Effect of Dispersion on Adsorption of Atrazine by Aqueous Suspensions of Fullerenes

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S Supporting Information

ABSTRACT: With the widespread application of fullerenes, it is critical to assess their environmental behaviors and their impacts on the transport and bioavailability of organic contaminants. The effects of fullerene particle size, chemistry of the solution, and natural organic matter on the adsorption of atrazine by aqueous dispersions of fullerenes (C_{60}) were investigated in this work. The results showed that the Polanyi-Manes model could fit the adsorption isotherms well. Smaller sizes of fullerene particles led to increased available sites and, consequently, enhanced the adsorption of atrazine on C_{60} . However, intensely dispersed C_{60} systems might not possess suitably high adsorptive capacities due to surface chemistry change. Adsorption of atrazine by aqueous dispersions of C_{60} increased with a decrease in the pH of the solution. Introduction of humic acid significantly reduced the size of the C_{60} particles, and resulted in the increase of the adsorption amount. Fullerene materials, once released into the aquatic environment, are inclined to form aqueous suspensions with different degrees of dispersion, which would greatly affect the transport and fate of organic contaminants.

INTRODUCTION

Fullerenes (C_{60}) and other carbon-based nanomaterials, due to their distinctive and unique chemical and physical properties, have drawn intensive research interest and large-scale applications in a variety of areas.^{1–3} Meanwhile, the widespread use of these nanomaterials has triggered some concerns about their potential adverse effects on both environment and human health. Aqueous suspensions of well-dispersed C_{60} can be formed under certain circumstances^{4–6} in spite of its extremely low solubility in water.⁷ Dispersed C_{60} could be stable and mobile in aqueous systems^{8–10} and be toxic to some aquatic organisms.^{11,12}

In addition to the toxicity of carbonaceous nanomaterials, the potential synergistic effects of contaminants adsorbed on them are also of high concern.^{2,13,14} The complexation of nanomaterials with the adsorbed contaminants might result in enhanced toxicity.¹² Therefore, the adsorptive property of fullerenes could be a crucial aspect that changes the fate and bioavailability of environmental contaminants. Compared to other carbonaceous materials, such as activated carbons, fullerenes have theoretically much high surface area (SA) and could be large capacity adsorbents. However, previous studies have shown that fullerenes generally have very limited adsorptive capacity.^{13,15} Nevertheless, adsorptive capacity can be improved when the initial fullerene agglomerates are broken into smaller masses.¹⁵ Moreover, the salinity and pH of the solution, in addition to the existence of natural organic matter, are reported to change the aggregate status of the nanoparticles and consequently lead to varying effects on the adsorption of polycyclic aromatic

hydrocarbons (PAHs) onto aqueous suspensions of C_{60} .¹⁶ The phenomenon of desorption hysteresis of fullerenes has also been observed, which was attributed to the formation of closed interstitial spaces in the spherical fullerene aggregates.^{13,15} Hence, formation of interstices could be a key process to explain the adsorption mechanism of fullerenes.

In general, nanomaterials have a great tendency for self-aggregation. The relative stability of dispersed nanomaterials depends on specific conditions, such as the dispersion method and dispersive agent used. The dispersive-aggregative status of nanomaterials plays a critical role in their physical and chemical behaviors. Most of the current studies related to the adsorption of nanomaterials were carried out without sophisticated dispersion treatment of the nanomaterials. Only a few studies^{15,16} have indicated that the dispersive status could change the adsorption capacities of C_{60} aqueous suspensions for some organic compounds. Humic acid (HA), which is ubiquitous in natural waters, has been found to be able to efficiently disperse C_{60} suspensions.^{17–20} Therefore, dispersion of fullerenes is believed to occur once they are released into the aquatic environment.

This work investigated the influence of dispersivity on the adsorptive properties of C_{60} aqueous suspensions. Both extended hydraulic stirring and solvent-exchange methods were used to

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Table 1. Selected Characterization Data of C₆₀ Dispersion Systems

sample ID	pH	concentration (g/L)	ZP ^a (mV)	SA ^b (m ² /g)	D[3,2] ^b (μm)
GRI/C ₆₀	6.06	1.00 ± 0.01 ^c	−9.4 ± 2.0	0.24 ± 0.01	15.28 ± 0.13
4DS/C ₆₀	6.07	0.98 ± 0.03	−8.3 ± 1.1	0.41 ± 0.05	8.90 ± 1.06
8DS/C ₆₀	6.10	0.94 ± 0.02	−16.8 ± 2.1	0.57 ± 0.01	6.36 ± 0.14
2WS/C ₆₀	6.39	1.02 ± 0.01	−22.9 ± 1.7	2.22 ± 0.36	1.64 ± 0.31
STI/C ₆₀	6.64	0.21 ± 0.01	−30.6 ± 0.6	11.39 ± 0.17	0.32 ± 0.05
SON/C ₆₀	6.64	0.24 ± 0.01	−33.1 ± 0.8	26.10 ± 0.42	0.14 ± 0.03
PH3/C ₆₀	3.03	1.28 ± 0.02	−8.9 ± 0.6	2.27 ± 0.10	1.60 ± 0.35
PH6.6/C ₆₀	6.60	1.28 ± 0.02	−25.6 ± 3.5	4.65 ± 0.05	0.78 ± 0.05
PH11/C ₆₀	11.02	1.28 ± 0.03	−28.1 ± 4.0	5.59 ± 0.01	0.65 ± 0.07
2.5HA/C ₆₀	7.11	0.97 ± 0.01	−16.5 ± 1.0	3.04 ± 0.02	1.20 ± 0.16
5HA/C ₆₀	7.29	0.97 ± 0.03	−20.5 ± 1.1	4.08 ± 0.04	0.89 ± 0.07
10HA/C ₆₀	7.41	0.99 ± 0.02	−24.1 ± 1.0	3.13 ± 0.01	1.16 ± 0.19

^a ZP is ζ potential. ^b Surface area calculated by laser particle-size analysis, SA = 6/(ρD[3,2]), where D[3,2] is surface weighted mean diameter, ρ is particle density. ^c Mean ± standard error.

obtain C₆₀ aqueous suspensions. A type of commercial humic acid was also used to elucidate its effect on the dispersion of fullerenes and the consequent impact on the adsorption of organic compounds. C₆₀ suspensions were characterized through different techniques, such as laser particle-size analysis, transmission electron microscopy (TEM), and in situ Raman spectroscopy. Atrazine, a widely used herbicide, and a frequently detected aqueous organic pollutant, was selected as the adsorption objective. The adsorption performances of different C₆₀ suspensions were systematically examined, and the possible adsorption mechanisms are discussed.

EXPERIMENTAL SECTION

Materials. Fullerene, C₆₀ (purity: 99.9%), was purchased from Yongxin Technology Co., Ltd. (Puyang, China). Atrazine, of analytical grade, and HA were purchased from Sigma-Aldrich. HA was purified before use (procedures are described in the Supporting Information, SI). The elemental composition and structural information of purified HA were characterized using elemental analysis and solid-state ¹³C nuclear magnetic resonance spectroscopy (instrumental information is provided in the SI and related data are presented in Tables S1 and S2 in the SI). Methanol (high performance liquid chromatography (HPLC) grade) was purchased from Fisher Scientific. All of the other chemicals used were of analytical reagent grade.

Preparation of C₆₀ Aqueous Suspensions. To evaluate the effect of particle size on adsorption, 1.0 g/L stock suspensions of fullerene were prepared by adding 260 mg of C₆₀ particles to 260 mL of 10 mM NaCl solution in a flask. The flask was wrapped with aluminum foil to avoid exposure to light. Magnetic stirring (at 600 rpm) was carried out for 4 days, 8 days, and 2 weeks, and the samples were denoted as 4DS/C₆₀, 8DS/C₆₀, and 2WS/C₆₀, respectively.

To evaluate the effect of intense dispersion on the adsorption of aqueous C₆₀, two types of C₆₀ systems were prepared by long-term stirring (denoted as STI/C₆₀) and solvent exchange (denoted as SON/C₆₀), respectively. To obtain STI/C₆₀, magnetic stirring of the stock suspension lasted for one month, and then the sample was collected by decanting the upper part of the suspension after settling for 10 h. The protocol used for the preparation of SON/C₆₀ was as follows: first, 300 mg of fullerene were dissolved in 300 mL toluene; then, an equivalent amount of

10 mM NaCl solution was added to the system. Solvent exchange was conducted with a water bath sonicator (power: 200 W) and the temperature was controlled by iced water. It was observed that there were large C₆₀ particles accumulated on the top layer during sonication; therefore, after toluene was completely removed, SON/C₆₀ sample was drawn from 2 cm below the surface to exclude large particles. The concentrations of both STI/C₆₀ and SON/C₆₀ systems were much lower than 1.0 g/L since relatively large particles were not collected (Table 1).

To investigate the effect of pH on the adsorption property of aqueous C₆₀ dispersions, a batch of aqueous C₆₀ stock suspension (1.5 g/L) was stirred for a month and allowed to settle for 3 h. Then, the upper part containing only small aggregates was collected. The pH values of the suspensions were adjusted to 3.03, 6.60, and 11.02 by adding 0.1 M HCl or 0.1 M NaOH solution, followed by an additional mixing for four days. The samples were denoted as PH3/C₆₀, PH6.6/C₆₀, and PH11/C₆₀, respectively.

For the batch of C₆₀ with HA as dispersant, the preparation procedure was identical with 2WS/C₆₀ except that the background electrolyte solution for C₆₀ stock was replaced by a series of diluted HA stock solutions. The concentrations of HA were 2.5, 5.0, and 10 mg/L, and the corresponding samples were denoted as 2.5HA/C₆₀, 5HA/C₆₀, and 10HA/C₆₀, respectively. The HA concentration was confirmed by total organic carbon analysis (TOC-VCPH, Shimadzu, Japan). The HA-dispersed C₆₀ suspensions were used for adsorption experiments within 2 weeks after preparation.

Determination of Concentration of C₆₀ Aqueous Suspensions. The C₆₀ concentrations of all of the prepared suspensions that were used for adsorption experiments were measured by ultraviolet (UV) absorbance. Before the measurement of absorbance, a toluene-extraction step²¹ was carried out with slight modifications as follows: the extraction system, containing one volume of C₆₀ suspension, one volume of 4% NaCl solution, and ten volumes of toluene, was sealed and vigorously mixed. The UV absorbance of C₆₀ in toluene was measured at 334 nm using a spectrophotometer (U-2910, Hitachi, Japan). Concentrations of C₆₀ of all of the experimental systems are given in Table 1.

Characterization of Particles and Aqueous Suspensions of C₆₀. The particle size distribution of the C₆₀ suspensions was measured using a laser particle-size analyzer (Mastersizer 2000, Malvern, UK). The sizes of the particles in the C₆₀ suspensions

Figure 1. Particle-size distribution of C_{60} dispersion systems: (A) Effect of stirring time and grinding, (B) comparison of STI/ C_{60} and SON/ C_{60} , (C) effect of pH value, and (D) effect of humic acid concentration. Data given as the mean of triplicates.

were tested just before these suspensions were used, and all measurements were triplicated. TEM (H-7500, Hitachi, Japan) was performed to observe the particle structure and morphology, in addition to confirming the particle size. Samples were prepared by dropping the C_{60} suspension on copper grids and allowing the sample to air-dry in a dust-free box at room temperature. The surface charges of the C_{60} suspensions were measured by a ζ -potential analyzer (Zetasizer 2000, Malvern, UK).

Since most C_{60} dispersions in this investigation were prepared through extended stirring, Fourier-transform infrared (FTIR) and energy-dispersive X-ray (EDX) spectroscopy techniques were used to evaluate the possible changes of surface functional groups and elemental composition of C_{60} particles before and after the one-month stirring. The FTIR result (Figure S1 of the SI) shows that no noticeable functional group was formed even after one month of mixing; and no remarkable increase of oxygen was found by EDX (Table S3 of the SI). Thus, surface oxidation of C_{60} aqueous suspensions might not be a factor of greatly influencing the adsorption results in this study.

Adsorption of Atrazine onto C_{60} Aqueous Suspensions. Adsorption isotherms of atrazine on the C_{60} dispersions were obtained using a batch technique. Ten milliliters of C_{60} suspension were taken from the respective stock flask into 15-mL amber glass vials with Teflon-lined screw caps. Then, adsorption was initiated by adding a predetermined amount of atrazine stock solution (predissolved in methanol); the volume of injected methanol was less than 0.2% to avoid cosolvent effect.²² Blank control experiments were set up by replacing the C_{60} stock suspensions with corresponding background solution. Adsorption processes were conducted in a rotary shaker (at 25 ± 1 °C and 200 rpm) and allowed to equilibrate for 5 days (adsorption

kinetics demonstrate that 5 days were sufficient for reaching equilibrium; Figure S2 of the SI). With the exception of the experiments involving STI/ C_{60} and SON/ C_{60} , centrifugation at 13000 rpm with Teflon tubes for 30 min at 25 °C was used to separate the C_{60} particles. The supernatants were withdrawn to determine the concentrations of atrazine by HPLC, details of which were described in a previous study.²³ The adsorbed atrazine was calculated by the difference in mass between the initial and the equilibrium solutions. Adsorption isotherms were fitted by Freundlich (FM), Langmuir (LM) and Polanyi-Manes models (PMM) (model formulas are listed in Table S4 of the SI).

For the adsorption systems of STI/ C_{60} and SON/ C_{60} , the experimental procedure was modified as follows: instead of using high-speed centrifugation to separate C_{60} , a 0.02- μ m polycarbonate filter (Whatman, England) was used to remove C_{60} after the adsorption process, and the filtrates were collected for atrazine measurement. The effect of filtration on the concentration loss of atrazine was evaluated by testing blank samples before and after passing through a filter, and the loss was less than 2%.

RESULTS AND DISCUSSION

In this work, the adsorption properties of different C_{60} dispersion systems were comparatively studied with their corresponding particle size distributions. Particle size distribution curves and corresponding adsorption isotherms of different C_{60} systems are presented in Figures 1 and 2, respectively. Detailed discussions are given in the following sections.

Adsorption Model Selection. Three nonlinear models, FM, LM, and PMM, were used to fit the adsorption isotherms of atrazine by the different C_{60} suspensions (shown in Figures S3

Figure 2. Isotherms of adsorption of atrazine onto C_{60} aqueous suspensions: (A) Effect of stirring time and grinding, (B) comparison of STI/ C_{60} and SON/ C_{60} , (C) effect of pH value, and (D) effect of humic acid concentration. Solid lines represent Polanyi-Manes Model fitting.

and S4 of the SI and Figure 2, respectively), and fitting parameters are listed in Table S5 of the SI. A thorough comparison of the R^2 values and mean weighted square errors of the fitting results shows that the applicability of the three models is significantly different. Both LM and FM failed to fit some of the isotherms. Only PMM, a suitable adsorption model for carbonaceous materials,^{23,24} fits all of the isotherms well, which suggests that adsorption sites of C_{60} are heterogeneous and both surface adsorption and pore filling could occur in these adsorption process.²⁵

Effect of Particle Size on Adsorption. First, the adsorption capacities of as-received fullerenes (RAW/ C_{60}) and hand-ground C_{60} particles (GRI/ C_{60}) were compared (the related operation procedures are described in the SI). GRI/ C_{60} had much higher adsorptive capacity for atrazine (Figure 2A) than RAW/ C_{60} , whose adsorption amount was extremely low (data not shown). The relatively higher surface area of GRI/ C_{60} can be verified by the N_2 adsorption–desorption isotherms (Figure S5 of the SI). The adsorption differences between GRI/ C_{60} and RAW/ C_{60} could be attributed to the increased surface area and pore volume after grinding of the raw product (Table S6 of the SI) since there is no obvious change of surface characteristics of C_{60} after pulverization (Figure S6 of the SI and related experimental details and discussion are provided in SI).

During the hydraulic stirring of the fullerenes, the C_{60} particles gradually reduced in size with an increase of stirring time (Figure 1A). For 4DS/ C_{60} , two clear peaks of size distribution were detected, with numerous particles still having sizes above $100\ \mu\text{m}$, which were inefficiently dispersed. In addition, an equivalent amount of aggregates with sizes less than $50\ \mu\text{m}$ existed. In the case of 8DS/ C_{60} , most of the particles had sizes less than $100\ \mu\text{m}$, indicating 8 days are required to break up the

raw C_{60} clusters. After 2 weeks of stirring, a small peak appeared at the nanolevel. However, most particles were below $100\ \mu\text{m}$ in size and were centered around $4\ \mu\text{m}$. The TEM images (Figure S7A–D of the SI) show that the particles in these suspensions were still mainly in the form of tightly combined blocks (not sufficiently dispersed), which was obviously different from the C_{60} clusters with large amount of pores and interstices. Such pores and interstices were formed through rearrangement of well dispersed C_{60} particles (to be discussed below).

All of the C_{60} systems were negatively charged and the surface charge changed with the stirring duration (Table 1). Negative ζ potential of aqueous C_{60} particles could be induced by charge transfer mechanism, oxygen in water molecules as electron donor, and C_{60} as electron acceptor.²⁶ The ζ potential of C_{60} particles became more negative with stirring time lasting longer, and more negative ζ potential is favorable for stabilizing small particles. Figure 2A shows that adsorption of atrazine onto C_{60} suspensions significantly increased with the stirring time. By plotting the SA of C_{60} against estimated adsorption capacities (Q^b) obtained from PMM fitting (Figure S8 of the SI), it could be said that the enlargement of the SA with the broken of raw C_{60} particles was a significant factor for the increase of atrazine adsorption.

Figure 1B shows that most particles in SON/ C_{60} have finer sizes than those in STI/ C_{60} , and the SA of SON/ C_{60} is higher than that of STI/ C_{60} (Table 1). However, it is striking to find that SON/ C_{60} adsorbed less atrazine than STI/ C_{60} (Figure 2B). Previous studies have found strong desorption hysteresis for fullerene systems, and it was ascribed to the entrapment of adsorbate in closed interstices formed during the rearrangement of fullerene aggregates.^{13,15} This suggests that interstitial spaces in fullerenes are important adsorption sites. Hence, the adsorption

Figure 3. TEM images of (A) STI/C₆₀ and (B) SON/C₆₀.

difference between SON/C₆₀ and STI/C₆₀ in the present work might be explained by the distinct structural arrangement of C₆₀ particles in the two suspensions. The TEM images (Figure 3) display that the structures of the C₆₀ aggregates in these two suspensions were still heterogeneous, although their sizes were smaller than the other C₆₀ systems. As shown in the insets (images of relatively large aggregates) of Figure 3, particle aggregates in SON/C₆₀ and STI/C₆₀ exhibit distinct different structures. The particles of STI/C₆₀ are irregularly combined. However, the lattice frame of SON/C₆₀ particles indicates that these fullerenes existed in tightly arranged crystalline forms, which may resemble the structure of raw C₆₀ material. (The crystalline structure of raw and hand-ground C₆₀ particles can be evidenced by the SEM images and XRD patterns presented in Figures S9 and S10 of the SI). In both systems, larger particle clusters are consisted of smaller aggregates with sizes less than 50 nm. Compared with the irregularly combined aggregates in STI/C₆₀, the aggregates arranged in crystalline form in SON/C₆₀ have fewer interstices as available sites for adsorption. According to the PMM, pore-filling is an important adsorption mechanism.²⁴ Irregularly combined aggregates in STI/C₆₀ could trap more adsorbate into its accessible pores and interstices via rearrangement of particles, and thus result in the adsorption difference with SON/C₆₀.

Briefly, with the increased extent of dispersion, C₆₀ particles could adsorb more atrazine, as the adsorption sites increased with dispersion. For well-dispersed C₆₀ particles, porous structure could form through rearrangement. However, the microstructure of small particles could be different due to different dispersion methods, which can affect the adsorption property of fullerene systems.

Effect of pH on Adsorption. Compared with the above-discussed systems, the dispersions used to study the effects of pH were obtained by hydraulic stirring for a duration lasting one month so that the particles were dispersed more uniformly. Figure 1C shows that the size distributions of the three pH-adjusted dispersions were less than 20 μm. Both PH6.6/C₆₀ and PH11/C₆₀ contained particles of sizes less than 300 nm, with most centered around 20 μm, whereas in PH11/C₆₀, the nanoscale fraction constituted a larger percentage than that in pH6.6/C₆₀. In PH3/C₆₀, there existed no particle fraction less than 300 nm, but the position of its main peak is rather close to those of PH6.6/C₆₀ and PH11/C₆₀. The missing of nanoscale particles in PH3/C₆₀ could be explained by the much less negatively charged surface of PH3/C₆₀ system (Table 1). Chen et al.²⁷ also demonstrated that aggregation increased with the decrease of pH.

Nevertheless, in this case, larger SA (Table 1) did not result in greater adsorption of atrazine to C₆₀ dispersions. The adsorption isotherms (Figure 2C) show that the amount of atrazine adsorbed was gradually reduced as the pH of the suspensions increased. Under the pH range of this work, atrazine (pK_a of 1.68²⁸) predominately exists in its neutral molecular form. Therefore, the speciation of atrazine could not be a main factor influencing its adsorption change with pH. Instead, the predominant factor could be attributed to the status of C₆₀ aggregation at different pH. The change of particle aggregation status with pH could be observed through the TEM images of these systems (Figure S7E–G of the SI). With pH adjustment, previously dispersed small C₆₀ aggregates may undergo different rearrangement pathways. With the decrease of pH, well-dispersed small particles intended to form larger aggregates due to the reduction of surface charge and consequently more interstices and pores could be developed, and vice versa. The increased adsorption of C₆₀ systems with the decrease of pH could be partly explained by the increased volumes of interstices and pores with decreasing pH. The structural differences of C₆₀ systems at different pH were also suggested by in situ Raman spectra (Figure S11 of the SI, related discussion was also given in the SI).

Effect of HA Concentration on Adsorption. The size distributions of C₆₀ dispersions containing 2.5, 5.0, and 10.0 mg/L HA are presented in Figure 1D. With a stirring duration of 2 weeks, all the C₆₀ systems dispersed in a solution containing dissolved HA yielded a narrower size-distribution peak than 2WS/C₆₀, which lacked HA (compared with Figure 1A). This result shows that addition of HA can greatly promote the dispersion of aggregates of C₆₀. When HA concentration increased from 2.5 to 5.0 mg/L, the main size-distribution peak moved toward lower-size, and the proportion of particles at nanoscale level increased. When HA concentration reached 10 mg/L (10HA/C₆₀), aggregates larger than 20 μm disappeared. However, both the main and the nanoscale peaks moved toward larger-size. Many previous reports suggested that the dispersing function of HA could be attributed to steric repulsion.^{19,20} On the basis of Table 1, the electrical charge of the HA-C₆₀ complexes become more negative as the concentration of the dissolved HA increased, which indicated that HA played an important role in stabilizing the C₆₀ systems. Furthermore, molecular bridging by HA was also reported in HA-C₆₀ systems containing calcium ions,¹⁹ which could possibly affect the dispersivity of C₆₀ under high HA concentrations.

The adsorption isotherms of this batch of experiments are shown in Figure 2D (model fitting parameters are presented in Table S5 of the SI). Among the three dispersions, SHA/C₆₀ and 10HA/C₆₀ had the highest and the lowest adsorption capacities, respectively, for atrazine. When HA concentration increased from 2.5 to 5 mg/L, the HA enhanced the dispersion of C₆₀ particles and resulted in increased adsorption sites. With the HA concentration increased to 10 mg/L, the effect of bridging-blockage of available sites might overtake that of dispersion. With large numbers of HA molecules existing in the pores and interstices of C₆₀ aggregates, the volume of pores and interstices accessible for adsorption could be significantly reduced. The TEM images (Figure S7H–J of the SI) also corroborated the different aggregation structures of HA/C₆₀ systems.

In addition, all of the C₆₀ systems containing dissolved HA had higher quantities of adsorbed atrazine than 2WS/C₆₀ (without HA). Lu et al.²⁹ reported that sorption of atrazine on HA-coated mineral nanoparticles was apparently lower than that on original particles. They found that the surface area of HA-coated nanoparticles was reduced due to the pore-blockage effect. Shi et al.³⁰ observed that HA-dispersed multiwalled carbon nanotubes (MWNTs) had a greatly reduced adsorption capacity for atrazine. The surface chemistry change of MWNTs by HA was considered to be the primary reason for such adsorption reduction. Wang et al.³¹ found no striking changes in the adsorption of hydrophobic organic compounds (HOC) on carbon nanotubes after coating with HA. They proposed that the reduced accessibility from polar moieties of HA was offset by the newly exposed sites from enhanced inter-CNT particle repulsion. However, the finding in the present work is apparently different from the above results in terms of the effect of HA on nanomaterial adsorption. The binding between dissolved HA and PAHs were previously reported to be very weak.^{32,33} In order to verify the interaction between atrazine and HA, control experiments were conducted and no adsorption was detected after atrazine was introduced into solutions containing HA in the concentration range of 1–10 mg/L. Moreover, the relatively low HA concentration in our work, compared to that of the adsorbent, could not greatly influence the adsorption result. Thus, it can be inferred that the positive role of HA played in the adsorption of the C₆₀ aqueous suspensions was mainly through favorable particle dispersion and rearrangement. The role of HA in enhancing C₆₀ dispersion could be verified through comparison of the TEM images of 2WS/C₆₀ (Figure S7D of the SI) and HA/C₆₀ series (Figure S7H–J of the SI): large solid blocks still existed in 2WS/C₆₀, but not in HA/C₆₀ series.

Further Discussion on the Adsorption Mechanisms. On the basis of Figure S8 of the SI, the total twelve C₆₀ systems studied in this work could be classified into three categories. Category I involves eight systems (GRI/C₆₀, 4DS/C₆₀, 8DS/C₆₀, 2WS/C₆₀, pH6.6/C₆₀, 2.SHA/C₆₀, SHA/C₆₀, and 10HA/C₆₀). In this category, there exists a positive correlation between adsorption capacity and SA, which indicated that SA could account for a large part of the adsorption differences among these systems. Category II includes three C₆₀ systems (STI/C₆₀, SON/C₆₀, and PH11/C₆₀). One distinct characteristic of this category is that the three systems were much better dispersed than all other ones. Category III includes only PH3/C₆₀. If SA-normalized adsorption were compared, then the order in decreasing sequence is as follows: category III > category I > category II.

Further comparison of SA-normalized adsorption isotherms of systems in category I (Figure S12 of the SI) reveals that the

SA-normalized isotherms of GRI/C₆₀, 4DS/C₆₀ and 8DS/C₆₀ nearly overlapped, which meant their surface property had not significantly changed. While the other five suspensions (2WS/C₆₀, 2.SHA/C₆₀, SHA/C₆₀, 10HA/C₆₀, PH6.6/C₆₀), which were prepared with stirring time of no less than 2 weeks, had relatively lower adsorbed amount per SA. This result suggested that the surface chemistry of these systems might have shifted to be less hydrophobic during the long-term dispersing process, which was also implied by the more negative ζ potentials of these systems (Table 1). Meanwhile, such surface chemistry change (ζ potentials being more negative) might also partially explain why the systems of category II could not possess suitably high adsorptive capacities in terms of their much higher SA values. As for category III (PH3.3/C₆₀), its significantly higher adsorption per SA could be attributed to the less negative ζ potentials and more porous structure of this system.

■ ASSOCIATED CONTENT

S Supporting Information. Additional details of the experimental methods and results as well as other supporting tables and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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