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# The correlation between structural characteristics of activated carbons and their adsorption of organic solutes from aqueous solutions

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**Abstract** Adsorption is controlled by an array of attractive forces between adsorbent, adsorbate, and solvent molecules. Such forces work interactively, making the interpretation and prediction of sorption processes difficult. By carefully designing the experimental matrix, the effects of adsorbent surface chemistry and pore structure on the adsorption of aromatic compounds were isolated from the complicated web of interactions. Two parameters, $\gamma$ and $\delta$, were created to describe the relative adsorption affinity index of activated carbons to adsorbates and the occupancy rate of activated carbons by active sites that can lead to formation of water clusters. Taking the space availability and the relative adsorption affinity index into account, a correlation between the Freundlich adsorption affinity coefficient and the characteristics of adsorbent was established. With this correlation, if the Freundlich adsorption affinity coefficient of a compound on one carbon is known, its adsorption affinity coefficient on another carbon might be predictable if the surface chemistries and pore structures of both carbons are available.

**Keywords** Activated carbon · Adsorption affinity · Physical structure · Surface chemistry · Correlation

## 1 Introduction

Adsorbent-adsorbate interactions are controlled by an array of factors, including the nature of the adsorbent (e.g., pore and surface structures, surface functional groups, and ash content), the nature of the adsorbate (e.g., polarity, planarity, solubility, molecular size, functional groups, and acid-base dissociation ability), and the characteristics of the bulk solution (e.g., pH, ionic strength, concentration of background organic and inorganic compounds, and oxygen availability) (Belfort 1979; Weber et al. 1991; Karanfil et al. 1998; Karanfil and Kilduff 1999). All of these factors can contribute in the sorption processes, resulting in a complex web of interactions. Despite the voluminous research focused on exploring the roles of physical factors and chemical interactions involved in the sorption of organic compounds by various carbonaceous adsorbents (Radovic et al. 1997; Pelekani and Snoeyink 2000; Jonker and Smedes 2000; Haghseresht et al. 2002; Li et al. 2002; Terzyk 2003; Moreno-Castilla 2004; Cornelissen et al. 2004a, 2004b; Dastgheib et al. 2004; Carrott et al. 2005; Derylo-Marczewska et al. 2008; Erto et al. 2010), there is still limited quantitative description of the mechanisms involved in the sorption processes. The ability to quantify adsorption interactions is more important for engineering design and practical applications. The limitations in many previous studies are attributable to a combination of factors: inappropriate selection of adsorbate/adsorbent matrix leading to simultaneous occurrence of different interactions; insufficient characterization of adsorbents' physical and chemical characteristics; and insufficient understanding of the potential impact of solvent effect on adsorption.

In this study, we carefully designed an experimental matrix to quantify the role of the nature of adsorbents on the adsorption of adsorbates from aqueous solutions. Two types of

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**Table 1** Molecular parameters of AOCs and their HPLC analysis conditions

| AOC | Molecular size[a] (Å × Å × Å) | $S_W$[b] (μmol $L^{-1}$) | $V_{AOC}$ ($cm^3$ $mol^{-1}$) | $H_2O$:MeOH[c] (%:%) | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | $\lambda_{UV}$ (nm) |
|---|---|---|---|---|---|---|---|
| PN | 8.1 × 6.7 × 3.5 | 881947 | 87.87 | 60:40 | 276 | 296 | 270 |
| NB | 8.8 × 6.8 × 3.5 | 15433 | 102.34 | 50:50 | n.a. | n.a. | 267 |
| BP | 11.8 × 6.8 × 4.7 | 39.6 | 155.45 | 20:80 | 260 | 315 | 248 |
| 2PP | 11.8 × 7.8 × 5.4 | 4113 | 140.32 | 40:60 | 290 | 340 | 245 |
| 2CP | 11.7 × 7.6 × 5.7 | 28.6 | 191.73 | 35:65 | 280 | 365 | 242 |
| 2NP | 11.7 × 8.4 × 6.7 | 111.4 | 165.59 | 35:65 | n.a. | n.a. | 232 |

[a] Simulated with ChemBioOffice 2008 (CambridgeSoft Corporation) with the MM2 module

[b] Water solubility

[c] Mixture of distilled and deionized water ($H_2O$) and methanol (MeOH) employed as eluent. The concentrations of AOCs were detected at maximum fluorescence excitation wavelength ($\lambda_{ex}$), fluorescence emission wavelength ($\lambda_{em}$) and UV wavelength ($\lambda_{UV}$) with both fluorescence and UV detectors

activated carbons (ACs), granular activated carbons (GACs) and activated carbon fibers (ACFs), were selected as the adsorbents. Six aromatic compounds (AOCs) with different properties were used as probe molecules. The relations between the structural characteristics of adsorbents and their adsorption affinities to AOCs were investigated by correlating the adsorption affinity coefficient with the physical structure and surface chemistry of adsorbents.

## 2 Materials and methods

### 2.1 Materials

A coconut shell-based GAC, OLC (Calgon Carbon Co.), and a phenol formaldehyde-based ACF, ACF10 (American Kynol Co.), were pretreated with two methods prior to use: (i) heat treatment at 1173 K for 2 h under hydrogen flow to remove surface functional groups and, (ii) oxidation of the carbons in 4 M nitric acid at 90 °C for 1 h to add surface functional groups. The heat-treated ($H_2$) and oxidized (NO) ACF10 and OLC were labeled as ACF10_$H_2$, ACF10_NO, OLC_$H_2$, and OLC_NO, respectively. Prior to adsorption, the OLC was ground to particles in the size range of 150–180 μm. ACF10 was used directly in strands of fiber.

Phenol (PN, 99.5+ %), nitrobenzene (NB, 99.0+ %), biphenyl (BP, 99.5+ %), 2-phenylphenol (2PP, 99+ %), 2-nitrobiphenyl (2NP, 97+ %), were purchased from Sigma-Aldrich Chemical Co. Analytical standard grade 2-chlorobiphenyl (2CP) was purchased from Fluka Chemical Co. The molecular sizes of the AOCs were simulated with ACD-LABS 11.0 (Advanced Chemistry development Inc.). The molecular sizes and some key properties of the AOCs are summarized in Table 1.

### 2.2 Characterization of ACs

Nitrogen adsorption at 77 K, water vapor and benzene adsorption at 273 K were performed with a physisorption analyzer (Micromeritics ASAP 2010) to characterize the physical structure, surface polarity, and adsorption energy of the ACs. Prior to measurement, the samples were degassed under vacuum for 24 h at 523 K. The Brunauer-Emmett-Teller (BET) equation, *t*-plot method, Dubinin-Astakhov (DA) model, and the Frenkel-Halsey-Hill (FHH) equation were used to calculate surface area, pore volume, pore size, and surface fractal dimension from nitrogen adsorption isotherm.

Elemental analysis was performed with an EA1112 elemental analyzer (Thermo Electron Co.). Certain amounts of ACs were calcined in a furnace at 650 °C for 3 h to calculate the ash content. Batch equilibrium experiments were employed to determine the pH of the point of zero charge ($pH_{PZC}$) of the ACs. Boehm titration and acid/base uptake were used to determine the surface functional groups of the ACs. Each acid/base solution (20 ml) was mixed with 0.1 g AC, and shaken for three days in an anaerobic chamber to reach equilibrium. A portion of 10 mL of supernatant was titrated with 0.05 M NaOH/HCl solution by using an autotitrator (Titrino 721 from Metrohm Inc.).

### 2.3 Liquid phase adsorption experiments

Constant carbon dose isotherm experiments were performed in 255 mL glass bottles with Teflon-lined screw caps. The bottles containing about 1 mg of ACs were first filled with distilled and deionized water to nearly full, and then spiked with predetermined volumes of stock AOC solution while keeping the volume percentage of the methanol stock solution below 0.1 % (v/v) to minimize any co-solvent effect. The bottles free of headspace were then placed into a tumbler for 7 d. The supernatants in bottles were analyzed using

**Table 2** Structural characteristics of the ACs

| AC | Elemental composition (%) | | | | | $pH_{pzc}$ (–) | meq[a] (mmol/g) | | $\delta$ (%) | SA[b] ($m^2\,g^{-1}$) | | PV[c] ($cm^3\,g^{-1}$) | | $F$[d] (–) | PW[e] (mm) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N | C | H | O | Ash | | NaOH | HCl | | $S_{BET}$ | $S_{mic}$ | $V_{total}$ | $V_{mic}$ | | $D_{BJH}$ | $D_{DA}$ |
| ACF10_H$_2$ | 0.000 | 95.459 | 0.868 | 0.148 | 0.062 | 9.94 | 0.077 | 0.446 | 2.31 | 1066 | 971 | 0.445 | 0.381 | 2.98 | 2.79 | 1.31 |
| ACF10_NO | 0.678 | 75.789 | 1.786 | 16.62 | 0.080 | 3.15 | 2.226 | 0.000 | 9.73 | 1058 | 946 | 0.437 | 0.372 | 2.97 | 2.82 | 1.32 |
| OLC_H$_2$ | 0.262 | 96.097 | 0.616 | 0.084 | 0.245 | 10.26 | 0.064 | 0.460 | 2.47 | 1080 | 883 | 0.484 | 0.353 | 2.96 | 3.21 | 1.37 |
| OLC_NO | 0.529 | 87.057 | 0.804 | 7.362 | 0.206 | 3.52 | 1.525 | 0.039 | 7.17 | 1030 | 838 | 0.453 | 0.336 | 2.96 | 3.20 | 1.37 |

[a] Acid/base uptake

[b] SA: surface area, $S_{BET}$ and $S_{mic}$ are the BET specific surface area and micropore surface area. The $S_{BET}$ was calculated with the BET model by plotting $1/(V[(P_0/P)-1])$ versus $P/P_0$ ($V$ is adsorbed amount, $P/P_0$ represents relative pressure.). The $S_{mic}$ was obtained from the $t$-plot with the Harkins and Jura equation

[c] PV: pore volume, $V_{total}$ and $V_{mic}$ are the total and micropore volumes obtained from the $t$-plot method

[d] The fractal dimensional obtained from the FHH model

[e] PW: pore width, $D_{BJH}$ and $D_{DA}$ are the BJH desorption average pore width and DA median pore width

a high performance liquid chromatograph (HPLC) analyzer. Detailed HPLC analysis conditions are provided in Table 1. The bottles without any adsorbent were served as blanks to monitor the loss of adsorbates during the experiment, which was found to be negligible. All experiments were performed at room temperature and the solution pH was around 6.7 without any adjustment.

### 2.4 Data modeling

The empirical Freundlich model was employed in this work to simulate the adsorption isotherms of AOCs on the four carbons.

$$q_e = K_F \cdot C_e^n \tag{1}$$

where $q_e$ (mmol $g^{-1}$) is the equilibrium concentration of the adsorbate in the adsorbent, $C_e$ ($\mu mol\,L^{-1}$) is the equilibrium concentration of the adsorbate in solution, $K_F$ ($mmol\,g^{-1}\,\mu mol^{-n}\,L^n$) is a unit-capacity parameter, and $n$ is a constant known as the heterogeneity factor that is related to the surface heterogeneity.

The modeling was performed with Origin 8 Software (OriginLab Corporation). Reduced chi-square ($\chi^2$) and coefficient of determination ($R^2$) were used to evaluate the goodness of fit.

$$\chi^2 = \sum_{i=1}^{N} \frac{(q_{e,exp} - q_{e,fit})^2}{q_{e,fit}} \tag{2}$$

where $q_{e,exp}$ and $q_{e,fit}$ are experimental and model fitted equilibrium concentration of the adsorbate in the adsorbent.

## 3 Results and discussion

### 3.1 Characteristics of ACs

The chemical characterization results of the ACs are summarized in Table 2. As compared to the heat-treated ACs, the oxidized ACs had lower $pH_{pzc}$ values, higher oxygen contents, and higher oxygen-containing surface functional groups. The sum of the oxygen and nitrogen contents has been used to express the polarity of adsorbents because both oxygen- and nitrogen-containing surface functional groups can serve as hydrogen-bond donor and/or acceptor sites that facilitate water adsorption (Karanfil and Kilduff 1999; Li et al. 2002). The hydrophobic adsorbents, e.g., ACs with a low oxygen- and nitrogen-containing functional group content (<2–3 $mmol\,g^{-1}$), were more effective for the removal of both hydrophilic and hydrophobic adsorbates from aqueous solutions. Ash constituents also can serve as hydrophilic sites (Arafat et al. 1999). However, the quantitative relation between the elemental composition and the hydrophilic sites is not clear. Acid and base uptakes directly correspond to the amount of active sites where hydrogen proton can be removed from or added to the surface functional groups of the carbon. Therefore, the acid and base uptakes were employed in this study to calculate the number of sites where water clusters can form. Here, every active site was assumed to combine with one water molecule with a diameter of 0.276 nm (Zhang and Xu 1995). Consequently, the occupancy rate of surface or pore volume of AC by the active sites that can form water clusters can be calculated with the following equation:

$$\delta = \frac{[O+N] \times 10^{-3} \cdot A \cdot M_m}{\mu} \times 100\,\% \tag{3}$$

where $\delta$ is the surface coverage or pore volume occupancy of the active sites on the adsorbent by combining one water molecule; $[O + N]$ (mmol $g^{-1}$) is the sum of acid and base uptakes which mainly come from oxygen- and nitrogen-containing functional groups on the adsorbent; $A$ is the Avogadro's number; $M_m$ is the molecular parameter of water, which can be expressed either by molecular area, $S_m$ ($m^2$), or molecular volume, $V_m$ ($cm^3$); $\mu$ is the space availability parameter of the adsorbent, which can be expressed either by specific surface area, $S_C$ ($m^2\,g^{-1}$), or pore volume, $V_C$ ($cm^3\,g^{-1}$).

A typical configuration for the water molecules bonded on one surface site of the AC was proposed by McCallum and coworkers in their molecular model for adsorption of water on AC (1999). In this configuration, the O atom in the water molecule attached to the well bonding site on the carbon surface was surrounded with four small spheres arranged tetrahedrally. The four spheres represent the two H atoms and the two lone-pair electrons. Therefore, each water molecule can be H-bonded with up to four other water molecules (two through its two lone pairs, and two through its two hydrogen atoms). In such a way, large water clusters could be formed. According to the acid/base uptake listed in Table 2, there was about 0.3–1.2 active sites/$nm^2$ on the surface of ACs. The adsorption capacities of AOCs on ACs under the given experimental conditions were up to 3.0 mmol $g^{-1}$, indicating that there might be 1.8 AOC molecules on per $nm^2$ AC surface. The density of AOCs and oxygenated sites on the surface of ACs implied that most of water molecules were repelled by AOCs during the adsorption process. This is reasonable, because there was strong hydrophobic effect in the AOC-water-AC system. Therefore, we assume that each active site was occupied by a water cluster with five water molecules. As a result, the space availability of the adsorbent consequently turns to be $\mu(1 - 5\delta)$.

Nitrogen adsorption analysis was performed to obtain the accessibility parameters of adsorbents. As illustrated in Fig. 1, the four ACs possess similar adsorption behaviors to nitrogen. The surface area, pore volume, and pore size information of the ACs obtained from the nitrogen adsorption isotherms are summarized in Table 2. As shown by these parameters, the four ACs were highly microporous with similar physical structures. Fractal dimension ($F$) is an index of self-similarity in structure. The $F$ values of the four ACs were close to 3, indicating a highly uniform porous structure.

The similarity in nitrogen adsorption demonstrated that the heat-treatment and nitric acid oxidation of the ACs did not cause significant effect on their pore structures. However, the effects on their surface chemistry were well documented: heat-treatment under $H_2$ flow removed surface functional groups from the carbon surface while nitric acid oxidation generated a large amount of oxygen-containing functional groups on the carbons (Dastgheib and Karanfil 2005). This was already proved by the chemical analyses as summarized in Table 2. In terms of adsorption, the change in surface chemistry (surface polarity) was well reflected by the water vapor adsorption isotherms (Fig. 2). For the two heat-treated ACs, there was almost no adsorption at low-to-moderate relative pressures, but there was a sharp increase of adsorption at relative pressures between 0.5–0.7. Such adsorption isotherms are of type V in the IUPAC classification (Sing et al. 1985). For the two surface-oxidized ACs, adsorption started at low relative pressures and the isotherm can be decomposed into type I and type V contributions (Carrasco-Marin et al. 1997). The difference in adsorption behaviors of water vapor could be explained by the water-surface site interaction and the H-bonding between water and pre-adsorbed water (McCallum et al. 1999). At low pressures single water molecules adsorbed on individual surface sites. The presence of oxygen-containing functional groups facilitated such interaction. With increased pressure, water molecules attached to ACs by forming H-bonds to pre-adsorbed water molecules. The simultaneous bonding of water molecules to a surface site and a pre-adsorbed water molecule led to the sharp increase in the adsorption isotherm. As a result, water clusters formed. As the pressure further increased, the pores were filled with water. Though different at low pressures, the isotherms of the same type of ACs (ACF10_$H_2$ vs ACF_10NO, OLC_$H_2$ vs OLC_NO) showed some similarity at the water cluster formation and pore filling stages. In other words, the adsorption of water vapor at low pressures was largely controlled by surface chemistry while the formation of water clusters and the pore-filling are mainly controlled by the pore structure. Stoeckli and coworkers reported that water vapor adsorption isotherms of both types I and V can be described within the framework of Dubinin's theory (Stoeckli et al. 1994).

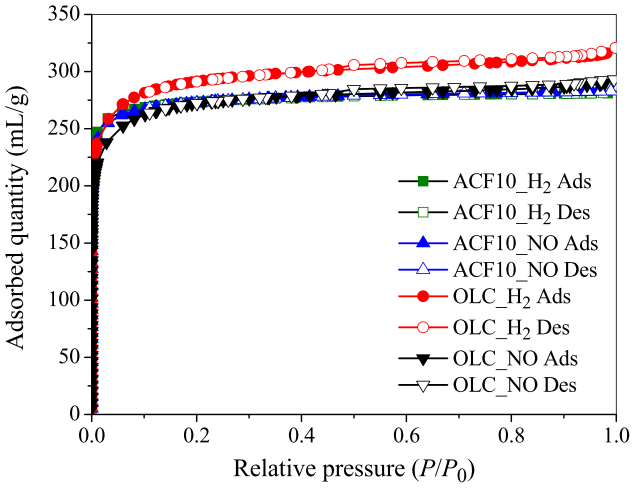

**Fig. 1** Nitrogen adsorption isotherms of the ACs at 77 K

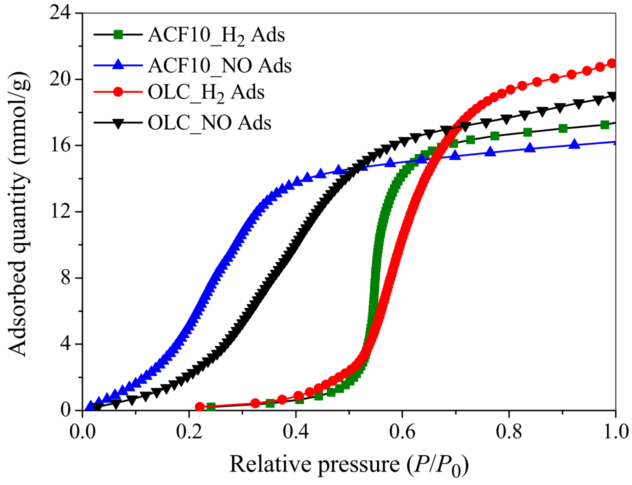

**Fig. 2** Water vapor adsorption isotherms of the ACs at 273 K

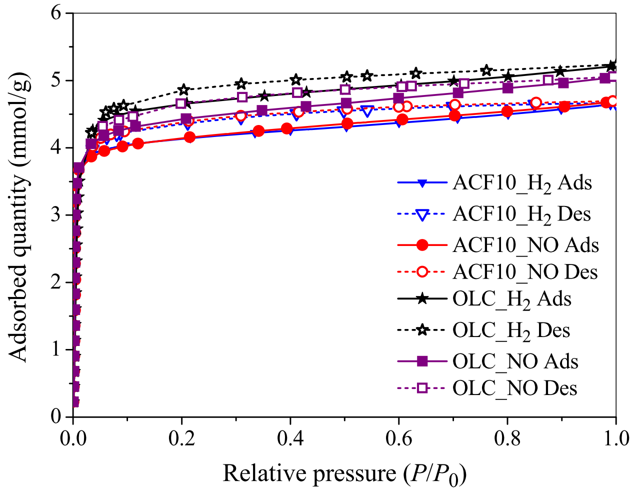

**Fig. 3** Benzene adsorption isotherms of the ACs at 273 K

According to the potential theory of adsorption, the adsorbed amount of a given adsorbate on an adsorbent under equilibrium conditions is a function of the adsorption potential ($\varepsilon = RT \ln(P_0/P)$). By combining the theory of micropore filling of Dubinin into the adsorption potential theory, the following DA model was established:

$$W = W_0 \exp\left[-\left(\frac{RT \ln(P_0/P)}{E}\right)^B\right] \tag{4}$$

where $W$ is the adsorbed gas volume at a relative pressure of $P/P_0$; $W_0$ is the maximum volume of adsorbed gas in micropores; $R$ is the universal gas constant (0.008314 $\text{kJ mol}^{-1}\,\text{K}^{-1}$); $T$ is the analysis temperature (K); $E$ is the adsorption energy ($\text{kJ mol}^{-1}$), usually expressed as $\beta E_0$; $\beta$ is known as similarity or affinity coefficient, which is dependent on the adsorptive; $E_0$ is the characteristic adsorption energy; and $B$ is an exponent usually varying from 1 to 3. Values of $B$ equal or above 3 represent molecular sieve carbons with narrow pores, whereas values less than 2 belong to less microporous carbons with wider pore size distributions.

The adsorption system in the present study was composed of activated carbon-water-aromatics. The water vapor adsorption at 273 K could partially reflect the interactions between water molecules and ACs. Benzene is the parent structure of the studied AOCs. The benzene adsorption isotherms should be useful for the prediction of the AC-AOC interactions. As illustrated in Fig. 3, no significant differences were observed among the benzene adsorption isotherms of the heat-treated and surface-oxidized ACs, suggesting that the benzene adsorption was not sensitive to the surface chemistry of ACs.

By fitting the nitrogen, benzene, and water vapor adsorption isotherm data to the DA equation, parameters of the DA equation for the given combination of adsorbate-adsorbent were obtained. As usually performed, benzene was taken as the reference compound with $\beta_{\mathrm{BZ}} = 1.00$. The $\beta$ values of nitrogen and water were obtained as ratios of $E_{\mathrm{W}}$ (water) and $E_{\mathrm{N}}$ (nitrogen) to $E_{\mathrm{BZ}}$ (benzene). It should be noted that the selection of isotherm range should be performed with care in order to obtain a meaningful micropore volume. The values of $B$ and $E$ were sensitive to the selected range. As shown in Table 3, the average $\beta$ values of water and nitrogen on the four carbons were 0.11 and 0.30, respectively, which are consistent with values previously reported in the literature (Dastgheib and Karanfil 2005).

It is pointed by Stoeckli and coworkers that for water isotherms of type V, $\beta$ loses its meaning and consequently only $E$ is used. To take into account of the effects caused by both pore structure and surface chemistry, an affinity index ($\alpha$) with the following form was extracted from the DA model to serve as a functional parameter for the adsorbate-adsorbent interaction:

$$\alpha = \exp\left[-(1/E)^B\right] \tag{5}$$

As listed in Table 3, the $\alpha$ values of benzene and nitrogen on the four carbons were close to unity, whereas there were significant differences among the $\alpha$ parameters of water. The adsorption isotherms in Figs. 1, 2, and 3 have already demonstrated that the adsorption of benzene and nitrogen was mainly controlled by pore structure while the adsorption of water depended on both surface chemistry and pore structure. Since the four studied ACs had similar pore structure but different surface polarity, their $\alpha$ parameters for benzene and nitrogen were close to 1 while the parameters for water deviated from 1 to various extents depending on the surface functional group contents. Therefore, we can say that the $\alpha$ parameter is a valid index for the interaction strength between adsorbate and adsorbent. In essence, adsorption is a competitive process between the adsorbent and the solvent for the adsorbate. Since the studied adsorbates in this work are all aromatics and the adsorption was performed in aqueous solutions, the ratio of $\alpha$ parameters for

**Table 3** DA parameters of gas phase adsorption isotherms of the ACs

| AC | Benzene ($_{BZ}$) | | | | Water ($_W$) | | | | Nitrogen ($_N$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E$ | $B$ | $\beta$ | $\alpha$ | $E$ | $B$ | $\beta$ | $\alpha$ | $E$ | $B$ | $\beta$ | $\alpha$ |
| ACF10_H$_2$ | 32.97 | 1.74 | 1.00 | 0.998 | 2.72 | 2.28 | 0.07 | 0.903 | 8.73 | 2.11 | 0.26 | 0.990 |
| ACF10_NO | 26.48 | 2.01 | 1.00 | 0.999 | 6.68 | 1.73 | 0.16 | 0.963 | 8.38 | 1.96 | 0.32 | 0.985 |
| OLC_H$_2$ | 28.22 | 1.55 | 1.00 | 0.994 | 1.94 | 2.03 | 0.06 | 0.770 | 7.38 | 1.73 | 0.26 | 0.969 |
| OLC_NO | 21.20 | 1.93 | 1.00 | 0.997 | 3.68 | 1.85 | 0.13 | 0.914 | 7.70 | 1.71 | 0.36 | 0.970 |

benzene and water on one adsorbent can serve as a relative adsorption affinity index ($\gamma$) between the adsorbent and the adsorbate in aqueous solutions.

$$\gamma = \alpha_{BZ}/\alpha_W \tag{6}$$

## 3.2 Adsorption isotherm modeling

The liquid phase adsorption isotherms of AOCs on the four adsorbents are illustrated in Fig. 4. The Freundlich model was employed to simulate these isotherms.

The low $\chi^2$ and high $R^2$ of the Freundlich fits (Table 4) suggest that the modeling results were reasonable. The $K_F$ can be used as a measure of relative interaction strengths between the adsorbent and the adsorbate.

The four ACs employed in the present work are very close in surface area, pore volume and pore size, but are significantly different in surface chemistry (Table 2 and Fig. 2). For this set of adsorbents, it is clear that surface chemistry effects will dominate over pore structure effects. For a given adsorbate, it is the surface and pore structural characteristics of the adsorbent that determine the space availability and relative adsorption affinity to the adsorbate. Taking the space availability and relative adsorption affinity index into account, an equation between the $K_F$ and the characteristics of adsorbents was established as:

$$K_F = K \cdot \mu \cdot (1 - 5\delta) \cdot \gamma \tag{7}$$

where $K_F$ is the Freundlich adsorption affinity coefficient; $\mu$ (space availability parameter of the adsorbent) is the same as that in (3); $\delta$ and $\gamma$ are the two affinity index parameters with definitions in (5) and (6); $K$ is a primitive adsorption coefficient reflecting the adsorption affinity of one basal adsorption site to the adsorbate, which is independent of the pore structure and surface chemistry of the adsorbent, and therefore is assumed to be the same for all ACs. The $K$ term is currently only theoretically valid. It is impossible for us to obtain an ideal adsorbent with all sites homogeneous to the adsorbates. As an alternative, the $K$ term might be obtained statistically from a data set with a large amount of adsorbents with well described characteristics, such as the precise knowledge of pore structure, species and location of the surface functional groups.

The term $\mu$ represents the total number of adsorption sites. Whether surface area or pore volume should be chosen depends on which mechanism predominates in the adsorption, surface coverage or pore filling. For adsorbents with quite different pore size distributions, this term will be much more complicated than those expressed here merely by specific surface area or total pore volume. Further efforts are warranted on the elucidation of pore structure effects in our future work. The four ACs employed in the present study were deliberately selected with similar pore structures. Even though, the system is so complex that some simplifications in the model are essential at this stage. It is assumed that the adsorbent surface area (or pore volume), not occupied by water clusters, is accessible to adsorbates. The effect caused by water cluster formation was adjusted by the $\delta$ term.

As aforementioned, the $K$ term is unavailable with the limited sample size in the present work. To check whether the correlation expressed in (6) is valid or not, we normalized the Freundlich adsorption affinity parameter, $K_F$, with the other three terms in (6). If the correlation is valid, we can expect such an equation:

$$\frac{K_{Fi}}{K_{Fj}} \cdot \frac{\mu_j}{\mu_i} \cdot \frac{(1 - 5\delta_j)}{(1 - 5\delta_i)} \cdot \frac{\gamma_j}{\gamma_i} = 1 \tag{8}$$

where $i$ and $j$ are labels of ACs. The $K_{Fi}/K_{Fj}$ term is the Freundlich adsorption affinity ratio of AC $i$ to AC $j$, whereas the whole part in the left hand side of (8) is the normalized ratio with terms $\mu$, $\delta$, $\gamma$ to adjust the difference caused by the difference in pore structure and surface chemistry of the two ACs.

As illustrated in Fig. 5, the original $K_F$ ratios of the AC pairs (a: ACF10_H$_2$ vs. OLC_H$_2$, b: ACF10_NO *vs* OLC_NO, c: ACF10_H$_2$ vs. ACF10_NO, and d: OLC_H$_2$ vs. OLC_NO) had a wide range while their normalized counterparts (a′, b′, c′, d′) leveled to 1, suggesting that the correlation expressed in (7) was valid. It is worth noting that ratios of the AC pairs with similar surface chemistry were more close to 1 than those of the pairs with the same precursor but different surface chemistry. This is consistent with our expectation in the experimental design: surface chemistry effects determine the adsorption difference among the

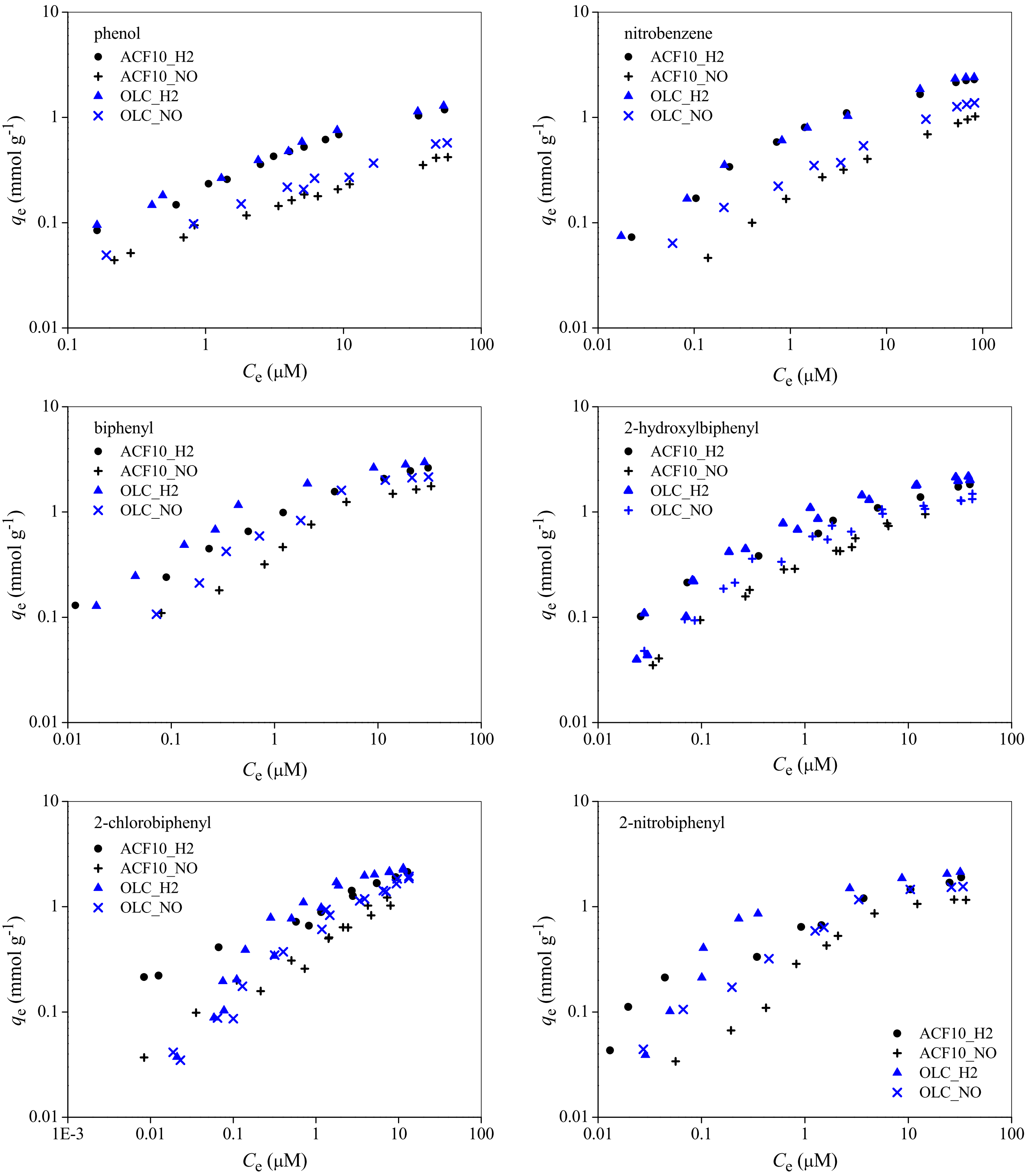

**Fig. 4** Adsorption isotherms of AOCs on the four ACs from aqueous solutions. The AC dosage was about 1 mg in 255 mL of AOC solutions with initial concentrations ranging from 1.6E–4 to 0.12 mmol L$^{-1}$

given sorbent-sorbate combinations. It should be noted that the correlation in (7) was developed from the aspect of adsorbents. In terms of adsorbates, their molecular configurations and sizes determine their accessibility to the sorption sites while their functional groups may affect their specific interactions with adsorbents. The linear solvation energy relationship will be employed to address this issue in our future work.

**Table 4** Freundlich modeling parameters of AOC adsorption on the ACs

| | | $K_F$ | $n$ | $\chi^2$ | $R^2$ | $N$[a] |
|---|---|---|---|---|---|---|
| PN | ACF10_H$_2$ | 0.263 ± 0.014 | 0.385 ± 0.017 | 0.002 | 0.982 | 12 |
| | ACF10_NO | 0.091 ± 0.003 | 0.381 ± 0.009 | 0.000 | 0.995 | 14 |
| | OLC_H$_2$ | 0.282 ± 0.019 | 0.391 ± 0.020 | 0.003 | 0.984 | 10 |
| | OLC_NO | 0.115 ± 0.007 | 0.405 ± 0.018 | 0.000 | 0.988 | 10 |
| NB | ACF10_H$_2$ | 0.645 ± 0.046 | 0.297 ± 0.018 | 0.011 | 0.986 | 10 |
| | ACF10_NO | 0.190 ± 0.009 | 0.383 ± 0.012 | 0.001 | 0.996 | 10 |
| | OLC_H$_2$ | 0.658 ± 0.047 | 0.309 ± 0.018 | 0.011 | 0.987 | 10 |
| | OLC_NO | 0.268 ± 0.015 | 0.380 ± 0.014 | 0.001 | 0.995 | 10 |
| BP | ACF10_H$_2$ | 0.878 ± 0.055 | 0.336 ± 0.022 | 0.015 | 0.984 | 9 |
| | ACF10_NO | 0.517 ± 0.071 | 0.372 ± 0.047 | 0.027 | 0.936 | 9 |
| | OLC_H$_2$ | 1.229 ± 0.120 | 0.289 ± 0.035 | 0.075 | 0.943 | 9 |
| | OLC_NO | 0.742 ± 0.102 | 0.344 ± 0.048 | 0.055 | 0.925 | 9 |
| 2PP | ACF10_H$_2$ | 0.608 ± 0.034 | 0.308 ± 0.018 | 0.006 | 0.986 | 9 |
| | ACF10_NO | 0.319 ± 0.013 | 0.331 ± 0.022 | 0.002 | 0.982 | 14 |
| | OLC_H$_2$ | 0.776 ± 0.055 | 0.292 ± 0.023 | 0.036 | 0.942 | 20 |
| | OLC_NO | 0.492 ± 0.035 | 0.291 ± 0.023 | 0.014 | 0.942 | 18 |
| 2CP | ACF10_H$_2$ | 0.895 ± 0.028 | 0.345 ± 0.015 | 0.006 | 0.987 | 15 |
| | ACF10_NO | 0.422 ± 0.030 | 0.491 ± 0.044 | 0.007 | 0.953 | 14 |
| | OLC_H$_2$ | 1.011 ± 0.072 | 0.374 ± 0.036 | 0.058 | 0.921 | 19 |
| | OLC_NO | 0.624 ± 0.034 | 0.443 ± 0.026 | 0.010 | 0.979 | 18 |
| 2NP | ACF10_H$_2$ | 0.639 ± 0.051 | 0.319 ± 0.027 | 0.014 | 0.970 | 10 |
| | ACF10_NO | 0.369 ± 0.057 | 0.352 ± 0.052 | 0.020 | 0.903 | 10 |
| | OLC_H$_2$ | 0.899 ± 0.103 | 0.274 ± 0.039 | 0.064 | 0.906 | 10 |
| | OLC_NO | 0.570 ± 0.079 | 0.315 ± 0.048 | 0.038 | 0.900 | 10 |

[a] Sample size

Since $K_F$ is a unit-capacity parameter, its value depends on the concentration units of $C_e$ and is related to the $n$ value. One may quest what it would be if $C_e$ was not expressed in the units of $\mu\text{mol}\,\text{L}^{-1}$. To check the validity of the three adjustment factors in a wide concentration range, another two parameters, distribution coefficient ($K_d$) and solubility-normalized $K_F$ ($K_{FS}$), were employed in (8) to substitute the $K_F$. $K_d$ is one of the simplest and most commonly used parameter for estimating the migration potential of adsorbates from solution to adsorbents. For adsorption not obeying to Henry's law, its value depends on $C_e$. Since $K_F$ and $K_{FS}$ correspond to the adsorption capacities at $C_e$ of 1 $\mu\text{mol}\,\text{L}^{-1}$ and the saturated concentrations of AOCs, we selected a middle point, $C_e$ of 10 $\mu\text{mol}\,\text{L}^{-1}$, from the adsorption isotherms of AOCs on ACs to check the model validity for $K_d$ values.

$$K_d = q_e/C_e = K_F \cdot C_e^{n-1} \tag{9}$$

$$K_{FS} = K_F \cdot S_w^n \tag{10}$$

From the above equations, we can see that $K_d$ and $K_{FS}$ values equal to $K_F$ at the specific concentration levels of adsorbate: $C_e = 1$ and $C_e = S_w$, respectively. Similar to the ratios of $K_F$, the ratios of $K_d$ and $K_{FS}$ between the AC pairs were leveled to 1 after normalized with the three adjustment factors in (8), demonstrating that the empirical equation is valid in a wide concentration range: from 1 $\mu\text{mol}\,\text{L}^{-1}$ to the saturated concentration of the adsorbate. Such a range covers the concentrations usually met in adsorption systems.

## 4 Conclusions

Quantitative structure-activity relationships that are able to predict specific properties of chemicals with representative descriptors of molecular structure and/or properties are a useful tool in many applicability domains. However, due to the complexity of the liquid phase adsorption system, quantitative description of adsorption processes based on the structure of adsorbents is still very limited. As a preliminary attempt, an empirical equation was developed in this work to relate the structural characteristics of an adsorbent with its adsorption affinity to aromatic compounds. For this purpose, some simplifications were employed in

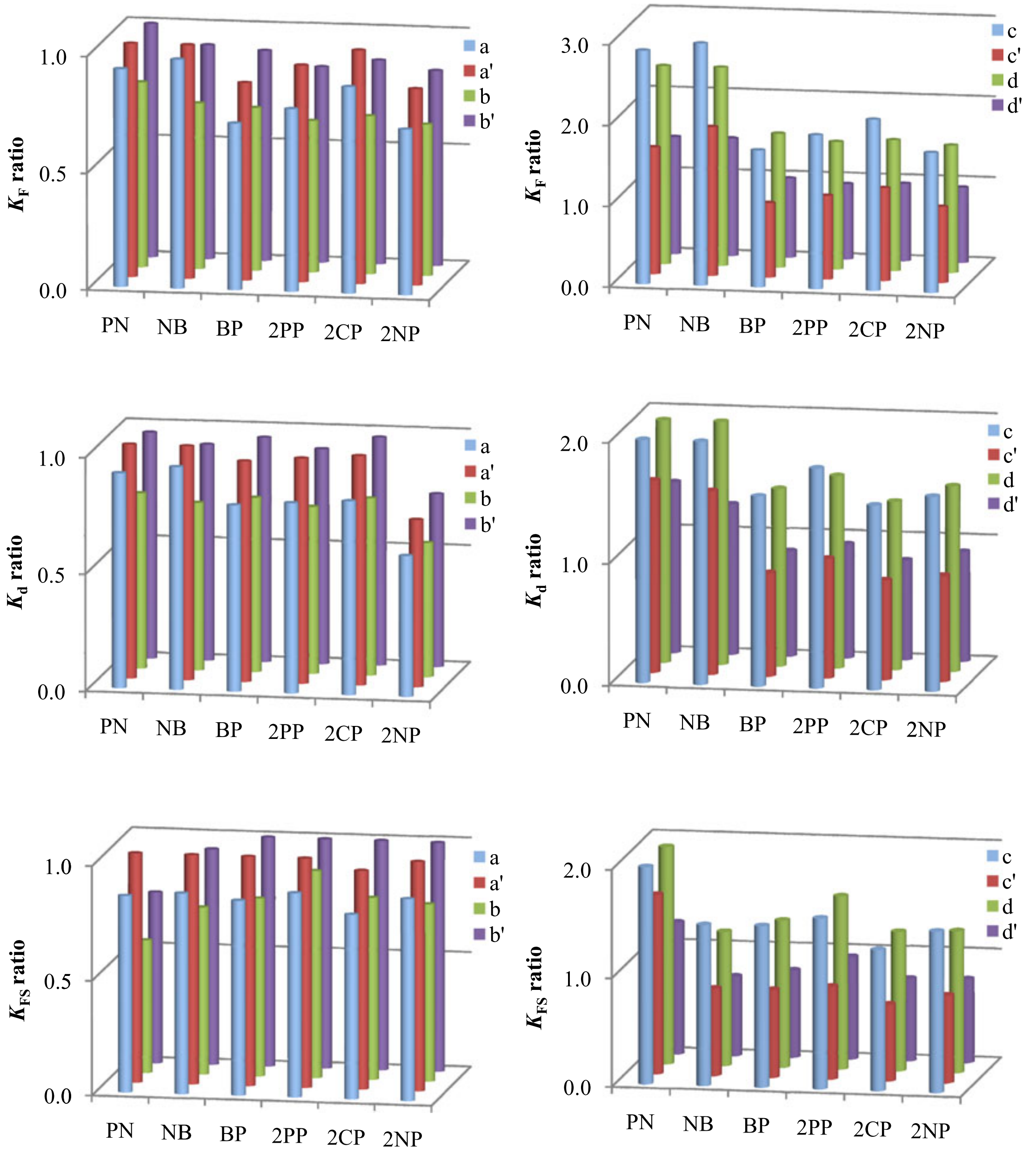

**Fig. 5** The original and normalized adsorption coefficient ratios. $a$, $b$, $c$, $d$ represent the ratios of AC pairs: ACF10_H$_2$ vs. OLC_H$_2$, ACF10_NO vs. OLC_NO, ACF10_H$_2$ vs. ACF10_NO, and OLC_H$_2$ vs. OLC_NO, respectively. $a'$, $b'$, $c'$, d′ are the normalized counterparts of $a$, $b$, $c$, $d$. $S_{\mathrm{BET}}$ values were used as $\mu$ in the normalization

the modeling: (1) The adsorbent surface area (or pore volume), not occupied by water clusters, is accessible to adsorbates; (2) The effect caused by water cluster formation could be adjusted by the $\delta$ term; (3) The $\gamma$ parameters derived from benzene and water vapor adsorption on one adsorbent can serve as a relative adsorption affinity index between the adsorbent and the adsorbate in aqueous solutions. With the developed terms, if the adsorption affinity coefficient of a compound on one carbon is known, its adsorption affinity coefficient on another carbon can be deduced from their surface chemistries and pore structures. The empirical equations established in this work provide us the possibility to predict the adsorption affinities of carbons whose physical structures and surface chemistry were well characterized. This equation could be further improved by incorporating the detailed pore structure effects in the model.

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