Adsorption of Estrogen Contaminants by Graphene Nanomaterials under Natural Organic Matter Preloading: Comparison to Carbon Nanotube, Biochar, and Activated Carbon

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Supporting Information



ABSTRACT: Adsorption of two estrogen contaminants (17 β -estradiol and 17 α -ethynyl estradiol) by graphene nanomaterials was investigated and compared to those of a multi-walled carbon nanotube (MWCNT), a single-walled carbon nanotube (SWCNT), two biochars, a powdered activated carbon (PAC), and a granular activate carbon (GAC) in ultrapure water and in the competition of natural organic matter (NOM). Graphene nanomaterials showed comparable or better adsorption ability than carbon nanotubes (CNTs), biochars (BCs), and activated carbon (ACs) under NOM preloading. The competition of NOM decreased the estrogen adsorption by all adsorbents. However, the impact of NOM on the estrogen adsorption was smaller on graphenes than CNTs, BCs, and ACs. Moreover, the hydrophobicity of estrogens also affected the uptake of estrogens. These results suggested that graphene nanomaterials could be used to removal estrogen contaminants from water as an alternative adsorbent. Nevertheless, if transferred to the environment, they would also adsorb estrogen contaminants, leading to great environmental hazards.

1. INTRODUCTION

Graphene, as a two-dimensional (2D) single-layer sheet of sp²hybridized conjugated carbon atoms, is a basic unit for construction of carbon allotropes, such as zero-dimensional (0D) fullerenes, one-dimensional (1D) nanotubes, or threedimensional (3D) graphite.^{1,2} Graphene has received the bulk of scientific attention since its discovery as a result of its unique structure and excellent electronic, mechanical, and optical properties.³⁻⁶ It has been reported that these scale applications of graphene nanomaterial are expected to increase exponentially in the next decade.⁷ An additional unusual physical property of graphene nanomaterial compared to other carbonaceous nanomaterials is a high specific surface area (SSA, 2630 m²/g) and flat morphology.^{8,9} Therefore, they are expected to serve as excellent adsorbents for organic compounds. For examples, Pavagadhi et al. reported that graphene could be used as an adsorbent to remove algal toxins from water;¹⁰ Wu et al. prepared a functionalized graphene oxide (GO), which could be an efficient adsorbent for methylene blue (MB) removal from real wastewater;¹¹ and Chen et al. found that reduced graphene oxide (rGO) was a powerful adsorbent for removal of nitroaromatic compounds from water.¹²

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Estrogens, including 17β -estradiol (E2) and 17α -ethynyl estradiol (EE2), have been identified to possess serious endocrine-disrupting activity among endocrine-disrupting chemicals (EDCs). As reported, they are capable of causing negative responses to organisms, even at low concentrations, such as sex reversal of males, fish egg production inhibition, and collapse of local fish populations.^{13,14} However, there are only a small amount of peer-reviewed research papers on the uptake of estrogens.¹⁵⁻¹⁸ Considering the predicted high-yield production of graphene, investigating adsorption of estrogens by this material has multiple important environmental significances, including evaluating (i) the potential of using graphene nanomaterial as an adsorbent in pollution control, (ii) the fate and transportation of estrogens by graphene nanomaterial in the environment, and (iii) the potential toxicological impacts of graphene nanomaterial on the environment if this material is discharged and adsorbs estrogen pollutants.

In natural waters, the adsorption behaviors of graphenes are likely to be influenced by natural organic matter (NOM). NOM is ubiquitous in surface and ground waters, originating from internal (i.e., excretion or photosynthetic products of microorganisms) and/or external (i.e., decomposition of plants, animal residues, and terrestrial biomass) sources in waters.¹⁹ NOM is a heterogeneous mixture of chemically complex polyelectrolytes, such as humic substances, proteins, hydrophilic acids, lipids, carboxylic acids, carbohydrates, hydrocarbons, and amino acids. Because of the carboxylic and phenolic moieties distributed throughout the entire molecule, NOM generally carries a negative charge in fresh waters.² Thus, the presence of NOM has definite impacts on the adsorption of estrogen contaminants. As reported, there are two opposite impacts on organic contaminant uptake: an increase in uptake because of the enhanced dispersion of the adsorbent in the presence of NOM and/or a decrease in uptake because of direct site competition and/or pore blockage.² However, no attention has been paid to examine the influence of NOM on estrogen adsorption, although graphenes, carbon nanotubes (CNTs), biochars (BCs), and activated carbon (ACs) have been used to explore the adsorption properties of estrogens. Thus, the specific objectives of this research were to (i) investigate the adsorption behavior of estrogen contaminants, such as E2 and EE2, on graphene materials in ultrapure water and in the presence of NOM and (ii) compare the adsorption property of graphene nanomaterial to other common carbonaceous adsorbents, including multi-walled carbon nanotube (MWCNT), single-walled carbon nanotube (SWCNT), two BCs, powdered activated carbon (PAC), and granular activate carbon (GAC).

2. EXPERIMENTAL SECTION

2.1. Materials. The samples used in this research included two rGOs (rGO₁ and rGO₂, with laboratory preparation described in the Supporting Information), CNTs (MWCNT and SWCNT, Chengdu Organic Chemicals Co., Ltd.), two BCs (BC₁ and BC₂, with laboratory preparation described in the Supporting Information), and ACs (PAC and GAC, Sinopharm Chemical Reagent Co., Ltd.). rGOs, CNTs, BCs, and PAC were used as obtained, while the GAC was smashed to 150–225 μ m size before use.

E2 (\geq 98%) and EE2 (\geq 98%), two selected adsorbates in this research, were purchased from Sigma-Aldrich Chemical Co. The 3D molecular structures and selected physical-chemical properties of the two compounds are listed in Table S1 and

Figure S1 of the Supporting Information, respectively. Ultrapure water generated by a Milli-Q water filtration system (Millipore, Billerica, MA) was applied to the preparation of all of the solutions.

Humic acid (HA, Suwannee River II standard and Leonardite standard) and fulvic acid (FA, Suwannee River II standard and Nordic lake reference) were provided by the International Humic Substances Society. NOM stock solution was prepared by adding a known amount of HA and FA (weight ratio of 1:1) into ultrapure water with stirring 24 h. Dissolution of NOM was promoted by adding NaOH to increase the solution pH to 7.¹⁹ After measurements of the specific ultraviolet absorbance (SUVA₂₅₄) and the dissolved organic carbon (DOC), the solution was diluted to the desired NOM concentration (see Table S2 of the Supporting Information).

2.2. Adsorbent Characterization. Adsorbents were characterized by several instrumental analyses to examine their physical-chemical properties, including elemental analysis, ζ potential meter, Fourier transform infrared (FTIR) spectrum, and Brunauer-Emmett-Teller (BET) method. Oxygen contents of adsorbents was examined using an elemental analyzer (Vario EL III, Elementar, Germany). ζ potential measurements were performed with a ζ potential meter (Zetasizer Nano-ZS90, Malvern). Besides, pH of the point of zero charge (pH_{P7C}) of adsorbents was investigated via the pH equilibration technique.²² FTIR measurements were conducted using a Nicolet 5700 spectrometer in the KBr pellet at room temperature. The porosities of the samples were determined at liquid nitrogen temperature using a surface area and porosity analyzer (Micromeritics, ASAP 2020 M+C) after evacuation of the samples at 150 °C for 12 h. The BET equation was applied to calculate the specific surface area (SSA). The total pore volumes (PVs) were determined from the adsorbed volume of N₂ near the saturation point $(P/P_0 =$ 0.99). Pore size distributions (PSDs) of samples were obtained from the N₂ isotherms via using the density functional theory (DFT) model.

2.3. Batch Adsorption Experiments. The stock solutions were prepared by dissolving an appropriate amount of E2 and EE2 in methanol. Constant dose batch adsorption isotherms for E2 and EE2 were performed through 250 mL amber glass bottles with Teflon-lined screw caps. Two kinds of isotherm experiments were carried out at room temperature $(25 \pm 1 \,^{\circ}C)$.

For ultrapure water experiments, bottles with about 1 mg of adsorbents were first filled with ultrapure water to nearly no free headspace. Afterward, known volumes of estrogen stock solutions were directly spiked into the bottles. For the graphene experiments, the bottles with samples were first half-filled with ultrapure water. After ultrasonication for 30 min, the bottles nearly filled with ultrapure water before spiking estrogens. The volume percentage of methanol in spiked solution remained below 0.1% (v/v) to avoid the co-solvent effect, as used by reported papers.²³⁻²⁵ According to studies from our group, 24 h was sufficient to reach equilibrium for estrogen adsorption.^{26,27} Therefore, the prepared bottles were placed in a shaker bath with an agitation speed of 170 rpm for 24 h. The initial pH values in aqueous solutions were kept around 6.5. The desired solution pH was adjusted by negligible volumes of HCl and NaOH solution through a pH meter (PHSJ-5, China).

The NOM influence on estrogen adsorptions by selected adsorbents was investigated under preloading conditions. Specifically, NOM was added 4 days in advance before spiking

				DFT PV distribution				$\mathrm{pH}_{\mathrm{PZC}}$
adsorbent	SSA (m^2/g)	$PV (cm^3/g)$	V _{micro} (<2 nm, %)	V _{meso} (2–50 nm, %)	V _{macro} (>50 nm, %)	oxygen content (%)	pristine	NOM preloading
rGO_1	244	0.155	25.1	69.2	4.7	16.69	4.8	4.5
rGO ₂	167	0.109	18.8	73.9	7.3	10.33	5.6	4.3
MWCNT	175	0.664	7.0	65.4	27.6	2.99	7.5	5.5
SWCNT	557	1.043	16.1	77.8	6.1	4.94	6.7	4.5
BC_1	85	0.057	13.4	75.7	10.9	24.27	3.3	3.1
BC ₂	142	0.185	11.5	69.8	18.7	21.95	4.1	3.8
PAC	1255	0.757	37.0	61.9	1.1	28.01	3.2	2.8
GAC	1354	0.778	42.6	56.4	1.0	21.92	4.1	3.5







Figure 1. Adsorption isotherms in ultrapure water: (A) E2 mass basis, (B) EE2 mass basis, (C) E2 SSA normalized, (D) EE2 SSA normalized, (E) E2 oxygen content normalized, and (F) EE2 oxygen content normalized.

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estrogens, which stood for severe competition of NOM. To examine the effect of preloading NOM on adsorption, bottles with about 1 mg samples were initially nearly filled with 3.4 mg of DOC/L of NOM stock solution, buffered with 1 mM

1E-4

1E-5

 NaH_2PO_4 H_2O/Na_2HPO_4 ·7 H_2O and adjusted pH to 7.0. Further, the bottles were placed in a shaker bath with an agitation speed of 170 rpm for 4 days. The residual NOM was examined using DOC analysis through a Shimadzu TOC- VCPH analyzer (Shimadzu Co., Japan). After that, the bottles were directly spiked with known volumes of estrogen stock solutions and then continuously shocked for 24 h.

2.4. Analyses. After adsorption for a predetermined time, the solutions (10 mL) were separated from the adsorbents by centrifugation. The estrogen concentration in supernatants was measured by high-performance liquid chromatography (HPLC) with fluorescence detectors (Agilent 1100 Series, Santa Clara, CA). The analytical column was a C18 reverse-phase column (5 mm, 4.6×150 mm, Agilent). The mobile phase flow rate was set at 1 mL/min; the column temperature was kept at 30 °C; and the sample injection volume was 20 μ L. The mobile-phase solvent profile was 45% ultrapure water acidified with 10 mM H_3PO_4 and 55% methanol. Then, detection was carried out at an excitation wavelength of 280 nm and an emission wavelength of 310 nm for both E2 and EE2. Furthermore, bottles without any adsorbents were served as blanks to monitor the loss of adsorbates during the experiment, which was found to be negligible. The description of the HPLC method used in this research has been reported elsewhere.^{28,29}

2.5. Isotherm Modeling. In this work, four common nonlinear isotherm models, such as Freundlich model (FM), Langmuir model (LM), Langmuir—Freundlich model (LFM), and Polanyi—Manes model (PMM), were applied to interpret the adsorption isotherm data (Table S3 of the Supporting Information). The residual root-mean-square error (RMSE), χ^2 test, and coefficient of determination (R^2) values suggested that FM showed goodness of fitting the experimental data (Tables S4 and S5 of the Supporting Information). Thus, FM parameters were used to evaluate adsorption data further.

3. RESULTS AND DISCUSSION

3.1. Adsorbent Characterization. The selected physicochemical properties of all adsorbents, such as SSA, PV, PSD, and oxygen content, were listed in Table 1. As seen, rGO1 had a higher oxygen content (16.69%) than rGO₂ (10.33%) and the SSA of rGO₁ and rGO₂ were 244 and 147 m^2/g , respectively, which indicated that the SSA of rGOs was considerably enhanced after exfoliation of graphite (4.5 m²/g).³⁰ However, the SSA gap between this obtained value and the theoretical maximum value of thin graphene (single-layered graphene, $2630 \text{ m}^2/\text{g})^{31}$ might be as result of the aggregation tendency of graphene layers during the reduction process as a result of the strong van der Waals force between single graphene layers. Consequently, they formed bundles, resulting in decreasing the SSA. Although the aggregation characteristics might change the SSA, rGOs had an increasing distribution of micropores (<2 nm) and a relatively high total PV as a result of the massive space within its house-of-cards-type structure.⁷ In addition, pH_{PZC} of rGOs was a low acidic pH, which was consistent with the presence of a high oxygen content.

The properties of rGOs were compared to those of other samples used in this research (Table 1), including CNTs, BCs, and ACs. Clearly, rGOs, SWCNT, and ACs were hybrid in meso- and micropores, while the proportion of mesopores of ACs was higher; MWCNT was dominated with meso- and macropores; and BCs had the highest heterogeneity in the porous structure with a wide distribution range of PVs. Furthermore, no major gap was found in PVs besides the significantly low PV of BC₁. The SSA of the researched adsorbents followed the order of GAC > PAC > SWCNT > rGO₁ > MWCNT > rGO₂ > BC₂ > BC₁. As reported, micropores had a higher surface area than that of the meso- and macropores.³² Thus, the larger pores in the rGOs, CNTs, and BCs resulted in relatively smaller SSA than those of ACs. Besides, the N₂ adsorption isotherms of these adsorbents are shown in Figure S3 of the Supporting Information. In terms of physical structures, as illustrated by the nitrogen adsorption isotherms, ACs and BCs were microporous adsorbents. However, SWCNT and rGO exhibited both micro- and mesoporous properties. Furthermore, the isotherm pattern of the MWCNT suggested that it is abundant in macropores and has less micro- and mesopores than the SWCNT and rGO. It is reported that the adsorption behavior in micropores depend upon not only the fluid-wall interactions but also the attractive forces between fluid molecules, resulting in capillary (pore) condensation.³³ In addition, the FTIR analysis (Figure S2 of the Supporting Information) illustrated the existence of the C-O group at 1096 cm⁻¹, C=O group at 1641 cm⁻¹, and O-H group at 3443 cm⁻¹ on rGOs, CNTs, BCs, and ACs.

3.2. Adsorption of E2 and EE2 by Graphene Nanomaterials in Ultrapure Water. Adsorption isotherms of E2 and EE2 in ultrapure water are exhibited in Figure 1, and the Freundlich isotherm parameters are listed on Table 2. K_d values (q_e/C_e) , as the single point adsorption descriptors, were also calculated at different equilibrium concentrations, such as at 0.1, 1, 10, and 25% of estrogen aqueous solubility and listed in Table S6 of the Supporting Information. Clearly, adsorption capacities for EE2 were lower than those for E2 for all adsorbents, as represented by $K_{\rm F}$ of the Freundlich model. This might be ascribed to the higher hydrophobicity of E2 than that of EE2 as reflected by the higher octanol-water distribution coefficient (log K_{ow}) value of E2 (Table S1 of the Supporting Information). To further examine the effect of the hydrophobic interaction in adsorption, two parameters $(K_{F-C_{ex}}$ and $K_{\text{F-log }K_{\text{ow}}}$) as the solubility-normalized and hydrophobicitynormalized $K_{\rm F}$ values, respectively, were applied (Table S7 of the Supporting Information). As illustrated, the difference for $K_{\rm F-C_{sw}}$ and $K_{\rm F-\log K_{ow}}$ between E2 and EE2 was narrowed. Nevertheless, these parameters were not nearly the same after the above normalization. Thus, although the hydrophobic interaction was influential on adsorption, it was not the sole factor affecting estrogen uptake.

In addition, rGO₂ showed higher E2 and EE2 adsorption ability than rGO₁, even after SSA normalization. This might be attributed to the more nonpolar surface of rGO₂ as a result of the less oxygen content. As reported, oxygen-containing functional groups of adsorbents could reduce the accessibility for hydrophobic organic compounds via decreasing the available number of adsorption sites because of the formation of water clusters on their surface.³⁴ A similar phenomenon was also found in the uptake of aromatic organic and halogenated aliphatic contaminants by graphene materials.^{7,35,36} To further investigate the difference between rGO_1 and rGO_2 uptake, K_d values at different equilibrium concentrations were also investigated (Table S6 of the Supporting Information). With increasing equilibrium concentrations, the gaps in estrogen uptake between rGO1 and rGO2 narrowed, which might be ascribed to the stronger hydrophobic effect and $\pi - \pi$ interactions between estrogen contaminants and the graphene surface. Thus, with increasing estrogen concentrations, a number of water molecules that were clustered around the oxygen-containing functional groups might be displaced by estrogen molecules and then the estrogen molecules could be better coated on the surface of graphene nanosheets.

												in ultrap	oure water			in NOM	l solution	
	$K_{ m F}~({ m mg/g})$	/(mg/L) ^N	${ m K_{F_2}^{K_{F_2}} \over { m L}}$		$(\mathrm{mg/m}^{K_{\mathrm{F}-\mathrm{h}}}))/$	$(\mathrm{mg/L})^N$	$R_{ m SSA}$ ((%o)	$R_{\rm NOM}$	(%)	V	ь	R^2		Ν		M	2
dsorbent	E2	EE2	E2	EE2	E2	EE2	E2	EE2	E2	EE2	E2	EE2	E2	EE2	E2	EE2	E2	EE2
GO1	64.39	38.68	0.26	0.16	44.36	23.39	4.0	4.1	68.9	60.5	0.698	0.524	0.9942	0.9956	0.889	0.656	0.9982	0.9855
GO_2	77.86	61.41	0.47	0.37	43.76	33.94	6.0	6.0	56.2	55.3	0.611	0.698	0.9958	0.9965	0.836	0.782	0.9975	0.9951
MWCNT	43.54	22.68	0.25	0.13	16.33	9.93	5.7	5.7	37.5	43.8	0.651	0.690	0.9943	0.9691	0.795	0.778	0.9983	0.9919
SWCNT	103.81	74.66	0.19	0.13	47.75	29.68	1.8	1.7	46.0	39.8	0.505	0.476	0.9991	0.9935	0.601	0.670	0.9973	0.9973
BC1	6.56	1.52	0.08	0.02	2.60	0.72	12.2	13.2	39.6	47.4	0.747	0.844	0.9796	0.9980	0.895	0.910	0.9728	0.9872
BC_2	9.19	2.85	0.06	0.02	3.84	1.27	6.5	7.0	41.8	44.6	0.728	0.851	0.9971	0.9939	0.776	0.993	0.9986	0.9918
PAC	132.73	114.05	0.11	0.09	58.66	49.59	0.8	0.8	44.2	43.5	0.392	0.326	0.9938	0.9679	0.522	0.469	0.9967	0.9873
GAC	29.30	12.21	0.02	0.01	9.70	5.18	0.7	0.7	33.1	42.4	0.759	0.496	0.9795	0.9501	0.762	0.590	0.9882	0.9797

Table 2. Freundlich Isotherm Parameters of Estrogen Adsorption in Ultrapure Water and NOM Solution

Article

3.3. Comparison of E2 and EE2 Adsorption by rGOs, CNTs, BCs, and ACs in Ultrapure Water. In comparison of graphenes to other carbonaceous nanomaterials, the order of both E2 and EE2 adsorption abilities was provided (PAC > $SWCNT > rGO_2 > rGO_1 > MWCNT > GAC > BC_2 > BC_1$), as illustrated by $K_{\rm F}$. This suggested that the adsorption of estrogens seriously depended upon the physiochemical characteristics of carbonaceous nanomaterials. To investigate the effect of the surface area of all of the adsorbents, SSA normalization was investigated (Table 2 and Figure 1). Two parameters, $K_{\rm F-SSA}$ and $R_{\rm SSA}$, as the surface-area-normalized $K_{\rm F}$ values and the ratio of $K_{\text{F-SSA}}/K_{\text{F}}$, respectively, were analyzed to quantify the effect of SSA on the estrogen uptake by various adsorbents. The lower R_{SSA} value exhibited a greater impact of SSA on adsorption. As illustrated, the differences in $K_{\text{F-SSA}}$ were suppressed after SSA normalization. In particular, the gap between BCs and other adsorbents was obviously narrowed, indicating that SSA was a great factor influencing estrogen uptake by BCs. In addition, R_{SSA} values of ACs and SWCNT were smaller than other adsorbents, which reflected a stronger decrease in the estrogen uptake by ACs and SWCNT. This suggested that SSA played an important role in the uptake of estrogens. Furthermore, the adsorption isotherms were further normalized on the basis of the oxygen content. As seen, notable differences were still observed among these isotherms (Figure 1). Interestingly, microporous adsorbents (ACs, SWCNT, and rGOs) still exhibited higher E2 and EE2 adsorption after SSA and oxygen content normalization, which might be attributed to the desirable filling of micropores by estrogen molecules. These investigations suggested that the factors affecting estrogen uptake by graphene materials in ultrapure water were similar to those of CNTs, BCs, and ACs. These results demonstrated that the overall adsorption behavior of these adsorbents relied on their SSA, PSD, oxygen content, and hydrophobicity of estrogens.

3.4. Adsorption of E2 and EE2 by Graphene Nanomaterials under NOM Preloading. To study the influence of NOM on estrogen adsorption by graphene nanomaterials, adsorption of E2 and EE2 by rGOs was investigated under NOM preloading. The adsorption isotherms in the presence of NOM are illustrated in Figure 2. For comparison, isotherms of graphenes in ultrapure water are also exhibited in the same figure. Freundlich isotherm parameters in NOM solution are also summarized in Table 2. $K_{\text{F-NOM}}$ and R_{NOM} , as K_{F} values of adsorption in NOM solution and the ratio of $K_{\rm F-NOM}/K_{\rm F}$, respectively, were used to quantify the influence of NOM on the estrogen adsorption by different adsorbents. The lower R_{NOM} values suggest a greater reduction of the adsorption ability because of the presence of NOM. The percent reduction $(R_{K_{d}})$ in the K_{d} value in the presence of NOM, as compared to $K_{\rm d}$ in ultrapure water, was also investigated (Table S6 of the Supporting Information). Previous studies reported that NOM with a higher aromatic content and lower polarity tended to sorb on aromatic moieties of graphene materials presumably through $\pi - \pi$ interactions and/or hydrophobic interactions. ${}^{37-39}$ Adsorption of E2 and EE2 by graphene nanomaterials reduced in the presence of NOM, which might suggest the direct competition between NOM contaminants with E2 and EE2 for the available uptake sites on aromatic moieties of rGOs. In addition, as indicated by lower R_{NOM} values of rGO₂, the influence of NOM on the adsorption capacity of rGO₂ was stronger than that of rGO₁. Meanwhile, rGO₁ showed a



Figure 2. Adsorption isotherms in NOM solution: (A) E2 mass basis and (B) EE2 mass basis.

comparable adsorption capacity under NOM preloading conditions and in ultrapure water, as exhibited by $R_{\rm NOM}$ values (68.9 and 60.5%) of rGO₁ for E2 and EE2, respectively. These observations might be ascribed to (i) the electrostatic repulsive force between the acidic-charged rGO1 surface (pHPZC 4.8; Table 1) and negatively charged NOM molecules, resulting in less NOM aligning on the rGO₁ surface, as reflected by Table S8 of the Supporting Information, (ii) the better dispersed rGO₁ nanosheets as a result of the polarity of surface oxides, which led to decreasing the effect of NOM on estrogen adsorption in water, and (iii) the reduced hydrophobicity of rGO₂ because NOM preloading introduced more polar functionalities and negative charges on the rGO₂, as illustrated by lower pH_{PZC} of rGO₂ after NOM preloading (Table 1). The N value of the Freundlich model suggests the heterogeneity of the surface, and a higher N value exhibits a homogeneous surface with narrow distributions of the adsorption site.⁴⁰ The increase in the N values of rGO2 was 37% for E2 and 12% for EE2, while the increase in N values of rGO_1 was 27 and 25%, respectively. Small enhancements in the N values indicated that the NOM aligning did not notably alter the surface heterogeneity of graphene nanomaterials. Moreover, R_{NOM} as a result of NOM preloading in E2 uptake was higher than that in EE2 for rGOs, which might be ascribed to the stronger hydrophobic effect of the E2 molecule than that of the EE2 molecule to graphene nanomaterials.

3.5. Comparison of E2 and EE2 Adsorption by rGOs, CNTs, BCs, and ACs under NOM Preloading. Adsorption of estrogens by rGOs, CNTs, BCs, and ACs in the presence of NOM was also compared (Table 2 and Figure 2). The order of E2 adsorption capacity indicated by $K_{\rm F-NOM}$ was PAC > SWCNT > rGO_1 > rGO_2 > MWCNT > GAC > BC_2 > BC_1 , and the order of EE2 adsorption capacity indicated by $K_{\rm F-NOM}$ was PAC > rGO_2 > SWCNT > rGO_1 > MWCNT > GAC > $BC_2 > BC_1$. These findings in the presence of NOM illustrated that, in terms of engineering application, graphene nanomaterials showed comparable or better adsorption ability than CNTs, BCs, and ACs; thus, they could be considered as alternative adsorbents for eliminating estrogen contaminants from aqueous solution, and in terms of environmental implication, if transferred to an environment, they would enrich estrogen contaminants, leading to great environmental hazards.

Past studies reported that the attractive interactions between NOM and CNTs, BCs, and ACs are largely driven by $\pi-\pi$ and hydrophobic interactions.^{19,41–43} In addition, the adsorption capacity, especially of ACs, is also determined by SSA of the porous structure available for adsorption.^{44,45} As illustrated in

Table 2, R_{NOM} values for E2 and EE2 of rGOs were higher than those of CNTs, BCs, and ACs, which suggested that the influence of NOM preloading conditions on rGOs was lower than that on CNTs, BCs, and ACs. NOM preloading could reduce the pH_{P7C} of all samples, as exhibited in Table 1, which facilitated the formation of water clusters through adsorbing water to hydrophilic sites, causing less availability for hydrophobic estrogens. The order of pH_{PZC} after NOM preloading was CNTs < rGOs < BCs ~ ACs, which could explain the higher influence of NOM preloading on BCs and ACs than that on rGOs. Besides, as reported by Newcombe et al., pore blockage, especially for the micropore, caused by NOM can also be expected to decrease the adsorption capacity through restricting access to adsorption sites for the target contaminants.⁴⁶ In comparison to ACs, rGOs possessed much less microporous structure, which resulting in less hindrance of estrogen access to the adsorption sites. As presented by Table S8 of the Supporting Information, the adsorbed amount of NOM on CNTs was higher than that of rGOs after 4 days of preloading as a result of the lower oxygen content, which was prone to adsorption through $\pi - \pi$ interactions and hydrophobic interactions. This indicated that less adsorption sites took place by NOM on rGOs compared to CNTs, which resulted in less effect of NOM preloading on rGOs. Furthermore, it has been reported that CNTs are more hydrophobic compared to rGOs, as reflected by Table 1, and prefer to aggregate as compact bundles as a result of the unavoidable van der Waals interactions along the length axis.^{47,48} The much less compact bundle structure for graphene nanomaterials resulted in a lower influence of the NOM preloading condition on rGOs in comparison to CNTs. A similar phenomenon was also found in the adsorption of aromatic organic and halogenated aliphatic contaminants.^{7,35,36} Furthermore, as indicated by Table S6 of the Supporting Information, $R_{K_{d}}$ increased with a decrease in adsorbate equilibrium concentrations. This suggested that NOM molecules preferentially took up high-energy adsorption sites, and then the replacement of binded NOM molecules would be harder with enhancing estrogen concentrations, considering that the NOM concentration of 3.4 mg of DOC/L (Table S2 of the Supporting Information) selected to preloading was 2-3 orders of magnitude higher than estrogens at the low-concentration ranges. Moreover, as exhibited by increasing Freundlich N values (Table 2), surface heterogeneity of all samples reduced during NOM preloading. Nevertheless, there were no significant trends observed in enhancing N values. Among all samples, ACs was affected the most under NOM preloading. As indicated by R_{K_1} values in Table 2, the reductions of estrogen adsorption by ACs in the presence of

NOM were maintained at a high level (>50%) at all of the different equilibrium concentrations. This clear decrease might be ascribed to the microporous structure of ACs, where NOM preloading might led to a combination of pore condensation and site competition for estrogen uptake.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b00073.

Preparations of rGO and biochar, selected properties of estrogens (Table S1), characteristics of NOM solution (Table S2), nonlinear adsorption isotherm models (Table S3), nonlinear simulations of adsorption isotherms in ultrapure water and NOM solution (Tables S4 and S5), single-point adsorption coefficients (K_d) for different levels of E2 and EE2 water solubilities of ultrapure water and NOM solution isotherms (Table S6), solubility-normalized and hydrophobicity-normalized $K_{\rm F}$ values $(K_{\rm F-C_{sw}} \text{ and } K_{\rm F-\log K_{ow}})$ of estrogen adsorption in ultrapure water (Table S7), NOM adsorption capacities after 4 days of preloading (Table S8), 3D molecular configurations of E2 and EE2 (Figure S1), FTIR spectra of the rGOs, CNTs, ACs, and BCs (Figure S2), and nitrogen adsorption isotherms of the rGOs, CNTs, ACs, and BCs (Figure S3) (PDF)

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