

AN EMPIRICAL EQUATION TO RELATE THE ADSORPTION AFFINITY AND STRUCTURAL CHARACTERISTICS OF CARBONACEOUS ADSORBENTS

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Introduction

Adsorbent-adsorbate interaction is well known to be controlled by an array of factors [1], including the nature of the adsorbent (pore and surface structures, surface functional groups, ash content, etc.), the nature of the adsorbing species (polarity, planarity, solubility, molecular size, functional groups, acid-base dissociation ability, etc), and the property of the bulk solution (pH, ionic strength, concentration of compounds, oxygen availability, etc). All of these factors take part 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 aromatic compounds by various carbonaceous adsorbent, there is still a lack of a comprehensive understanding of the mechanisms involved in the sorption processes. In the present work, an experimental matrix was carefully designed to quantify the role of the nature of adsorbents on the adsorption of AOCs from aqueous solutions. A granular activated carbon (GAC) and an activated carbon fiber (ACF) were selected as the adsorbents. Six aromatic chemicals (AOCs) with quite different properties were selected as the adsorbing probes. An empirical equation was developed to predict the adsorption affinities of adsorbents based on their structural characteristics.

Experimental

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. One method was to heat treat the carbons at 1173 K for 2 h under hydrogen flow to remove surface functional groups. Another one was to oxidize the carbons in 4 M nitric acid at 90oC for 1 h to add surface functional groups. The heat-treated and oxidized ACF10 and OLC were labeled as ACF10_H₂, ACF10_NO, OLC_H₂, and OLC_NO, respectively. Prior to adsorption, the OLC was ground to particles with size in the range of 150-180 μm. ACF10 was used directly in strands of fiber.

The structural characteristics of the carbons were characterized with nitrogen gas adsorption at 77 K and are summarized in Table 1. The elemental composition of carbons was determined by an elemental analyzer and the surface functional groups were quantified with NaOH and HCl titration with results shown in Table 2. Benzene and water vapor adsorption experiments were performed at 273 K to determine the surface polarity of carbons. The Dubinin-

Astakhov (DA) model was used to analyze the benzene and water adsorption isotherms.

$$W = W_0 \exp \left[- \left(\frac{RT \ln(P_0 / P)}{E} \right)^B \right] \quad (1)$$

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 ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is the analysis temperature (K); E is the adsorption energy (kJ mol^{-1}), usually expressed as βE_0 ; β is known as similarity or affinity coefficient; E_0 is the characteristic adsorption energy; and B is an exponent usually varying from 1 to 3.

An affinity index (α) with the following form is expected to be a reliable functional parameter for the adsorbate-adsorbent interaction:

$$\alpha = \exp \left[- (1/E)^B \right] \quad (2)$$

Table 1. Physical structural parameters of adsorbents.

Carbon	Surface Area ^a					Pore Volume ^b	
	S_{BET}	S_{mic}	S_{DFT}	$S_{<1}$	$S_{>3}$	V_{total}	V_{mic}
ACF10_H ₂	1066	971	883	789	0	0.445	0.381
ACF10_NO	1058	946	879	757	1	0.437	0.372
OLC_H ₂	1080	883	879	680	5	0.484	0.353
OLC_NO	1030	838	770	613	5	0.453	0.336

^a Total, microporous, DFT surface area and surface area fraction in pore size range (< 1 nm and > 3 nm), unit: m²/g.

^b Total and microporous volume in unit of mL/g.

Table 2. Chemical structural parameters of adsorbents.

Carbon	elemental %			pH _{pzc}	uptake (mmol/g)	
	N	O	Ash		NaOH	HCl
ACF10_H ₂	0.00	0.15	0.06	9.94	0.08	0.45
ACF10_NO	0.68	16.62	0.08	3.15	2.23	0.00
OLC_H ₂	0.26	0.08	0.24	10.26	0.06	0.46
OLC_NO	0.53	7.36	0.21	3.52	1.52	0.04

Table 3. Molecular properties and HPLC determination conditions for adsorbates.

AOC	S_w (μM)	V_{AOC} (mL/mol)	H ₂ O:MeOH (%:%)	λ_{ex}	λ_{em}	λ_{UV}
				(nm)		
PN	881947	87.87	60:40	276	296	270
NB	15433	102.34	50:50	n.a.	n.a.	267
BP	39.6	155.45	20:80	260	315	248
2PP	4113	140.32	40:60	290	340	245
2CP	28.6	191.73	35:65	280	365	242
2NP	111.4	165.59	35:65	n.a.	n.a.	232

Phenol (PN), nitrobenzene (NB), biphenyl (BP), 2-phenylphenol (2PP), 2-nitrobiphenyl (2NP), were purchased from Sigma-Aldrich Chemical Co. The 2-chlorobiphenyl (2CP) was purchased from Fluka Chemical Co. The molecular properties together with HPLC determination conditions for the AOCs are summarized in Table 3.

Constant carbon dose aqueous phase isotherm experiments were conducted using 255 mL glass bottles with Teflon-lined screw caps. All experiments were performed at room temperature and without any pH adjustment.

Results and Discussion

All the isotherms of AOCs on the four carbons were nonlinear when the q_e vs C_e values were plotted on linear coordinates. The Freundlich model was employed to describe the adsorption isotherms:

$$q_e = K_F C_e^n \quad (3)$$

where K_F ($\text{mmol g}^{-1} \mu\text{mol}^{-n} \text{L}^n$) is a unit-capacity parameter and n is a constant known as the heterogeneity factor that is related to the surface heterogeneity, whose value ranges between 0 and 1.

As illustrated in Fig. 1, the K_F ratios of each two carbons were quite different although they had very similar surface and pore structures, suggesting that the surface chemistry of the carbons played an important role in their adsorption to AOCs. Therefore, two parameters were introduced here to reflect the roles of surface polarity and hydrophilic sites of the carbons in adsorption.

Since the studied adsorbates in this work are all aromatics and the adsorption were performed in aqueous solutions, the ratio of α parameters of benzene and water on one adsorbent can be served as a relative adsorption affinity index ($\gamma = \alpha_{\text{BZ}}/\alpha_{\text{w}}$) between the adsorbent and the adsorbate in aqueous solutions.

The acid and base uptakes as well as ash content were employed in the present work to calculate the amount of sites where water clusters can form.

$$\delta = \frac{[O + N] \times 10^{-3} \cdot A \cdot M_w}{\mu} \times 100\% + \text{ash\%} \quad (4)$$

where δ is the surface coverage or pore volume occupancy of the active sites on adsorbent by combining one water molecule; $[O + N]$ (mmol g^{-1}) is the concentration of oxygen- and nitrogen-containing functional groups on the adsorbent, equal to the sum of acid and base uptakes; A is the Avogadro's number; M_w is the molecular parameter of water, which can be expressed either by molecular area, S_w (m^2), or molecular volume, V_w (cm^3); μ is the space availability parameter of the carbonaceous adsorbent, which can be expressed either by specific surface area, S_C ($\text{m}^2 \text{g}^{-1}$), or pore volume, V_C ($\text{cm}^3 \text{g}^{-1}$).

The obtained γ and δ values are shown in Table 4.

Table 4. The γ and δ parameters of adsorbents.

Carbon	β_{BZ}	α_{BZ}	β_{w}	α_{w}	γ	δ (%)
ACF10_H ₂	1.00	0.998	0.07	0.919	1.09	2.31
ACF10_NO	1.00	0.999	0.16	0.981	1.02	9.73
OLC_H ₂	1.00	0.994	0.06	0.735	1.35	2.47
OLC_NO	1.00	0.997	0.13	0.928	1.07	7.17

Since each water molecule can be H-bonded with up to four other molecules (two through its two lone pairs, and two through its two hydrogen atoms) [2], each active site may form a water cluster with five water molecules. The possible space availability of the adsorbent consequently turns to be $\mu \cdot (1-5 \cdot \delta)$.

Taking the space availability and relative adsorption affinity index into account, a correlation between the K_F and the characteristics of adsorbents was established as:

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

where i and j are labels of carbons.

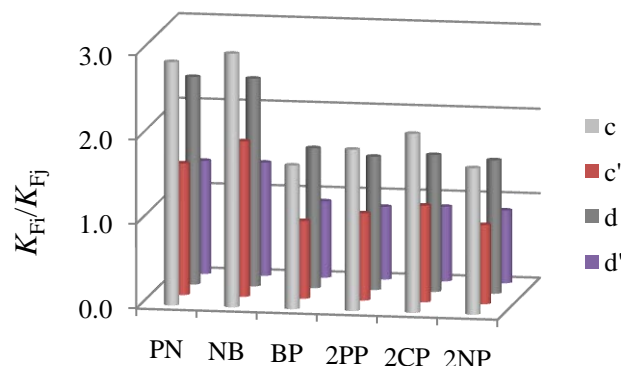


Fig. 1 The K_F ratios and normalized K_F ratios of AOCs on carbons. c and d represent the ratio of ACF10_H₂ to ACF10_NO, and OLC_H₂ to OLC_NO, respectively. c' and d' are the corresponding ratios normalized with equation 5.

As illustrated in Figure 1, after normalization with equation 5, the K_F ratios between different carbons approach to unity, suggesting that the correlation between the K_F and the characteristics of carbon expressed in equation 5 was valid.

Conclusions

Two parameters, γ and δ , were created to describe the relative adsorption affinity index of activated carbons to adsorbates and the occupancy rate of activated carbons by active sites, which can lead to formation of water clusters. Taking the space availability and relative adsorption affinity index into account, a correlation between the Freundlich adsorption coefficient and the characteristics of adsorbent was established. The empirical equations established here provide us the possibility to predict the adsorption affinities of carbons whose physical structures and surface chemistry were well characterized. This possibility will be of great significance to engineering design and application.

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