Graphical abstract

Prediction model:

$$\log q_e = \log Q^0 - (\varepsilon/E)^b$$

$$Q^0 = f(A, R_{\text{meso}}, \mathbf{MP}, N)$$

$$E = f(\alpha_m, R_{\text{meso}}, \pi^*)$$

$$b = f(\alpha_m, R_{\text{meso}}, \pi^*)$$

$$\varepsilon = -RT \ln(C_e/C_s)$$

Correlation and prediction of adsorption capacity and affinity of aromatic compounds on carbon nanotubes

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Abstract: Adsorption of 22 nonpolar and polar aromatic compounds on 10 carbon nanotubes (CNTs) with various diameters, lengths and surface oxygen-containing group contents was investigated to develop predictive correlations for adsorption, using the isotherm fitting of Polanyi theory-based Dubinin-Ashtakhov (DA) model. Adsorption capacity of aromatic compounds on CNTs is negatively correlated with melting points of aromatic compounds, and surface oxygen-containing group contents and surface area ratios of mesopores to total pores of CNTs, but positively correlated with total surface area of CNTs. Adsorption affinity is positively correlated with solvatochromic parameters of aromatic compounds, independent of tube lengths and surface oxygen-containing group contents of CNTs, but negatively correlated with surface area ratios of mesopores to total pores of CNTs. The correlations of adsorption capacity and adsorption affinity with properties of both aromatic compounds and CNTs clearly have physical significance, can be used successfully with DA model to predict adsorption of aromatic compounds on CNTs from the well-known physiochemical properties of aromatic compounds (i.e., solvatochromic parameters, melting points) and CNTs (i.e., surface area and total acidic group contents), and thus can facilitate the environmental application of CNTs as sorbents and environmental risk assessment of both aromatic contaminants and CNTs.

Keywords: carbon nanotubes; aromatic compounds; adsorption; correlation; prediction; DA model

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26 1. Introduction

27 Due to the large surface area and high surface activity, carbon nanotubes (CNTs) show high
28 adsorption capacity and affinity towards organic compounds (Yang and Xing, 2010) and thus could be
29 used as superior sorbent in water treatment (Peng et al., 2003; Lu et al., 2005; Mauter and Elimelech,
30 2008; Pan et al., 2008a) and solid-phase extraction (Pyrzyska, 2008; Niu et al., 2007). The currently
31 available experimental adsorption data are far limited for the organic compounds of huge number
32 currently in use (Crittenden et al., 1999), even without considering different types of CNTs. In addition,
33 obtaining the experimental data can be costly, time-consuming and laborious as well as potentially
34 dangerous due to the toxicity of both organic compounds and CNTs. Therefore, correlations that can
35 be applied to predict adsorption isotherms of organic compounds on CNTs with the physiochemical
36 properties of both organic compounds and CNTs are of great importance to promote the applications of
37 CNTs as superior sorbent. These correlations are also essential for the prediction and assessment of the
38 environmental and health risks of both CNTs and organic compounds because they are toxic and will
39 be released into the environment in their production, transportation, storage, use and disposal (Kam et
40 al., 2004; Yang and Lin, 2014).

41 To date, there are only a few studies have focused on the correlations and prediction of adsorption
42 of organic compounds by CNTs (Yang et al., 2008; Xia et al., 2010; Apul et al., 2013; Huffer et al.,
43 2014; Zhao et al., 2014). Linear solvation energy relationships (LSERs) based on the solute
44 solvatochromic parameters has been proposed as a useful approach to develop the predictive
45 correlations. LSERs between logarithmic values of CNTs-water distribution coefficients (i.e., $\log K$, K
46 is the ratio of adsorbed concentration to solution concentration of solute at equilibrium) and solute
47 solvatochromic parameters were reported to develop the predictive correlations for adsorption of
48 organic compounds by CNTs (Xia et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014).

49 However, there are four limitations of this approach. First, the $\log K$ could have little physical
50 significance for the nonlinear surface sorption of organic compounds on CNTs (Pan et al., 2008a;
51 Yang and Xing, 2010). Generally, at least two parameters are needed to describe the nonlinear sorption
52 behavior, such as the Langmuir model and Freundlich model (Yang and Xing, 2010). One sorption
53 parameter ($\log K$) could only be able to describe the linear sorption behavior, but not be enough to
54 interpret the nonlinear surface sorption behavior of organic compounds on CNTs and thus could not
55 reveal the underlying adsorption mechanism. Second, $\log K$ values vary with the equilibrium solute
56 concentration due to the nonlinear isotherms of organic compounds by CNTs (Yang and Xing, 2010),
57 thus, the coefficients in LSERs are solute concentration-dependent (Xia et al., 2010; Apul et al., 2013;
58 Huffer et al., 2014; Zhao et al., 2014). However, the developed correlations between the LSERs
59 coefficients (e.g., intercepts) and solute concentrations are largely varied and have no physical
60 significance (Xia et al., 2010; Apul et al., 2013; Zhao et al., 2014). Third, the π - π interaction, a very
61 important adsorption interaction observed between CNTs and aromatic compounds (Pan and Xing,
62 2008b; Yang and Xing, 2010), was largely neglected in these reported correlations based on $\log K$.
63 Moreover, the important roles of CNT properties (e.g., outer diameters, surface area and pore
64 distribution, acidic groups) in adsorption of organic compounds on CNTs as reported by previous
65 studies (Pan and Xing, 2008b; Yang and Xing, 2010; Wu et al., 2012) were not used in these predictive
66 correlations (Xia et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014). Therefore,
67 predictive correlations for adsorption of organic compounds on CNTs with following characteristics
68 are surely needed: 1) being with parameters having clear physical significance to capture adsorption
69 mechanism, 2) being independent of the equilibrium solute concentration, and 3) considering not only
70 the properties of organic compounds but also the properties of CNTs.

71 Adsorption of an organic compound on CNTs should be described in two aspects, adsorption
72 capacity (i.e., maximum adsorbed amount) and adsorption affinity (i.e., strength of adsorption
73 interactions between organic molecules and CNTs) (Yang and Xing, 2010; Wu et al., 2013). Polanyi
74 theory has been regarded as the most powerful theory dealing with aqueous adsorption of organic
75 compounds on CNTs (Yang et al., 2006a; Pan et al., 2008a; Yang and Xing, 2010), and the fitted
76 isotherm parameters of the Polanyi theory-based Dubinin-Ashtakhov (DA) model can be used to
77 identify the adsorption capacity and affinity of organic compounds on CNTs (Yang and Xing, 2010).
78 In our previous study (Yang et al., 2008), a LSERs based on DA model fitted isotherm parameters and
79 solute solvatochromic parameters was developed for adsorption of aniline, phenol and their substitutes
80 by a multi-walled CNTs sample. The LSERs was a significant multiple linear relationship between the
81 DA model fitted adsorption affinity parameter (E and b) and the solute solvatochromic parameters,
82 while the DA model fitted adsorption capacity parameter ($\log Q^0$) of these organic compounds were
83 relatively constant. Interestingly, LSERs based on Polanyi theory and solute solvatochromic
84 parameters have also been successfully used to modeling adsorption of organic compounds by
85 activated carbons (Crittenden et al., 1999). Parameters of the LSERs have clear physical significance
86 and meaning to capture adsorption mechanism. Since the fitted parameters of Polanyi theory-based
87 adsorption model are solute concentration-independent (Crittenden et al., 1999; Yang et al., 2008;
88 Yang and Xing, 2010), the established LSERs will also be independent of solute concentration, and
89 therefore pave the way in this study to predict adsorption of organic compounds by CNTs. However,
90 whether the reported LSERs (Yang et al., 2008) could be applicable for other CNTs or not is unclear
91 and needs to be examined. Correlations of this LSERs parameters and the adsorption capacity with the
92 properties of CNTs also need to be developed for the accurate adsorption prediction.

Besides the properties of organic compounds (i.e., solvatochromic parameter), the structural (e.g., outer diameter, tube length, surface area and pore distribution) and surface chemical properties (e.g., oxygen-containing groups) of CNTs play crucial roles in adsorbing organic compounds (Cho et al., 2008; Pan and Xing, 2008b; Yang and Xing, 2010; Wu et al., 2012). It was reported that adsorption capacity of organic compounds on CNTs increased proportionally as the surface area of CNTs increased (Pan and Xing, 2008b; Yang and Xing, 2010; Wu et al., 2012). Surface oxidation of multi-walled CNTs reduced the surface area-normalized adsorption capacity of organic compounds significantly because of the competition of water molecules, but did not alter the adsorption affinity (Cho et al., 2008; Wu et al., 2012). Thus, accurate prediction for adsorption of organic compounds on CNTs without combining the properties of CNTs will be largely hindered when it comes to a new CNTs sample with very different properties. However, there is no predictive correlation developed on the basis of CNTs properties at present, though it is of great importance for understanding the underlying adsorption mechanism, promoting the application of CNTs as superior sorbent and facilitating the assessment of environmental and health risks of both CNTs and organic compounds.

Therefore, in order to develop solute concentration-independent predictive correlations for adsorption of aromatic compounds on CNTs combining properties of both organic compounds and CNTs, and further to outline the underlying adsorption mechanism, adsorption of 22 typical aromatic compounds including polycyclic aromatic hydrocarbons, nitroaromatic compounds, phenolic compounds, and aromatic amines (Table S1) on 10 CNTs with different diameters, tube lengths and surface oxygen-containing group contents (Table S2) was investigated. These organic compounds were chosen also due to their notable concentrations and high toxicity in the aqueous environment (Neilson, 1999). The LSERs approach based on DA model and solute solvatochromic parameters as properties of organic compounds was applied here to develop the predictive correlations.

116 2. Experimental

117 2.1. Chemicals

118 Naphthalene (+99%), nitrobenzene (+99%), 1,4-dinitrobenzene (+98%) and 4-chloroaniline (+98%)
119 were purchased from Acros Organics Co.; 2-chlorophenol (+99%), 4-chlorophenol (+99%), 4-
120 methylaniline (+99.7%), 2-chloroaniline (+98%) and 2-nitroaniline (+99%) were purchased from
121 Aladdin Reagent Co.; 3-nitroaniline (+98%) was purchased from Sigma-Aldrich Chemistry Co.; 4-
122 methyl nitrobenzene (+99.5%) and 4-chloronitrobenzene (+98%) were purchased from Fluka
123 Chemistry Co.; 1,3-dinitrobenzene (+99%) and 1,3,5-trinitrobenzene (wetted with 40% water) were
124 purchased from Tokyo Chemical Industry Co.; 2,4-dichlorophenol (+99.5%), 4-methylphenol (+98%),
125 2-nitrophenol (+99%), 3-nitrophenol (+99%), 4-nitrophenol (+99.5%) and 4-nitroaniline (+99.5%)
126 were purchased from Sinopharm Chemical Reagent Co.; aniline (+99.5%) was purchased from
127 Shanghai Reagent Co; and phenol (+99.7%) was purchased from Hangzhou Shuanglin Chemical Co.
128 All these organic chemicals are of reagent grade and were used as received. Selected properties of
129 these chemicals are listed in [Table S1](#).

130 2.2. Carbon nanotubes

131 Purified single-walled CNTs (SW), five purified multi-walled CNTs with different outer diameters
132 (<8nm: MW8; 8-15 nm: MW15; 20-30 nm: MW30; 30-50 nm: MW50; >50 nm: MW100), MW15
133 with short length (MW15-S), graphitized MW15 (MW15-G), hydroxylated MW15 (MW15-OH) and
134 carboxylated MW15 (MW15-COOH) were purchased from Chengdu Organic Chemistry Co. (China)
135 and used as received. Transmission Electron Microscope (TEM) images of CNTs were obtained with a
136 TEM (Philips TECNAI 10, Netherlands), using suspensions containing 25 mg/L CNTs in ethanol, to
137 show the sizes of these CNTs ([Fig. S1](#) and [Table S2](#)). Nitrogen adsorption isotherms on CNTs at 77 K
138 were determined by a physisorption analyzer (Quantachrome, AUTOSORB AS-1) to characterize the

139 surface area and pore distribution of CNTs. Surface area was calculated by the multi-point Brunauer-
140 Emmett-Teller (BET) method, while the surface area and pore distribution by the Density Functional
141 Theory (DFT) method for cylindrical pores (Zhang et al., 2010). Surface acidic groups (i.e., carboxyl,
142 hydroxyl, and lactonic groups) of CNTs were determined using the Boehm titration described in our
143 previous study (Wu et al., 2013). Dry-weight-based elemental compositions (C, H, N) of CNTs were
144 determined by an elemental analyzer (Flash EA 1112, ThermoFinnigan, Italy) and the oxygen contents
145 were calculated by mass difference. Their ash contents were measured by heating the CNTs at 900 °C
146 for 8 h. The measured properties of CNTs are listed in Table S2 and Fig. S1.

147 **2.3. Adsorption experiments**

148 Adsorption experiments were conducted at 25±1 °C using a batch equilibration technique as described
149 in our previous articles (Wu et al., 2012). Briefly, chemicals, except for naphthalene and 1,4-
150 dinitrobenzene, were dissolved in background solution containing 0.01mol/L CaCl₂ in deionized
151 distilled water. The CaCl₂ was used to maintain a constant ionic strength and simulate the natural water
152 environment (Sun et al., 2014). Naphthalene and 1,4-dinitrobenzene in methanol were added to the
153 background solution for adsorption. 8, 22 or 40 mL aqueous solutions of chemicals were mixed with
154 CNTs in 8, 22 or 40 mL screw cap vials, respectively. The added amounts of CNTs were adjusted to
155 achieve that more than 20% of the added organic compounds was adsorbed by CNTs. The pH of the
156 mixtures was adjusted by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solution. The final solution pH
157 after adsorption were 6.5 for naphthalene and nonionic nitroaromatic compounds (i.e., nitrobenzene, 4-
158 methylnitrobenzene, 4-chloronitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene and 1,3,5-
159 trinitrobenzene), 3.0 for phenol and its substitutes (i.e., 4-methylphenol, 2-chlorophenol, 4-
160 chlorophenol, 2,4-dichlorophenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol), and 8.0 for aniline
161 and its substitutes (i.e., 4-methylaniline, 2-chloraniline, 4-chloroaniline, 2-nitroaniline, 3-nitroaniline

and 4-nitroaniline) in order to avoid the dissociation of chemicals. The suspensions were shaken at 150 rpm for 5 days, since preliminary experiment indicated that adsorption of all 22 chemicals on CNTs can reach equilibrium within 2 days (Fig. S2). After 5-day equilibration, the mixtures were separated by centrifugation at 3500 g for 20 min. The compound concentrations in the supernatants were determined by a UV-spectrophotometer (Shimadzu, UV-2450) at their maximum adsorption wavelength ($\lambda_{\max}$, Table S1), except for naphthalene which was determined by a reverse-phase High Performance Liquid Chromatography (HPLC, Shimadzu, LC-20A series, XDB-C18, 4.6×150 mm) equipped with a fluorescence detector at the excitation and emission wavelengths of 218 and 324 nm, respectively. Experimental uncertainties were evaluated in vials without CNTs, which showed that total uncertainty was less than 4% of the initial concentrations. Therefore, the adsorbed amounts of organic compounds by CNTs were calculated directly by the mass difference of organic compounds in initial and equilibrium solutions.

2.4. Sorption model and isotherm fitting

The Dubinin-Astakhov (DA) model (Dubinin and Astakhov, 1971), which was used successfully in fitting adsorption isotherms of organic compounds on CNTs in previous studies (Pan et al., 2008a; Yang and Xing, 2010; Wu et al., 2012), was employed here to fit the experimental data (Equation 1).

$$\log q_e = \log Q^0 - (\varepsilon/E)^b \quad (1)$$

where q_e [mg/g] is the adsorbed amount of organic compound at equilibrium; Q^0 [mg/g] is the adsorption capacity of organic compound; ε [KJ/mol], $\varepsilon = RT \ln(\frac{C_s}{C_e})$, is the effective adsorption potential; C_e [mg/L] is the equilibrium concentration of organic compound in aqueous phase; C_s [mg/L] is the water solubility of organic compound; R [8.314×10^{-3} KJ/(mol·K)] is the universal gas constant; T [K] is the absolute temperature; E [KJ/mol] is the “correlating divisor” of the effective adsorption

184 potential (ϵ), i.e., the characteristic energy of adsorption (Dubinin and Astakhov, 1971); and b is a
185 fitting parameter. E and b are also parameters that can be successfully used to identify the adsorption
186 affinity of organic compounds (Yang et al., 2008; Yang and Xing, 2010; Wu et al., 2012). All
187 estimated model parameter values and their standard deviations were determined by a commercial
188 software program (Origin 7.0). Mean weighted square error (MWSE) and correlation coefficients (r^2)
189 were used to evaluate the goodness of fitting results (Wu et al., 2012).

190 ***2.5. Solvatochromic parameters, Linear Solvation Energy Relationships and regression analysis***

191 Solvatochromic parameters are useful parameters for predicting chemical properties, toxicity, mobility
192 and environmental behaviors (Kamlet et al., 1986; Kamlet et al., 1988; Hickey and Passino-Reader,
193 1991; Marcus, 1991; Crittenden et al., 1999). There are mainly two sets of solvatochromic parameters
194 being reported and used in the literature, i.e., Kamlet-Taft parameters and Abraham parameters. The
195 Kamlet-Taft parameters, including intrinsic molar volume (V_I), polarity/polarizability parameter (π^*),
196 hydrogen-bonding acceptor parameter (β_m) and donor parameter (α_m), were obtained by the
197 solvatochromic comparison method and derived from the solute-solvent interaction (Kamlet et al.,
198 1988), and have been successfully used to predict adsorption of organic compounds by a multi-walled
199 CNTs (Yang et al., 2008) and also by four activated carbons and three synthetic polymeric adsorbents
200 (Crittenden et al., 1999). While the Abraham parameters, including McGowan volume (V), excess
201 molar refraction parameter (R), polarity/polarizability parameter (π), hydrogen-bonding acceptor
202 parameter (β) and donor parameter (α), were calculated from water-solvent or gas-liquid partition
203 system (Abraham et al., 1999), and have been used to predict adsorption of organic compounds by
204 CNTs (Xia et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014). Since both Kamlet-
205 Taft parameters and Abraham parameters can quantitatively describe the ability of solute to form
206 hydrogen-bonding and π - π interactions with others (Kamlet et al., 1988; Abraham et al., 1999; Yang et

207 al., 2008; Yang and Xing, 2010), they are comparably applied to correlate with the adsorption affinity
208 of aromatic compounds on CNTs in this study (Table S1).

209 Multiple linear regressions, using the stepwise method for variable selection (Criteria:
210 Probability-of-F-to-enter ≤ 0.050 , Probability-of-F-to-remove ≥ 0.100), were conducted by a
211 commercial software program (SPSS 20.0) to establish the LSERs combining the DA model fitted
212 adsorption affinity parameter (E) with the solvatochromic parameters of organic compounds for the 10
213 selected CNTs, respectively. The best-fit parameters for correlations were determined by minimizing
214 the percent sample deviation (Crittenden et al., 1999). The percent sample deviation based on the
215 relative error between experimental data and the correlations was calculated using Equation 2,

$$216 \quad \% \text{ sample deviation (SDEV)} = \sqrt{\frac{\sum (\frac{W_{\text{cal}} - W_{\text{exp}}}{W_{\text{exp}}})^2}{N - 1}} \times 100 \quad (2)$$

217 where W_{cal} and W_{exp} are parameters determined from correlations and experimental data, respectively,
218 and N is the number of data points (Crittenden et al., 1999).

219

220 3. Results and discussion

221 3.1. Adsorption isotherms and DA model fitting results

222 Adsorption isotherms of the 22 aromatic compounds on all 10 CNTs and the DA model fitted
223 isotherms are presented in Figs. 1 and S3-S5. DA model fitted parameters (i.e., $\log Q^0$, E and b) of
224 these isotherms and their MWSE values are listed in Table S3. All the isotherms are nonlinear and can
225 be fitted well by the DA model, as indicated by the low MWSE values and high correlation
226 coefficients (r^2) (Table S3).

227 3.2. Correlations of adsorption capacity with the properties of aromatic compounds and CNTs

For a given CNTs, DA model fitted adsorption capacity parameters (Q^0) of the investigated organic compounds were not constant (Table S3), indicating that adsorption capacity of aromatic compounds could be influenced by their properties. There was a significantly negative linear relationship between Q^0 values and melting points (MP) of organic compounds on a given CNTs, (Equation 3, Figs. 2A and S6), indicated by the low P values (Table 1). The linear regression results for 10 CNTs are listed in Table 1.

$$Q^0 = S \times MP + Q^* \quad (3)$$

where S is the slope and Q^* is the intercept.

The negative coefficient S in Table 1 indicated that adsorption capacity of aromatic compound on CNTs decreased with increasing melting point. This could be attributed to the phase changes from solid phase to adsorbed phase and the consequent expansion of organic compound with higher melting point being greater than organic compound with lower melting point on CNT surface, since solid adsorbate packed less efficiently than its melt one on adsorbent (Chiou and Manes, 1974; Manes, 1998; Yang et al., 2006b).

The intercept of Equations 3 (Q^* , mg/g) is the adsorption capacity of aromatic compound with $MP=0^\circ\text{C}$ on CNTs. A significant multiple linear relationship between Q^* values (Table 1) with the surface area (A , m^2/g , Table S2) and the total acidic group contents (N , mmol/g , Table S2) of CNTs was observed.

$$Q^* = 0.721 (\pm 0.023) \times A - 85.3 (\pm 17.6) \times N - 8.59 (\pm 5.50) \quad (4)$$

($N=10$, $r^2 = 0.993$, $F=487$, $P<0.001$, $SD=8.58$)

Fig. 2B shows that the calculated Q^* values using Equation 4 are in agreement with the regressive Q^* values (Table 1) of organic compounds on CNTs. The positive coefficient of Q^* with A in Equation 4 suggested that adsorption capacity of organic compound on CNTs increased as the surface area of

251 CNTs increased, while the negative coefficient of Q^* with N suggested that the adsorption capacity
 252 decreased with elevated surface oxidation of CNTs, consistent with the observations in previous
 253 studies (Cho et al., 2008; Pan and Xing, 2008b; Yang and Xing, 2010; Wu et al., 2012). CNTs with
 254 larger surface area have more available sites for adsorption of organic molecules to give bigger
 255 adsorption capacity (Pan and Xing, 2008b; Yang and Xing, 2010). However, a fraction of sites on
 256 CNTs surface cannot be available for adsorption of organic molecules after these hydrophobic surface
 257 sites were oxidized to be hydrophilic oxygen-containing groups, due to the competition of water
 258 molecules with organic molecules on these oxidized sites, which resulted in the decrease of adsorption
 259 capacity of organic compounds on oxidized CNTs (Cho et al., 2008; Wu et al., 2012). It was observed
 260 in our previous study that water molecules had higher adsorption affinity than organic molecules on
 261 oxidized hydrophilic sites of CNTs and thus occupied these sites prior to organic molecules (Wu et al.,
 262 2012).

263 Additionally, S values on CNTs (Table 1) are positively correlated with the Q^* values in Table 1
 264 and also the ratio of mesopore surface area to total surface area of CNTs (R_{meso}) in Table S2.

$$\begin{aligned}
 265 \quad S &= -0.00414 (\pm 0.00021) \times Q^* \times R_{\text{meso}} + 0.0385 (\pm 0.0224) \\
 266 \quad (N=10, r^2 &= 0.980, F=387, P<0.001, SD=0.0378) \quad (5)
 \end{aligned}$$

267 Equation 5 and Fig. 2C indicated the expansion of organic compound in the process of phase change
 268 (i.e., from solid phase to solution, then to adsorbed phase) occurred in mesopores or bigger ones of
 269 CNTs but not in micropores. This could be attributed to the stronger interactions between organic
 270 molecules and CNTs surface in micropores than that in bigger pores according to the Polanyi theory
 271 (Dubinin and Astakhov, 1971; Manes, 1998; Yang and Xing, 2010), which may suppress the
 272 expansion of organic compound and result in organic molecules packing more efficiently in
 273 micropores (Manes, 1998).

Therefore, adsorption capacity (Q^0) of aromatic compounds on CNTs is negatively correlated with melting points of organic compounds, and oxygen-containing group contents and surface area ratios of mesopores to total pores of CNTs, but positively correlated with total surface area of CNTs. Based on Equations 3-5, therefore, Equation 6 can be obtained for prediction of adsorption capacity (Q^0) of aromatic compounds on CNTs.

$$Q^0 = (-0.00298 \times A + 0.353 \times N + 0.0356) \times R_{\text{meso}} \times MP + 0.0385 \times MP + 0.721 \times A - 85.3 \times N - 8.59 \quad (6)$$

Fig. 2D shows that the calculated Q^0 values using Equation 6 are in agreement with the experimental Q^0 values derived from DA model fitted isotherms of organic compounds on CNTs (Table S3).

3.3. Correlations of adsorption affinity with the properties of aromatic compounds and CNTs

The DA model fitted parameters (i.e., E and b) are to identify the adsorption affinity of organic compounds, i.e., the strength of adsorption interactions between organic molecules and CNTs (Yang et al., 2008; Yang and Xing, 2010; Wu et al., 2012). For a given organic compound, the E value on single-walled CNTs was significantly higher than that on MW8, and followed by that on other 8 multi-walled CNTs (Table S3). Moreover, the E values on the other 8 multi-walled CNTs were almost constant (Table S3). The relatively constant E values of MW15, MW15-G, MW15-OH and MW15-COOH (Table S3) suggested that influence of surface oxidation of CNTs on the adsorption affinity of organic compound was insignificant, which is in line with previous studies (Cho et al., 2008; Wu et al., 2012). The relatively constant E values on MW15 and MW15-S (Table S3) indicated that the influence of tube length of CNTs on the adsorption affinity can also be negligible. For a given CNTs, however, the E values were dependent on the organic compounds investigated (Table S3), suggesting the significant role of properties of aromatic compounds in their adsorption affinity on CNTs.

In our previous studies (Yang et al., 2008; Yang and Xing, 2010), it was observed that DA model fitted parameter E values of anilines and phenols on a MWCNT sample (MW15) correlated with the

297 Kamelt-Taft solvatochromic parameters (i.e., α_m and π^*) of these organic compounds by a multiple
 298 linear relationships (i.e., LSERs, Equation 7). The influence of molecular size (V_I) and hydrogen-
 299 bonding acceptor ability (β_m) of organic compounds on their adsorption affinity can be negligible, and
 300 thus β_m and V_I were ruled out from the LSERs by the stepwise method. The LSERs was also observed
 301 in this study for the investigated 10 CNTs (Equation 7 and Table 2). The organic compounds in the
 302 LSERs included not only anilines and phenols, but also PAHs and nitrobenzenes.

$$E = \beta_1 \times \alpha_m + \pi_1 \times \pi^* + C \quad (7)$$

304 where β_1 , π_1 are the regression coefficients and C is the intercept. Figs. 3A and S7 show that the
 305 calculated E values of organic compounds on a given CNTs, computed from the α_m and π^* values
 306 (Table S1) and their coefficients (Table 2) using Equation 7, agreed well with the experimental E
 307 values.

308 The variable selection results of the Kamlet-Taft solvatochromic parameters were the same for all
 309 the 10 selected CNTs, where only α_m and π^* were selected into these LSERs equations, while β_m and
 310 $V_I/100$ were ruled out by the stepwise method, as is in agreement with our previous studies (Yang et al.,
 311 2008; Yang and Xing, 2010). The obtained LSERs Equation 7 can be used to identify the relative
 312 contribution of different adsorptive interactions to the overall adsorption of aromatic compounds by
 313 CNTs. The regression coefficients of the selected solvatochromic parameters (i.e., α_m and π^*) and
 314 intercept in the LSERs Equation 7 could be used to quantitatively describe the adsorption potential of
 315 CNTs responsible for the adsorption affinity of aromatic compounds (Kamlet et al., 1986; Xia et al.,
 316 2010). Similar to the concepts of solute solvatochromic parameters, the regression coefficients of
 317 chemical hydrogen-bonding donor parameter α_m and polarity/polarizability parameter π^* (Equation 7)
 318 can be referred to as the hydrogen-bonding acceptor potential (signed as parameter β_1) and the

319 polarity/polarizability potential (signed as parameter π_1) of CNTs, respectively, while the regression
320 intercept (C) can be referred to as the nonspecific van der Waals force potential of CNTs.

321 Thus, the relatively constant E values of a given organic compound on multi-walled CNTs with
322 OD>8 nm (Table S3) should be attributed to the relatively constant β_1 , π_1 and C in LSERs Equation 7
323 (Table 2), indicating the same hydrogen-bonding acceptor ability, polarity/polarizability and van der
324 Waals force potential of these multi-walled CNTs for aromatic compounds. Therefore, the influence of
325 outer diameter, tube length and surface oxygen-content on the adsorption potential of multi-walled
326 CNTs (OD>8 nm) for aromatic compounds and thus the adsorption affinity of aromatic compounds on
327 these CNTs can be negligible. The intercepts (C) of LSERs Equation 7 for the 9 investigated multi-
328 walled CNTs were almost the same (Table 2). They were close to the DA model fitted E value (5.71)
329 of linear isotherm ($b = 1$) and thus can be attributed to the hydrophobic effects of organic compounds
330 (van der Waals force) on adsorption (Yang et al., 2008; Yang and Xing, 2010), because the linear
331 isotherm, a special form of DA model with $E = 5.71$ and $b = 1$, indicates that the solute adsorption is
332 limited by their solubility only (Yang et al., 2008; Yang and Xing, 2010). Therefore, hydrogen-
333 bonding interaction identified by α_m , π - π interaction identified by π^* , and hydrophobic interaction
334 identified by C , are responsible for the adsorption of organic compounds on multi-walled CNTs,
335 supported by previous studies (Chen et al., 2007; Pan and Xing, 2008b; Yang et al., 2008; Yang and
336 Xing, 2010; Wu et al., 2012).

337 The β_1 of the 10 CNTs were almost constant (Table 2), with a mean value of 11.11($\pm$ 0.50).
338 However, the E value (i.e., the adsorption affinity) of a given organic compound on SW was bigger
339 than that on multi-walled CNTs, showing the bigger values of both π_1 and intercept (C) in LSERs
340 Equation 7 (Table 2) and that both of the π - π interaction and van der Waals force between SW and
341 organic molecules were stronger relative to that between multi-walled CNTs and organic molecules. In

the previous studies (Hilding et al., 2003; Yang et al., 2013), it was reported that much more energy was required to separate the single-walled CNTs bundles than multi-walled CNTs bundles into single tubes due to the stronger π - π interaction and van der Waals force between the individual tubes of SW, implying that the tubes of SW could interact with organic molecules by stronger π - π interaction and van der Waals force than the tubes of multi-walled CNTs, too. The stronger π - π interaction and van der Waals force between organic compounds and SW could be attributed to the bigger surface area in micropores of SW than multi-walled CNTs (Table S2), because the micropore surface shows higher adsorption potential to organic compounds than the commonly flat surface (Zhang et al., 2010). This micropore adsorption mechanism was captured by Polanyi theory. In the Polanyi theory (Dubinin and Astakhov, 1971; Manes, 1998; Yang and Xing, 2010), it was assumed that the magnitude of the adsorption potential for a given molecule is dependent on its proximity to adsorbent atoms, and thus the adsorption potential is highest in the narrowest pores because of proximity to more adsorbent atoms. The bigger adsorption affinity (E) of a given organic compound on MW8 than that on other multi-walled CNTs (OD>8nm) could also be attributed to the larger micropore surface area of MW8 (Table S2). The relatively constant E values of a given organic compound on other multi-walled CNTs (OD>8nm) could be due to their small and relatively constant micropore surface area (Table S2). Therefore, significantly negative linear relationships of π_1 , C with R_{meso} were observed (Fig. 3B),

$$C = -13.7 (\pm 1.8) \times R_{\text{meso}} + 17.6 (\pm 1.6) \quad (N=10, r^2 = 0.874, F=55.6, P<0.001, SD=0.71) \quad (8)$$

$$\pi_1 = -6.63 (\pm 2.37) \times R_{\text{meso}} + 15.0 (\pm 2.0) \quad (N=10, r^2 = 0.496, F=7.9, P=0.023, SD=0.92) \quad (9)$$

Based on Equations 7-9, Equation 10 can be obtained for prediction of adsorption affinity (E) of aromatic compounds on CNTs,

$$E = 11.11 \times \alpha_m + (-6.63 \times R_{\text{meso}} + 15.0) \times \pi^* - 13.7 \times R_{\text{meso}} + 17.6 \quad (10)$$

Fig. 3C shows that the calculated E values using Equation 10 are in agreement with E values derived from DA model fitted isotherms of organic compounds on CNTs (Table S3). Therefore, adsorption affinity is positively correlated with solvatochromic parameters of organic compounds, independent of tube lengths and surface oxygen-containing group contents of CNTs, but negatively correlated with surface area ratios of mesopores to total pores of CNTs.

Additionally, there was a significant linear relationship between the DA fitted parameter b values with $(E-C) \times R_{\text{meso}}$ of all the 220 adsorption isotherms (Fig. S8),

$$b = 0.0838 (\pm 0.0048) \times (E-C) \times R_{\text{meso}} + 0.635 (\pm 0.052) \\ (N=220, r^2 = 0.587, F=309, P<0.001, SD=0.24) \quad (11)$$

Therefore, parameter b can be calculated using Equations 8, 10 and 11, i.e., Equation 12,

$$b = 0.0838 \times E \times R_{\text{meso}} + 1.148 \times R_{\text{meso}}^2 - 1.475 \times R_{\text{meso}} + 0.635 \quad (12)$$

Fig. 3D shows that the calculated b values using Equation 12 are consistent with b values derived from DA model fitted isotherms of organic compounds on CNTs (Table S3). The relationship in Equations 11 and 12 indicated that DA fitted parameter b value can be determined not only by the E value, but also by the pore distribution of CNTs. The more micropores in CNTs would make the b value smaller.

Besides Kamlet-Taft parameters, Abraham parameters were also used to correlate with adsorption of organic compounds by CNTs for prediction in previous studies (Xia et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014). For comparison of Abraham parameters and Kamlet-Taft parameters in predictive application of adsorption of organic compounds by CNTs, we also correlated adsorption affinity parameter E with Abraham parameters using the multiple linear regressions with stepwise method for variable selection. The results are listed in Table S4. Only V and α were selected into the LSERs based on Abraham parameters, while R , π and β were ruled out. The π - π interaction was ignored and ruled out (Table S4), consistent with the reported LSERs based on Abraham

parameters in the previous studies (Xia et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014). However, these regression results using Abraham parameters were not in agreement with the experimental observations, i.e., π - π interaction is significant and very important for adsorption of aromatic compounds on CNTs (Chen et al., 2007; Pan and Xing, 2008b; Yang and Xing, 2010). Moreover, it is difficult to correlate the varied LSERs coefficients (e.g., V and intercept B in Table S4) with the properties of CNTs, as was commonly ignored in previous studies (Xia et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014). Therefore, we suggest here that LSERs based on Kamlet-Taft parameters (Equation 7 and Table 2) would be better correlations for predicting adsorption of aromatic compounds on CNTs, although good fitting results of LSERs based on Abraham parameters were also obtained.

3.4. Prediction of adsorption of aromatic compounds by CNTs

The obtained correlations of adsorption capacity and affinity with the properties of both organic compounds and CNTs (i.e., Equations 6, 10, 12) were used to calculate and predict adsorption of aromatic compounds by CNTs using the well-known Kamlet-Taft solvatochromic parameters and melting points of organic compounds, the surface area and total acidic group contents of CNTs, and the Polanyi theory-based DA model (Equation 1). For example, the calculated adsorbed amounts ($\log q_{\text{ecal}}$) of the 22 organic compounds on the 10 CNTs at different solute concentrations investigated in this study using the correlations (Equations 1, 6, 10, 12) agreed well with the experimental adsorbed amounts of organic compounds ($\log q_{\text{exp}}$), indicated by the low SDEV values (Table S3 and Fig. 4A). More importantly, these correlations were also successfully used to calculate the adsorption of organic compounds on CNTs from the earlier reported studies (Yang et al., 2006a; Lin and Xing, 2008; Yang et al., 2008; Chen et al., 2009; Wang et al., 2009; Zhang et al., 2010; Wu et al., 2012) (Table S5 and Fig. 4B), indicating the applicability of these observed correlations for prediction. The CNTs in these

410 reported studies included single-walled and multi-walled CNTs with different outer diameters, surface
411 area and pore distribution, acidic group contents (Table S5). The organic compounds in these reported
412 studies included nonpolar organic compounds such as naphthalene and phenanthrene, polar organic
413 compounds such as nitrobenzene and 1,3-dinitrobenzene, and polar ionizable organic compounds such
414 as 4-nitrophenol, 4-chlorophenol, 2,4,6-trichlorophenol, 2-phenylphenol, 4-nitroaniline and 4-
415 chloroaniline, where phenanthrene, 2,4,6-trichlorophenol and 2-phenylphenol were not investigated in
416 this study (Table S5). Moreover, although some of the organic compounds above were also
417 investigated in this study, their sorption behaviors in previous studies should be different from that in
418 this study because of the quite different properties of CNTs used in previous studied compared with
419 that in this study. The good agreement of the calculated adsorbed amounts of organic compounds on
420 CNTs using the correlations (Equations 1, 6, 10, 12) with the experimental adsorbed amounts reported
421 in this study and in previous studies (Fig. 4) validated the application of these correlations to predict
422 adsorption of aromatic compounds on CNTs. As compared to the reported correlations (Xia et al., 2010;
423 Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014), the correlations developed in this study for
424 adsorption prediction of aromatic compounds on CNTs: 1) clearly have physical significance and
425 meaning, 2) are solute concentration-independent, and 3) include the properties of CNTs. Moreover,
426 the significant difference of the regression coefficients of the correlations in the reported studies (Xia
427 et al., 2010; Apul et al., 2013; Huffer et al., 2014; Zhao et al., 2014) would be largely eliminated in the
428 correlations developed in this study, since they are applicable for predicting the reported data (Fig. 4B).

429

430 **4. Conclusion**

431 Correlations of adsorption capacity and affinity of aromatic compounds by CNTs with the properties of
432 both organic compounds and CNTs were developed in this study. These correlations can be effectively

433 used to predict adsorption of aromatic compounds on CNTs from the commonly physiochemical
434 properties of both organic compounds (i.e., solvatochromic parameters, melting points) and CNTs (i.e.,
435 surface area and total acidic group contents). The adsorption prediction using these correlations will
436 greatly reduce the cost, time and labor that are needed to investigate the unknown adsorption behaviors
437 when it comes to new organic compounds and/or new CNTs. These correlations can also be applied to
438 guide the synthesis and surface modification of CNTs with desired physicochemical properties and the
439 applications of CNTs in water treatment and solid-phase extraction. Moreover, these correlations can
440 facilitate the assessment and prediction of the environmental and health risks of both CNTs and
441 aromatic compounds.

442

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448

449 **Appendix A. Supplementary data**

450 Supplementary data associated with this article can be found in the online version.

451

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Caption of Tables and Figures

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550 **Table 1.** Results of linear regressions between Q^0 and melting point of organic compounds

551 **Table 2.** Results of multiple linear regressions with stepwise method between E and Kamlet-Taft
552 parameters

553 **Fig. 1.** Adsorption isotherms of 22 selected organic compounds by MW15. Solid lines represent
554 isotherms fitted by the DA model.

555 **Fig. 2.** Prediction of adsorption capacity (Q^0) of aromatic compounds on CNTs. (A) Linear
556 relationship between Q^0 and melting points (MP) of 22 organic compounds on MW15 (as an example
557 of CNTs). (B) Correlation between calculated Q^* (Q^*_{cal}) by Equation 4 and regressive Q^* (Q^*_{reg}) in
558 Table 1. (C) Linear relationship between S and $Q^* \times R_{meso}$ of 10 CNTs. (D) Correlation between
559 calculated Q^0 (Q^0_{cal}) by Equation 6 and Q^0 (Q^0_{exp}) derived from DA model fitted isotherms of organic
560 compounds on CNTs. Solid lines in Figs. A and C are derived from linear regression. Solid lines in
561 Figs. B and D are the reference line, $y = x$. Dashed lines indicate the standard deviation (SD) values
562 from the reference line.

563 **Fig. 3.** Prediction of adsorption affinity (E and b) of aromatic organic compounds on CNTs. (A)
564 Correlation between calculated E (E_{cal}) using Equation 7 and its coefficients (Table 2) and E (E_{exp})
565 derived from DA model fitted isotherms of organic compounds on MW15 (as an example of CNTs).
566 (B) Relationships of π_1 and C with R_{meso} . (C) Correlation between calculated E (E_{cal}) by Equation 10
567 and E (E_{exp}) derived from DA model fitted isotherms of 22 organic compounds on 10 CNTs. (D)
568 Correlation between calculated b (b_{cal}) by Equation 12 and b (b_{exp}) derived from DA model fitted
569 isotherms of 22 organic compounds on 10 CNTs. Solid lines in Figs. A, C and D are the reference line,
570 $y = x$. Dashed lines indicate the standard deviation (SD) values from the reference line. Solid lines in
571 Fig. B are derived from linear regression.

572 **Fig. 4.** Correlations between calculated **Log q_e** (**Log q_{ecal}**) values by Equations 1,6,10, 12 and
573 experimental **Log q_e** (**Log q_{eexp}**) values for adsorption of organic compounds on CNTs in this study
574 according to Table S3 (A) and in the previous studies (Yang et al., 2006a; Lin and Xing, 2008; Yang et
575 al., 2008; Chen et al., 2009; Wang et al., 2009; Zhang et al., 2010; Wu et al., 2012) according to Table
576 S5 (B). The **q_e** is the adsorbed amount (mg/g). Solid lines are the reference line, $y = x$. Dashed lines
577 indicate the SD values from the reference lines.

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Table 1. Results of linear regressions between Q^0 and melting point of organic compounds^a

CNTs	<i>S</i>	<i>Q</i> [*]	<i>N</i>	<i>r</i> ²	<i>F</i>	<i>P</i>	<i>SD</i>
SW	-0.437(±0.189) ^b	268.9(±15.4)	22	0.211	5.4	0.031	42.1
MW8	-0.975(±0.208)	289.6(±17.0)	22	0.523	21.9	<0.001	46.5
MW15	-0.237(±0.034)	77.8(±2.8)	22	0.706	48.0	<0.001	7.6
MW30	-0.374(±0.078)	111.8(±6.4)	22	0.534	22.9	<0.001	17.5
MW50	-0.219(±0.047)	68.2(±3.9)	22	0.516	21.4	<0.001	10.6
MW100	-0.219(±0.039)	60.7(±3.2)	22	0.615	31.9	<0.001	8.6
MW15-S	-0.425(±0.074)	116.8(±6.0)	22	0.624	33.2	<0.001	16.5
MW15-G	-0.192(±0.039)	58.3(±3.2)	22	0.554	24.8	<0.001	8.6
MW15-OH	-0.152(±0.035)	54.5(±2.8)	22	0.486	18.9	<0.001	7.8
MW15-COOH	-0.123(±0.036)	47.8(±3.0)	22	0.364	11.4	0.003	8.1

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^aAll estimated parameter values and their standard deviations were obtained by a commercial software program (SPSS 20.0); ^bData in the parenthesis are standard deviations.

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Table 2. Results of multiple linear regressions with stepwise method between *E* and Kamlet-Taft parameters^a

CNTs	α_m^b	π^*b	C^c	<i>N</i>	r^2	F	P	SD	SDEV
SW	10.91 (±1.58) ^d	11.96 (±2.09)	11.25 (±2.27)	22	0.759	29.9	<0.001	2.17	8.0%
MW8	11.87 (±1.35)	10.15 (±1.79)	5.67 (±1.93)	22	0.818	42.6	<0.001	1.85	10.0%
MW15	10.61 (±1.12)	8.54 (±1.49)	5.51 (±1.62)	22	0.834	47.7	<0.001	1.55	9.9%
MW30	11.43 (±1.39)	9.74 (±1.84)	5.01 (±2.00)	22	0.796	37.0	<0.001	1.91	11.9%
MW50	11.36 (±1.36)	9.68 (±1.81)	5.13 (±1.96)	22	0.800	38.0	<0.001	1.87	11.8%
MW100	11.42 (±1.19)	8.46 (±1.57)	5.89 (±1.70)	22	0.836	48.4	<0.001	1.63	10.1%
MW15-S	10.99 (±1.32)	9.72 (±1.75)	5.02 (±1.89)	22	0.803	38.7	<0.001	1.81	11.3%
MW15-G	11.57 (±1.36)	9.62 (±1.80)	4.83 (±1.95)	22	0.806	39.4	<0.001	1.87	11.6%
MW15-OH	10.68 (±1.20)	8.28 (±1.59)	5.89 (±1.72)	22	0.816	42.1	<0.001	1.65	10.5%
MW15-COOH	10.25 (±1.10)	7.64 (±1.46)	6.58 (±1.58)	22	0.826	45.2	<0.001	1.52	9.4%

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^aAll estimated parameter values and their standard deviations were obtained by a commercial software program (SPSS 20.0); ^b α_m (hydrogen-bonding donor parameter) and π^* (polarity/polarizability parameter) are Kamlet-Taft parameters; ^c*C* is the intercept of regression equation; ^dData in the parenthesis are standard deviations.