Interaction Mechanisms of Antibiotic Sulfamethoxazole with Various Graphene-based Materials and Multiwall Carbon Nanotubes and the Effect of Humic Acid in Water

Fei Wang ^a, Shuai Ma ^a, Yang Si ^b, Lifu Dong ^c, Xilong Wang ^d, Jun Yao ^{a,e,*}, Huilun Chen ^a, Zhengji Yi ^a, Wenchuo Yao ^a, Baoshan Xing ^{f,**}

^a School of Energy & Environmental Engineering, and Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, University of Science and Technology Beijing, 30 Xueyuan Road, 100083 Beijing, China

^b PPSM, CNRS UMR 8531, ENS-Cachan, 61 av President Wilson, 94230 Cachan, France

^c School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Centre, Guangzhou 510006, China

^d Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

^e School of Water Resource and Environmental Engineering, Sino-Hungarian Joint Laboratory of Environmental Science and Health, China University of Geosciences (Beijing), 29 Xueyuan Road, Haidian District, 100083 Beijing, China

^f Stockbridge School of Agriculture, University of Massachusetts, Amherst, Massachusetts 01003 USA

Corresponding Author

* Corresponding author. Tel.: (86) 10 62333305; fax: (86) 10 62333305.

** Corresponding author. Tel.: (413) 545-5212; fax: (413) 545-3958.

E-mail addresses: yaojun@ustb.edu.cn (J. Yao), bx@umass.edu (B. Xing)

29 **Abstract**

30 We studied the interaction mechanisms between carbonaceous nanomaterials (CNMs) and
31 sulfamethoxazole (SMX) to elucidate their adsorption behaviors. Three graphene-based materials,
32 reduced graphene oxide (rGO), graphene oxide (GO), and graphene nanoplatelet pastes (GNP), and
33 five multiwalled carbon nanotubes (MWCNTs), MWCNT10, MWCNT15, MWCNT15-OH,
34 MWCNT15-COOH, and N-doped MWCNTs, were used as sorbents. Oxygen-containing functional
35 groups and graphene wrinkling suppressed SMX adsorption on GO and GNPs due to fewer Csp²
36 ring sites for π - π stacking and fewer accessible flat surface adsorption sites, respectively. Ring
37 current-induced ¹H NMR upfield chemical shifts increased as the π -donor concentration increased,
38 as well as π -donor strength of polycyclic aromatic hydrocarbons (PAHs) (pyrene > phenanthrene >
39 naphthalene) as model graphene compounds, suggesting that π - π interaction strength of SMX with
40 PAHs associated with π -donor strength. Moreover, ¹H NMR results further verified that carboxylic
41 and hydroxyl groups in PAHs (9-phenanthrol and 3-phenanthrenecarboxylic acid) weakened the
42 complexation between SMX and the graphitic surface. Additionally, the morphologies of rGO and
43 MWCNT10 were observed using AFM, and transformed from being linear to scattered as the
44 loading dose of the humic acid increased. Our results are useful to understand the distinct
45 interaction mechanisms and subsequent adsorption behaviors resulting from various carbon
46 nanomaterials with SMX in water.

53 **1. Introduction**

54 The rapid advancement of nanoscience and nanotechnology, as well as the application extension of
55 carbonaceous nanomaterials (CNMs), particularly graphene, have attracted increasing research
56 attention of application in various fields [1, 2]. The production of carbon nanotubes (CNTs) reached
57 4,600 t per annum (tpa) in 2011, and the estimated production of graphene will reach 1,200 tpa by
58 2019 [3]. Among the different types of CNMs, graphene and CNTs are developed most widely
59 because of their superior physicochemical properties [4]. The presence of sp^2 hybridized
60 nanocarbons in these materials contribute to their outstanding features, which trigger the interest of
61 both the scientific and technological communities [5]. Given their hydrophobicity and large surface
62 area, graphene and CNTs are promising sorbents for removing various organic chemicals, such as
63 aromatic amines, PAHs, and pesticides [6-10].

64 In contrast to CNTs, which were first reported in 1991 [11], graphene was only discovered in
65 2009 [12]. Hence, intensive studies are still needed to understand the interaction mechanisms
66 between graphene and organic compounds. Although CNTs and graphene are both carbon-based
67 nanomaterials, they are highly different nanomaterial entities, particularly in terms of shape (tubular
68 vs. planar) and dimensions (1D vs. 2D). Their chemical properties (aqueous dispersibility and
69 aggregation; e.g., stacking for graphene and bundling and tangling for CNTs) differ as well [4]. In
70 addition, graphene oxides (GO) and reduced graphene oxides (rGO), which are two common
71 members of the graphene family [13], typically possess a distinct range of functional groups, such
72 as epoxy (C–O–C), hydroxyl (OH), and carboxylic (COOH) groups, on their basal planes and edges
73 [9]. These oxygen-containing functional groups also exist in CNTs [14]. These
74 self-physicochemical characteristics can affect the adsorption behavior of CNMs for organic

75 chemicals, which in turn may alter their transport and fate in the environment. However, limited
76 systematic reports have been conducted on adsorption differences induced by the dissimilar
77 characteristics of grapheme and CNTs. CNMs can be released into the environment from their
78 products [15], and they have widely been detected from surface water, wastewater, sediments, and
79 soil [16]. Once entering into the environment, which based on their current application is yet highly
80 uncertain, CNMs are most likely to undergo various processes of surface modifications resulting
81 from UV irradiation, microbial activity or interaction with natural organic matter. Moreover,
82 industrial CNMs which widely applied in membranes and filtration system for water purification,
83 thermal management, photodetectors, etc., are more typical than small amount of synthesized
84 CNMs in research laboratories. Therefore, a systematic investigation must be conducted to reveal
85 the differences in the adsorption behaviors of organic chemicals to various industrial CNMs.

86 Sulfamethoxazole (SMX), which is a commonly administered sulfonamide antibiotics, is widely
87 used for human medicine and livestock production [17]. Often poorly metabolized and absorbed by
88 humans and animals, SMX tends to enter into the aquatic environment [18-20]. Consequently, the
89 environmental behavior of SMX has become a worldwide concern because of the potential
90 proliferation of resistant pathogens [21]. Few works have been conducted to investigate the
91 adsorption behaviors of SMX as an environmental contaminant to biochars [22], silica zeolites [23],
92 carbon nanotubes [24, 25], sediment [26], and graphene oxide and graphite [27]. In these studies,
93 π - π electron donor-acceptor (EDA) interactions were identified as the main mechanism controlling
94 adsorption. However, these reports merely mentioned π - π EDA interactions lack of spectroscopic
95 evidence for π - π interactions. The present work will address this problem with direct measurements
96 by proton nuclear magnetic resonance (^1H NMR) [28]. In addition, oxygen on the CNMs could
97 localize the π -electrons. Hence, whether functional groups (OH or COOH) on the surface of CNMs

98 affect π - π interactions, and to what extent, still remain unclear. Therefore, π - π EDA interaction, and
99 the effect of OH or COOH on this interaction, must be elucidated to predict the potential
100 environmental behavior of organic chemicals and various CNMs.

101 Dissolved organic matter (DOM) is an important aquatic component that significantly influences
102 the adsorption of aromatic compounds [29], perfluoroalkyl acids [30], and carbamazepine [31] by
103 acting as a competitor or modifying the surface properties of sorbents. Wang et al. reported that the
104 adsorption of DOM masked numerous adsorption sites on MWCNTs, thereby reducing their
105 adsorption for phenanthrene and 1-naphthol [29]. Similarly, SMX adsorption to CNTs was
106 significantly reduced by the aggregation induced by DOM, but was increased as they were
107 suspended as a result of stable dispersion [25]. These varying results indicate that tripartite
108 interaction systems are complex: that organic compounds bind with DOM adsorbed on adsorbates;
109 and that the morphology of CNMs alter with different coating degrees of DOM, which associate
110 with the degree of suspended CNMs due to the varying strength of electric repulsion from polar
111 functional groups on DOM. The literature, however, does not provide ample information as regards
112 morphology change of CNMs with different coating degrees of DOM. Moreover, few studies have
113 reported on the effect of DOM on the adsorption of antibiotics on graphenes.

114 The objectives of this study are as follows: (1) to investigate the adsorption distinction of SMX
115 on GO, rGO, GNPs, and various MWCNTs with the use of batch techniques; (2) to demonstrate the
116 interaction mechanisms by analyzing the characteristics of CNMs with the use of SEM/EDX, XPS,
117 FTIR, ^1H NMR methods; and (3) to evaluate the effect of DOM on the adsorption of SMX to
118 CNMs with the aid of AFM imaging.

119

120 2. Experimental Section

121 **2.1. Chemicals and Sorbents**

122 SMX, naphthalene (NAPH), phenanthrene (PHEN), pyrene (PYR), 9-phenanthrol,
123 3-phenanthrenecarboxylic acid, and HA was purchased from Sigma-Aldrich (St. Louis., MO, USA).
124 Eight types of CNMs, namely, three graphene-based materials and five multiwalled CNTs
125 (MWCNTs), which have distinct physical structures and chemical compositions, were used as
126 sorbents. The three graphene-based materials were reduced graphene oxide (rGO), graphene oxide
127 (GO), and graphene nanoplatelet pastes (GNP). The MWCNTs included MWCNT10 with an outer
128 diameter of <10 nm, three multiwall CNT with an outer diameter in the range of 8–15 nm
129 (MWCNT15, MWCNT15-OH, MWCNT15-COOH), and one N-doped MWCNTs with an outer
130 diameter in the range of 30–50 nm. MWCNT10 was purchased from Shenzhen Nanotech Port Co.,
131 China. The other CNMs were purchased from Chengdu Organic Chemistry Co., Chinese Academy
132 of Sciences. The physicochemical properties of the CNMs and SMX are summarized in Table S-1
133 and S-2 in the Supplementary Information (SI).

135 **2.2. Characterization of Carbonaceous Nanomaterials**

136 The surface morphology of CNMs was determined by using a Nova NanoSEM 450 (FEI Ltd.,
137 Holland), and the content of C and O in CNMs were semi-quantified with an energy dispersive
138 X-ray (EDX) spectrum. The abundance of surface functional groups on CNMs was obtained by
139 using an AXIS Ultra DLD X-Ray photoelectron spectrometer (Kratos Analytical Ltd., UK). The
140 surface area and porosity of CNMs were measured by using adsorption-desorption isotherms of N₂
141 at 77 K with a V-Sorb 2800P surface area and pore distribution analyzer (Gold APP Instruments Co.,
142 China). The surface characteristics of rGO with HA and SMX were investigated with a SEM/EDX
143 after a part of the suspension containing rGO was air-dried. Four samples from the interaction

144 systems with rGO and MWCNT10 containing 0.86 and 8.6 mg C/L HA were scanned with an
145 atomic force microscope (AFM) (5500, Agilent, USA). rGO and MWCNT10 without HA and SMX
146 in suspension were set as control samples.

147

148 **2.3. Adsorption Experiments**

149 The batch equilibrium adsorption experiments of SMX to CNMs were conducted in aqueous
150 solution, and performed in 15 mL glass vials with Teflon-lined screw caps at 25 °C. SMX was
151 dissolved in methanol to prepare the stock solution. The methanol content in the adsorption systems
152 was controlled to be below 0.1% (v/v) to avoid cosolvent effect. The background solution contained
153 200 mg/L NaN₃ to minimize bioactivity and 0.02 M NaCl to maintain a constant ionic strength. The
154 solid-to-liquid ratio for rGO was 2 mg per 15 mL aqueous solution, whereas that for GO, GNPs,
155 MWCNT10, MWCNT15, MWCNT15-OH, MWCNT15-COOH, and N-doped MWCNT was 7 mg
156 per 15 mL aqueous solution. The isotherm experiments were performed on a rotary shaker at 100
157 rpm for 5 days. After equilibration, the solution was filtered through a 0.2 µm PTFE filter. The
158 filtrate was quantified at 265 nm with a Shimadzu LC20AD high-performance liquid
159 chromatograph (HPLC) in conjunction with a SPD-20A UV detector (Kyoto, Japan), equipped with
160 a reversed-phase C8 column (5 µm, 4.6 mm × 150 mm). The mobile phase was 40:60 (v:v) of
161 acetonitrile and deionized water with 0.1% acetic acid, and the flow rate was 1 mL/min [25]. All
162 samples were run in duplicates. In view of the negligible mass loss (<3.0%) of the adsorbate during
163 the experiment, the adsorbed amount to the CNMs was calculated from the mass balance.

164 The HA stock solution was prepared according to the procedure in a previous work [32]. The
165 final HA solution was analyzed with a high-temperature TOC instrument, and a concentration of
166 43.3 mg C/L was obtained. The HA stock solution was stored in the dark at 4 °C prior to use. The

167 effect of HA on the adsorption of SMX on CNMs was performed at a given concentration of 7
168 mg/L SMX. The initial concentrations of HA were 0.86-34.4 mg C/L.

169 The initial and equilibrium pH values of a interaction system in the absence and presence of HA
170 were determined, and presented in Table S-3.

171

172 **2.4. Interaction of HA and SMX**

173 The binding of HA and SMX in the solution was assessed by fluorescence quenching technique [33].

174 The concentration of SMX was fixed at 10 mg/L, and the HA concentration was adjusted to be
175 within the range of 0.0–4.3 mg C/L. Their mixtures were thoroughly mixed for 24 h in the dark at
176 room temperature. Then, the fluorescence of SMX was measured on a Hitachi F4500
177 spectrofluorometer (Tokyo, Japan). The excitation wavelength (λ_{ex}) was 275 nm, and the emission
178 (λ_{em}) spectra were recorded at 220–550 nm. The excitation and emission slits were 5 nm, and the
179 detector voltage was 700 V. The fluorescence intensities at $\lambda_{\text{ex}}/\lambda_{\text{em}}$ of 275/340 nm without HA (F_0)
180 and with HA (F) were measured. The Stern-Volmer plot, $F_0/F = 1 + K_{\text{SV}} [\text{HA}]$, was constructed,
181 where K_{SV} is the Stern-Volmer constant and $[\text{HA}]$ is the concentration of HA [34].

182

183 **2.5. ^1H NMR Analysis of Complexation in the Solution**

184 The proton nuclear magnetic resonance (^1H NMR) spectra of SMX as π -acceptor were recorded in
185 methanol- d_4 (Acros) in mixture with model π -donor compounds (naphthalene, phenanthrene,
186 pyrene, 9-phenanthrol, and 3-phenanthrenecarboxylic acid) at room temperature on a Bruker-400
187 MHz nuclear magnetic resonance (NMR) spectrometer (Bruker, Switzerland). The spectrometer
188 was locked on the deuterium of the solvent, and the chemical shift (δ) was internally referenced to
189 the $-\text{CH}_3$ of SMX.

190

191 **2.6. Data Analysis**

192 The Langmuir and Freundlich models were used to fit the equilibrium adsorption isotherm data of
193 SMX by CNMs. Additional details these regarding models are presented in the SI. The distribution
194 coefficient, K_d (L/g), was calculated by dividing the adsorbed amount of the sorbate (q_e) by its
195 equilibrium concentration in aqueous phase (C_e), $K_d = q_e / C_e$.

196

197 **3. Results and Discussion**

198 **3.1. Characteristics of the Sorbents**

199 SEM images revealed that GO, rGO, and GNP tended to stack into few layers, and that they acted
200 like typical crumpled wave-like sheets to form groove regions (Fig. 1). rGO had slight aggregation
201 with loose wrinkles. Compared to rGO, GO and GNP displayed relatively flat surfaces, especially
202 GNP, which possessed the lowest pore volume of 0.06 cm³/g. These grooves and surfaces are
203 potential adsorption sites. By contrast, CNTs tend to form bundles or aggregates driven by van der
204 Waals forces along the length axis because of their high hydrophobicity (Fig. S1). As reported in a
205 previous study [35], the surface, groove, interstitial, and inner areas on CNTs offer adsorption sites
206 for organic chemicals. Except for GO (43.41%), the O content of other CNMs was relatively low
207 (1.93 to 4.95%) (Table S-1). The introduction of O-functional groups disrupted the π electronic
208 system of the graphene layer as a result of $sp^2 \rightarrow sp^3$ rehybridization, which breaks up the
209 delocalized π band structure of graphene and acts as a scattering center in the graphene lattice [36,
210 37]. The vast differences in the BET surface area (SA) of CNMs (ranging from 9.93 m²/g to 530
211 m²/g) are associated with their adsorption capacity.

212

Fig.1

Several oxygen-containing functional groups were identified at the surfaces of GO, rGO, GNP, and N-doped MWCNT, as revealed by the FTIR spectra (Fig. S2). The spectra displayed a number of peaks. In particular, the broad peak at $\sim 3500\text{ cm}^{-1}$ represented the bonded hydroxyl of phenol groups [22], and the peaks at 1721, 1593, and 1034 cm^{-1} were attributed to the stretching vibration of C=O, aromatic C=C, and asymmetric stretch of -COO^- , respectively [38, 39]. The FTIR spectra of MWCNT10, MWCNT15, MWCNT15-OH, and MWCNT15-COOH have been reported in our previous studies [32, 35], where these functional groups were included as well.

The surface functional groups of CNMs were analyzed by using XPS (Fig. 2 for C 1s, Fig. S3 for the wide scan, Fig. S4 for O 1s, and Fig. S5 for N 1s). The eight CNMs presented a conspicuously high peak at $\sim 284.8\text{ eV}$ because of the sp^2 -hybridized carbons in C=C/C-C [40, 41]. Except for GO, a small peak at $\sim 285.9\text{ eV}$ on other CNMs was attributed to C-O. However, only GO had a secondary peak at 287 eV , which indicated the presence of C=O [38], suggesting that GO was more hydrophilic than the rest. According to the intensity, rGO, GO, MWCNT15-COOH possessed a relatively higher content of the O-C=O group at 289 eV , but it was not detected from GNP and MWCNT10. As for the O 1s spectra, the peaks at ~ 533.4 and $\sim 532.08\text{ eV}$ were attributed to -C-O/-OH groups and C(O)O-/C=O, respectively [42]. The N1s spectra of N-doped MWCNT can be deconvoluted into pyridinic N at 398.47 eV , pyrrolic N at 399.33 eV , graphitic N at 400.19 eV , and oxidized N at 401.6 eV [43-45]. Pyridine-like and pyrrole-like N may contribute to the π -conjugated system with a pair of p-electrons in the graphene layers [44].

Fig.2

3.2. Adsorption of SMX on CNMs

The adsorption isotherms of SMX on rGO, GO, GNPs, MWCNT10, MWCNT15, MWCNT15-OH,

236 MWCNT15-COOH, and N-doped MWCNT are shown in Fig. 3. In general, the isotherms were
 237 fitted slightly better with the Freundlich rather than the Langmuir model; the regression parameters
 238 are listed in Table 1. Freundlich n values indicate the heterogeneity of the CNMs, and a lower n
 239 value is indicative of a heterogeneous surface with a wider adsorption site energy distribution [46].
 240 According to n values, the heterogeneity of CNMs followed this order: rGO > MWCNT10 >
 241 N-doped MWCNT > GO > MWCNT15 = MWCNT15-COOH > GNPs > MWCNT15-OH.

242 **Fig.3 and Table 1**

243 In order to compare the adsorption affinity for these CNMs at a specific concentration, the single
 244 point K_d was calculated at $C_e = 2$ mg/L according to the fitting results of the Freundlich model
 245 (Table 1). The K_d values followed this order: rGO > MWCNT10 > MWCNT15 >
 246 MWCNT15-COOH > N-doped MWCNT > MWCNT15-OH > GO > GNPs. Compared with
 247 Freundlich n values order, heterogeneity of the CNMs closely associated with adsorption affinity of
 248 rGO and MWCNT10 (Fig. S6). Their adsorption affinity decreased with decrement of n values.
 249 However, when n values were greater than 0.6, K_d kept the similar values. It means that the role of
 250 heterogeneous surface of MWCNT15, MWCNT15-COOH, N-doped MWCNT, MWCNT15-OH,
 251 GO and GNPs became limited for adsorption.

252 The physical properties of CNTs play important roles in the adsorption of organic contaminants
 253 [47]. Both graphene and CNTs are hydrophobic and primarily made up of sp^2 carbon atoms densely
 254 parked in a hexagonal honeycomb crystal lattice. Therefore, the hydrophobic properties and the sp^2
 255 structure suggest that hydrophobic and π - π interactions occur between CNMs and SMX. However,
 256 graphene can be converted from planar sheets into wrinkled and scrolled sheets [48], and CNTs can
 257 form bundles of randomly tangled individual tubes by means of aggregation [49]. The
 258 morphological changes of CNMs would alter the energy distribution of their adsorption sites, which

in turn may influence the adsorption behaviors of SMX. For example, Bai et al. found that rGO with varying wrinkling associated with their adsorption rate [50]. As such, rGO, GO, and GNP exhibited different stacking structures because of their distinct wrinkling degrees (Fig. 1), resulting in different pore size distributions (Table S-1). rGO showed a high wrinkling degree, leading to large values of SA (530 m²/g) and pore volume (2.19 cm³/g). By contrast, GNP are stacked tightly to form the flake structure, and resulting in a weak wrinkling degree. GNP possessed the lowest values of SA (9.93 m²/g) and pore volume (0.06 cm³/g), and showed the lowest adsorption of SMX. As for GO, smooth nanosheets were exfoliated and dispersed in water because of the abundant OH and COOH groups (Fig. S2). As opposed to high SA of GO (329 cm³/g), GO presented a very low adsorption affinity. Therefore, other interaction mechanisms aside from the varying physical structures of CNMs affected the adsorption behavior of CNMs and SMX.

The relationship between SA and K_d was plotted to further clarify the influence of the surface area of CNMs on SMX adsorption. The relationship was generally linear after GO was removed (Fig. S7), suggesting that SA played an important role in the adsorption of SMX on CNMs. Meantime, surface area-normalization reduced the difference in adsorption affinity (Fig. S8), but the normalized isotherms were still scattered, suggesting other interactions occurred.

To focus on molecular interaction mechanisms aside from the hydrophobic effect, the normalized adsorption coefficient (K_d/K_{HW}) of SMX on CNMs was calculated at different equilibrium concentrations (C_e) (Fig. S9). Hexadecane is a nonpolar organic solvent that is useful for examining intermolecular interactions (e.g., π - π interaction) in addition to hydrophobicity effect [47, 51]. The aromatic ring of SMX is an effective π -electron acceptor because of the attracting electron of electron-withdrawing sulfuric groups [22], and CNMs can serve as π -electron donors. The distinct K_d/K_{HW} - C_e plots indicated the different π - π interaction strength of a nanomaterial with SMX

282 molecules, and higher K_d/K_{HW} values indicated stronger interaction. So, π - π interaction was one of
283 other mechanisms for SMX adsorption on CNMs.

284 The dominated species of SMX were cationic, neutral, and anionic at pH < 1.7, around 3.7, and >
285 5.7, respectively [52]. Anionic SMX species increased with increment of solution pH. The pH of
286 interaction systems were around 7, except for GO (pH = 4.83) (Table S-3). Subsequently, the
287 electrostatic repulsion occurred between SMX and CNMs. Considering the high oxygen content of
288 GO, electrostatic repulsion should be one of main interaction mechanism to greatly decrease
289 adsorption of SMX on GO. As for other CNMs with low oxygen content, electrostatic repulsion
290 was not enough strong to alter the general adsorption of SMX.

291 H-bond interaction of NH_2 group in SMX with O-containing functional groups on CNP should
292 happened. However, considering the low adsorption affinity of SMX with GO and low percent of
293 oxygen content of other CNMs, H-bond interaction was not the key interaction in our interaction
294 systems.

295

296 **3.3. Effects of O-containing Functional Groups on the adsorption of SMX on CNMs and**

297 **Spectroscopic Studies of the π - π Interaction in Solution**

298 GO, MWCNT15-OH, and MWCNT15-COOH exhibited a low adsorption compared with that of
299 CNMs with the same structures, such as rGO and MWCNT15. This low adsorption may be
300 attributed to the O-containing functional groups. Aside from reducing the hydrophobicity of CNMs
301 to decrease their adsorption for SMX, the effects of O-containing functional groups on π - π
302 interaction also altered the adsorption of CNMs for SMX.

303 The π - π EDA interaction between SMX (π -electron acceptor) and aromatic compounds (as
304 models of π -electron donors on graphene surfaces), as well as the effects of O-containing functional

groups (OH and COOH) on π - π interaction, was further tested by performing liquid phase ^1H NMR experiments. As a nucleus was placed above or below the plane of an aromatic structure, electronic shielding would occur because of the “ring effect” [53]. Thus, upfield NMR chemical shifts (δ) induced by ring current effect can be used to support the “face-to-face” geometry of the π - π EDA complex. The ^1H NMR up-field shift was clearly observed for SMX ($-\text{CH}_3$ group on the N-heterocyclic moiety) in the mixture with PAHs (Fig. 4). The shift increased as the π -donor concentration increased, as well as π -donor strength of PAHs (pyrene > phenanthrene > naphthalene) [28, 54]. Meanwhile, OH (9-phenanthrol) and COOH (3-phenanthrenecarboxylic acid) can reduce the π - π EDA interaction strength, particularly for 3-phenanthrenecarboxylic acid, whose ^1H NMR chemical shift did not change as the concentration increased. It also was reported that oxygen on the surface of CNMs localizes the π -electrons, reducing the π - π interactions between the graphitic surface and benzene rings of aromatic organic chemicals [47]. Therefore, O-containing functional groups altered the adsorption of CNMs by reducing the hydrophobicity of CNMs and weakening the π - π interaction. Hence, the oxygen content of CNMs was responsible for the adsorption behavior.

Fig.4

The oxygen content of GO reached up to 43.41%, which is much higher than that of MWCNT15-OH (4.15%), MWCNT15-COOH (4.95%), and other CNMs (<4.0%). The effect of oxygen became obvious at high oxygen content of CNMs. This contributed to the low adsorption of GO for SMX (q_{max} 0.15 ± 0.02 mg/g), which is much lower than the adsorption capacity of 240 mg/g to SMX on GO (no data on oxygen content) reported by Chen et al., [22]. The huge differences possibly resulted from the amount of surface oxygen content. As the surface oxygen content of the MWCNTs increased, the adsorption of tetracycline increased to the maximum values (0%,

2.0-3.2%) and then decreased (0%, 3.2-5.9%) [55]. According to the effects of oxygen content on the adsorption of MWCNTs with similar SA (approximate 140 m²/g), the adsorption to SMX followed this order: MWCNT15 (3.43%) > MWCNT15-COOH (4.15%) > MWCNT15-OH (4.95%). It was because of that water cluster formation played a more important role in SMX adsorption than did dispersion, and thus the adsorption affinity for SMX decreased with the increasing oxygen content [55]. However, for the adsorption of N-doped MWCNT with low oxygen content (1.93%) and SA (52.9 m²/g), N-doping may enhance π - π interaction to maintain a higher adsorption than that of MWCNT15-OH. The reason is that the effective site of the sp² carbon of CNMs has abundant free-flowing π -electrons, which can be activated by conjugating with the long-pair electrons from the doped N atoms [43].

338

3.4. Effect of Dissolved Humic Acid

The effects of HA addition on the adsorption of SMX on CNMs were shown in Fig. 5. As HA concentration was increased from 0.86 mg C/L to 34.4 mg C/L, K_d initially decreased sharply and then smoothly because of the competition with HA and the distribution of SMX to free HA. HA could interacted with CNMs by hydrophobic, π - π , H-bonding and electrostatic interactions due to HA containing the aromatic fractions and O-containing functional groups (carboxyl and phenolic groups) [32, 56]. But, these interactions depended on the solution pH. As reported, DOM adsorption decreased with increasing pH due to electrostatic repulsive forces between negatively charged carboxylic acid functional groups on the O-MWCNT and NOM at pH 7, but the hydrophobic π - π was still dominant [57]. As for this study, the initial and equilibrium pH of interaction systems containing CNMs was around 7, except for GO (pH, around 4.5) (Table S-3). Hence, the electrostatic repulsion should be similar for CNMs due to the similar pH of solution and low

351 oxygen content of CNMs. Whereas, negative chargers of GO and HA were smaller at lower pH than
352 that at higher pH. Therefore, electrostatic repulsion between GO and HA should not be strong as
353 well. Subsequently, HA could adsorbed on CNMs and competed adsorption sites on CNMs with
354 SMX. Beside competition adsorption, free HA could bind SMX molecules with the Stern-Volmer
355 constant (K_{SV}) of 9×10^4 L/kg (Fig. S10). Thus, part of free SMX may bind again with the adsorbed
356 HA on CNMs in the adsorption system. But, considering the deceasing adsorption of SMX with the
357 increasing HA concentration, the binding interaction between SMX and HA should be weak.

358 **Fig.5**

359 As shown in the AFM images, with HA concentrations varying between 0.86 and 8.6 mg C/L
360 (Fig. 6 and Fig. S11), the thickness of rGO and MWCNT10 did not substantially increase, and the
361 thickness was similar under the same concentrations of rGO and MWCNT10 (Fig. 6C, 6E, 6G, and
362 6J). It indicates that the adsorption thickness of HA on CNMs tends to be a specific value and
363 independent on the HA concentration. Another interesting phenomenon is that linear CNMs were
364 observed (Fig. 6B and 6G), and few CNMs were scattered at 0.86 mg C/L (Fig. 6C and 6H).
365 However, CNMs became dispersed particles at 8.6 mg C/L. The different morphologies of CNMs at
366 two HA concentrations suggested that, as the HA level was low, it did not cover the entire CNP
367 surface. The presence of HA was not enough to disperse CNMs by disrupting the strong van der
368 Waals forces between CNP particles driven by electrostatic repulsion and steric hindrance of HA.
369 The driven forces increased as the HA concentration increased, ultimately dispersing the CNMs. As
370 reported, suspended CNTs increase with increasing DOM concentration [57]. The loose wrinkles
371 became stacked layers after HA and SMX were loaded on rGO (Fig. S12), consequently decreasing
372 the number of available adsorption sites of CNMs. Meanwhile the ratio of C and O also
373 demonstrated the adsorbates adsorbed on rGO. These results also gave the evidence that adsorption

374 of SMX on CNMs slowly decreased due to the high coating degree of HA on CNMs, when CNMs
375 were exposed to high HA concentration. For CNMs with completely coating of HA, the adsorption
376 of SMX maybe mainly originate from the free SMX binding with adsorbed HA on CNMs.

377 **Fig.6**

378 **4. Summary**

379 The interactions between graphenes and SMX were investigated in comparison with MWCNT10,
380 MWCNT15, MWCNT15-COOH, MWCNT15-OH, and N-doped MWCNT. As shown in this work,
381 rGO had high adsorption affinity for SMX, suggesting that it may strongly alter the transport
382 behavior of SMX through adsorption process. The ^1H NMR up-field shift of $-\text{CH}_3$ group on SMX
383 verified the π - π interaction strength as followed the order, pyrene-SMX > phenanthrene-SMX >
384 9-phenanthrol-SMX > naphthalene-SMX > 3-phenanthrenecarboxylic acid-SMX. It further proved
385 that oxygen-containing groups (e.g. OH and COOH) on the surface of CNMs reduced the π - π
386 interactions between the graphitic surface and SMX. The morphologies of rGO and MWCNT10
387 changed from linear to dispersed morphologies, observed by AFM, with increment of HA
388 concentration. It resulted from the varying coating degree of HA on CNMs, which induced the
389 different interaction strength of electrostatic repulsion and steric hindrance of HA. Additionally,
390 adsorbed HA on CNMs could bind with SMX. Therefore, both morphologies changes of CNMs and
391 binding interaction with SMX altered the varying adsorption behavior of SMX in the presence of
392 HA.

393

394 **Acknowledgements**

395 This work is supported in part by grants from the Key project from National Science Foundation of
396 China (41430106), National Natural Science Foundation of China (41473096, 41273092,

397 U1402234, 41273131), Public welfare project of Chinese Ministry of Environmental Protection
398 (201409042).

399

400

401

402

403 **References**

- 404 [1] Ren W, Cheng H-M. The global growth of graphene. *Nat Nano*. 2014;9(10):726-30.
- 405 [2] Novoselov KS, Falko VI, Colombo L, Gellert PR, Schwab MG, Kim K. A roadmap for
406 graphene. *Nature*. 2012;490(7419):192-200.
- 407 [3] Zurutuza A, Marinelli C. Challenges and opportunities in graphene commercialization. *Nat*
408 *Nano*. 2014;9(10):730-4.
- 409 [4] Bussy C, Ali-Boucetta H, Kostarelos K. Safety considerations for graphene: lessons learnt from
410 carbon nanotubes. *Accounts of Chem. Res*. 2013;46(3):692-701.
- 411 [5] Li Z, Liu Z, Sun H, Gao C. Superstructured assembly of nanocarbons: fullerenes, nanotubes,
412 and graphene. *Chem. Rev*. 2015;115(15):7046-117.
- 413 [6] Xiao F, Pignatello JJ. $\pi^+-\pi$ Interactions between (Hetero)aromatic amine cations and the
414 graphitic surfaces of pyrogenic carbonaceous materials. *Environ. Sci. Technol*.
415 2015;49(2):906-14.
- 416 [7] Shen X, Guo X, Zhang M, Tao S, Wang X. Sorption mechanisms of organic compounds by
417 carbonaceous materials: site energy distribution consideration. *Environ. Sci. Technol*.
418 2015;49(8):4894-902.
- 419 [8] Patiño Y, Díaz E, Ordóñez S, Gallegos-Suarez E, Guerrero-Ruiz A, Rodríguez-Ramos I.
420 Adsorption of emerging pollutants on functionalized multiwall carbon nanotubes. *Chemosphere*.
421 2015;136:174-80.
- 422 [9] Zhao J, Wang Z, White JC, Xing B. Graphene in the aquatic environment: adsorption,

423 dispersion, toxicity and transformation. *Environ. Sci. Technol.* 2014;48(17):9995-10009.

424 [10] Maliyekkal SM, Sreeprasad TS, Krishnan D, Kouser S, Mishra AK, Waghmare UV, et al.

425 Graphene: a reusable substrate for unprecedented adsorption of pesticides. *Small* (Weinheim an

426 der Bergstrasse, Germany). 2013;9(2):273-83.

427 [11] Iijima S. Helical microtubules of graphitic carbon. *Nature.* 1991;354(6348):56-8.

428 [12] Geim AK. Graphene: Status and Prospects. *Science.* 2009;324(5934):1530-4.

429 [13] Bianco A, Cheng H-M, Enoki T, Gogotsi Y, Hurt RH, Koratkar N, et al. All in the graphene

430 family – A recommended nomenclature for two-dimensional carbon materials. *Carbon.*

431 2013;65:1-6.

432 [14] Yang K, Xing B. Adsorption of organic compounds by carbon nanomaterials in aqueous phase:

433 polanyi theory and its application. *Chem. Rev.* 2010;110(10):5989-6008.

434 [15] Petersen EJ, Zhang L, Mattison NT, O'Carroll DM, Whelton AJ, Uddin N, et al. Potential

435 release pathways, environmental fate, and ecological risks of carbon nanotubes. *Environ. Sci.*

436 *Technol.* 2011;45(23):9837-56.

437 [16] Gottschalk F, Sun T, Nowack B. Environmental concentrations of engineered nanomaterials:

438 Review of modeling and analytical studies. *Environ. Pollut.* 2013;181(0):287-300.

439 [17] Thiele-Bruhn S. Pharmaceutical antibiotic compounds in soils – a review. *J. Plant Nutr. Soil*

440 *Sci.* 2003;166(2):145-67.

441 [18] Focazio MJ, Kolpin DW, Barnes KK, Furlong ET, Meyer MT, Zaugg SD, et al. A national

442 reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United

443 States — II) Untreated drinking water sources. *Sci. Total Environ.* 2008;402(2–3):201-16.

444 [19] Done HY, Halden RU. Reconnaissance of 47 antibiotics and associated microbial risks in

445 seafood sold in the United States. *J. Hazard. Mater.* 2015;282:10-7.

446 [20] Luo Y, Xu L, Rysz M, Wang Y, Zhang H, Alvarez PJJ. Occurrence and transport of

447 tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe river basin, China.

448 *Environ. Sci. Technol.* 2011;45(5):1827-33.

449 [21] Baquero F, Martínez J-L, Cantón R. Antibiotics and antibiotic resistance in water environments.

450 *Current Opinion Biotechnol.* 2008;19(3):260-5.

451 [22] Chen H, Gao B, Li H. Removal of sulfamethoxazole and ciprofloxacin from aqueous solutions

452 by graphene oxide. *J. Hazard. Mater.* 2015;282:201-7.

- 453 [23]Blasioli S, Martucci A, Paul G, Gigli L, Cossi M, Johnston CT, et al. Removal of
454 sulfamethoxazole sulfonamide antibiotic from water by high silica zeolites: A study of the
455 involved host–guest interactions by a combined structural, spectroscopic, and computational
456 approach. *J. Colloid Interface Sci.* 2014;419(0):148-59.
- 457 [24]Ji L, Shao Y, Xu Z, Zheng S, Zhu D. Adsorption of monoaromatic compounds and
458 pharmaceutical antibiotics on carbon nanotubes activated by KOH etching. *Environ. Sci.*
459 *Technol.* 2010;44(16):6429-36.
- 460 [25]Pan B, Zhang D, Li H, Wu M, Wang Z, Xing B. Increased adsorption of sulfamethoxazole on
461 suspended carbon nanotubes by dissolved humic acid. *Environ. Sci. Technol.*
462 2013;47(14):7722-8.
- 463 [26]Hou J, Pan B, Niu X, Chen J, Xing B. Sulfamethoxazole sorption by sediment fractions in
464 comparison to pyrene and bisphenol A. *Environ. Pollut.* 2010;158(9):2826-32.
- 465 [27]Wang C, Li H, Liao S, Zheng H, Wang Z, Pan B, et al. Coadsorption, desorption hysteresis and
466 sorption thermodynamics of sulfamethoxazole and carbamazepine on graphene oxide and
467 graphite. *Carbon.* 2013;65(0):243-51.
- 468 [28]Zhu D, Hyun S, Pignatello JJ, Lee LS. Evidence for π - π electron donor-acceptor interactions
469 between π -donor aromatic compounds and π -acceptor sites in soil organic matter through pH
470 effects on sorption. *Environ. Sci. Technol.* 2004;38(16):4361-8.
- 471 [29]Wang X, Tao S, Xing B. Sorption and competition of aromatic compounds and humic acid on
472 multiwalled carbon nanotubes. *Environ. Sci. Technol.* 2009;43(16):6214-9.
- 473 [30]Wang F, Shih K, Leckie JO. Effect of humic acid on the sorption of perfluorooctane sulfonate
474 (PFOS) and perfluorobutane sulfonate (PFBS) on boehmite. *Chemosphere.* 2015;118(0):213-8.
- 475 [31]Lerman I, Chen Y, Xing B, Chefetz B. Adsorption of carbamazepine by carbon nanotubes:
476 Effects of DOM introduction and competition with phenanthrene and bisphenol A. *Environ.*
477 *Pollut.* 2013;182(0):169-76.
- 478 [32]Wang F, Yao J, Chen H, Yi Z, Xing B. Sorption of humic acid to functionalized multi-walled
479 carbon nanotubes. *Environmental Pollution.* 2013;180(0):1-6.
- 480 [33]Wang F, Yao J, Yu C, Chen H, Yi Z, Choi MMF. Mutual effects of dialkyl Phthalate esters and
481 humic acid sorption on carbon nanotubes in aqueous environments. *ACS Sustain. Chem. Eng.*
482 2014;2(5):1219-27.

- 483 [34]Gauthier TD, Shane EC, Guerin WF, Seitz WR, Grant CL. Fluorescence quenching method for
484 determining equilibrium constants for polycyclic aromatic hydrocarbons binding to dissolved
485 humic materials. *Environ. Sci. Technol.* 1986;20(11):1162-6.
- 486 [35]Wang F, Yao J, Sun K, Xing B. Adsorption of dialkyl phthalate esters on carbon nanotubes.
487 *Environ. Sci. Technol.* 2010;44(18):6985-91.
- 488 [36]Chanda D, Hnat J, Dobrota AS, Pasti IA, Paidar M, Bouzek K. The effect of surface
489 modification by reduced graphene oxide on the electrocatalytic activity of nickel towards the
490 hydrogen evolution reaction. *Phys. Chem. Chem. Phys.* 2015;17(40):26864-74.
- 491 [37]Keith EW. Reversible graphene functionalization for electronic applications: a review. the
492 science and function of nanomaterials: from synthesis to application: American Chemical
493 Society 2014, p. 41-54.
- 494 [38]Wang J, Chen Z, Chen B. Adsorption of polycyclic aromatic hydrocarbons by graphene and
495 graphene oxide nanosheets. *Environ. Sci. Technol.* 2014;48(9):4817-25.
- 496 [39]Amir S, Jouraiphy A, Meddich A, El Gharous M, Winterton P, Hafidi M. Structural study of
497 humic acids during composting of activated sludge-green waste: Elemental analysis, FTIR and
498 ¹³C NMR. *J. Hazard. Mater.* 2010;177(1–3):524-9.
- 499 [40]Pei Z, Li L, Sun L, Zhang S, Shan X-q, Yang S, et al. Adsorption characteristics of
500 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, 2-naphthol and naphthalene on graphene and
501 graphene oxide. *Carbon.* 2013;51:156-63.
- 502 [41]Sun Y, Yang S, Chen Y, Ding C, Cheng W, Wang X. Adsorption and desorption of U(VI) on
503 functionalized graphene oxides: a combined experimental and theoretical study. *Environ. Sci.*
504 *Technol.* 2015;49(7):4255-62.
- 505 [42]Chen X, Chen B. Macroscopic and spectroscopic investigations of the adsorption of
506 nitroaromatic compounds on graphene oxide, reduced graphene oxide, and graphene
507 nanosheets. *Environ. Sci. Technol.* 2015;49(10):6181-9.
- 508 [43]Wang X, Qin Y, Zhu L, Tang H. Nitrogen-doped reduced graphene oxide as a bifunctional
509 material for removing bisphenols: synergistic effect between adsorption and catalysis. *Environ.*
510 *Sci. Technol.* 2015;49(11):6855-64.
- 511 [44]Sheng Z-H, Shao L, Chen J-J, Bao W-J, Wang F-B, Xia X-H. Catalyst-free synthesis of
512 nitrogen-doped graphene via thermal annealing graphite oxide with melamine and its excellent

electrocatalysis. ACS Nano. 2011;5(6):4350-8.

[45] Sui Z-Y, Meng Y-N, Xiao P-W, Zhao Z-Q, Wei Z-X, Han B-H. Nitrogen-doped graphene aerogels as efficient supercapacitor electrodes and gas adsorbents. ACS Appl. Mater. Interfaces. 2015;7(3):1431-8.

[46] Carter MC, Kilduff JE, Weber WJ. Site energy distribution analysis of preloaded adsorbents. Environ. Sci. Technol. 1995;29(7):1773-80.

[47] Apul OG, Karanfil T. Adsorption of synthetic organic contaminants by carbon nanotubes: A critical review. Water Res. 2015;68(0):34-55.

[48] Xu Z, Buehler MJ. Geometry controls conformation of graphene sheets: membranes, ribbons, and scrolls. ACS Nano. 2010;4(7):3869-76.

[49] Strachowski P, Bystrzejewski M. Comparative studies of sorption of phenolic compounds onto carbon-encapsulated iron nanoparticles, carbon nanotubes and activated carbon. Colloids and Surfaces A: Phys. Eng. Asp. 2015;467(0):113-23.

[50] Bai S, Shen X, Zhu G, Yuan A, Zhang J, Ji Z, et al. The influence of wrinkling in reduced graphene oxide on their adsorption and catalytic properties. Carbon. 2013;60:157-68.

[51] Pan B, Lin D, mashayekhi H, Xing B. Adsorption and hysteresis of bisphenol A and 17 α -ethinyl estradiol on carbon nanomaterials. Environ. Sci. Technol. 2008;42:5480-5.

[52] Zhang D, Pan B, Zhang H, Ning P, Xing B. Contribution of different sulfamethoxazole species to their overall adsorption on functionalized carbon nanotubes. Environ Sci Technol. 2010;44(10):3806-11.

[53] Chen J, Chen W, Zhu D. Adsorption of nonionic aromatic compounds to single-walled carbon nanotubes- effects of aqueous solution chemistry. Environ Sci Technol. 2008;42:7225-30.

[54] Ji L, Chen W, Zheng S, Xu Z, Zhu D. Adsorption of sulfonamide antibiotics to multiwalled carbon nanotubes. Langmuir. 2009;25(19):11608-13.

[55] Yu F, Ma J, Han S. Adsorption of tetracycline from aqueous solutions onto multi-walled carbon nanotubes with different oxygen contents. Sci. Rep. 2014;4:5326.

[56] Yang S, Li L, Pei Z, Li C, Shan X-q, Wen B, et al. Effects of humic acid on copper adsorption onto few-layer reduced graphene oxide and few-layer graphene oxide. Carbon. 2014;75:227-35.

[57] Smith B, Yang J, Bitter JL, Ball WP, Fairbrother DH. Influence of surface oxygen on the

543 interactions of carbon nanotubes with natural organic matter. Environ. Sci. Technol.
544 2012;46(23):12839-47.
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573

574 **List of captions for Table and Figures.**

575 **Table 1.** Langmuir and Freundlich model fitting parameters for adsorption of SMX by
576 carbonaceous nanomaterials

577

578 **Fig. 1.** The SEM/EDX images of reduced graphene oxide (rGO), graphene oxide (GO) and
579 graphene nanoplatelets pastes (GNP).

580

581 **Fig. 2.** C 1s XPS spectra of rGO, GO, GNP, MWCNT10, MWCNT15, MWCNT15-OH,
582 MWCNT15-COOH, and N-doped MWCNTs.

583

584 **Fig. 3.** Adsorption isotherms of SMX onto rGO, GO, GNP, MWCNT10, MWCNT15,
585 MWCNT15-OH, MWCNT15-COOH, and N-doped MWCNTs.

586

587 **Fig. 4.** ^1H nuclear magnetic resonance (NMR) chemical shifts (δ) of the $-\text{CH}_3$ group on SMX
588 (0.01M) vs the concentration of π -donors naphthalene (NAPH), phenanthrene (PHEN), pyrene
589 (PYR), 9-phenanthrol, 3-phenanthrenecarboxylic acid in methanol- d_4 .

590

591 **Fig. 5.** Effect of humic acid (HA) on the adsorption of SMX (7 mg/L) on rGO, GO, GNP,
592 MWCNT10, MWCNT15, MWCNT15-OH, MWCNT15-COOH, and N-doped MWCNTs.

593

594 **Fig. 6.** AFM images of rGO and MWCNT10 in aquatic environment.

595

596

597

598

599

Table 1.
Langmuir and Freundlich model fitting parameters for adsorption of SMX by carbonaceous
nanomaterials

	Langmuir model		r^2	Freundlich model			
	$q_{\max}$	K_L		K_f	n	r^2	K_d ($C_e=2\text{mg/L}$)
rGO	11.76±1.31	0.21±0.04	0.973	11.37±0.36	0.53±0.02	0.994	8.21
GO	0.15±0.02	0.01±0.01	0.956	0.19±0.03	0.87±0.07	0.960	0.17
GNP	0.08±0.01	-0.005±0.006	0.972	0.07±0.02	1.06±0.08	0.973	0.07
MWCNT10	3.03±0.52	0.11±0.04	0.938	3.70±0.29	0.59±0.04	0.976	2.78
MWCNT15	1.01±0.06	-0.01±0.004	0.992	1.02±0.1	1.03±0.04	0.992	1.04
MWCNT15-OH	0.79±0.06	-0.01±0.005	0.989	0.34±0.07	1.39±0.08	0.983	0.45
MWCNT15-COOH	0.54±0.04	-0.03±0.003	0.990	0.83±1.03	1.03±0.05	0.987	0.89
N-doped MWCNT	0.58±0.04	0.07±0.01	0.986	0.70±0.06	0.68±0.04	0.980	0.56

^a $q_{\max}$: mg/g; K_L : mL/mg; K_f : (mg/g)/(mg/mL)ⁿ. ^b Standard errors of $q_{\max}$, K_L , K_f and n , respectively. K_d was derived from the equilibrium concentration of SMX at 2 mg/L.

Fig. 1. The SEM/EDX images of reduced graphene oxide (rGO), graphene oxide (GO) and graphene nanoplatelets pastes (GNP).

647

648 **Fig. 2.** C 1s XPS spectra of rGO, GO, GNP, MWCNT10, MWCNT15, MWCNT15-OH,

649 MWCNT15-COOH, and N-doped MWCNTs.

650

651

652
653

654 **Fig. 3.** Adsorption isotherms of SMX onto rGO, GO, GNP, MWCNT10, MWCNT15,
655 MWCNT15-OH, MWCNT15-COOH, and N-doped MWCNTs. The q_e (mg/g) is the solid-phase
656 concentration and C_e (mg/L) is the equilibrium concentration.

657

658

659 **Fig. 4.** ^1H nuclear magnetic resonance (NMR) chemical shifts (δ) of the $-\text{CH}_3$ group on SMX
 660 (0.01M) vs the concentration of π -donors naphthalene (NAPH), phenanthrene (PHEN), pyrene
 661 (PYR), 9-phenanthrol, 3-phenanthrenecarboxylic acid in methanol- d_4 .

662

663

664

665 **Fig. 5.** Effect of humic acid (HA) on the adsorption of SMX (7 mg/L) on rGO, GO, GNP,

666 MWCNT10, MWCNT15, MWCNT15-OH, MWCNT15-COOH, and N-doped MWCNTs.

667

668

669

670 **Fig. 6.** AFM images of rGO and MWCNT10 in aquatic environment. (A) rGO, (B and C) rGO +
 671 0.86 mgC/L HA + 7 mg/L SMX, (D and E) rGO + 8.6 mgC/L HA + 7 mg/L SMX, (F) MWCNT10,
 672 (G and H) MWCNT10 + 0.86 mgC/L HA + 7 mg/L SMX, (I and J) MWCNT10 + 8.6 mgC/L HA +
 673 7 mg/L SMX.

Graphical Abstract