SURFACE CHEMISTRY AND ADSORPTION AFFINITY OF ACTIVATED CARBONS

Selcen Kose, Shujuan Zhang, and Tanju Karanfil

Department of Environmental Engineering and Science, 342 Computer Court, Clemson University, Anderson, SC 29625

Introduction

Activated carbon fibers (ACFs) have been used widely for the removal of synthetic organic compounds (SOCs) [1-3]. Adsorption of these compounds is controlled by physical and chemical interactions. Chemical interactions on the adsorption of SOCs, which include the chemical nature of the surface, the adsorbate, and the solvent, have been studied by many researchers [4-8].

In this study, adsorption of biphenyl (BP) and 2-hydroxybiphenyl (2HB) by heat-treated and oxidized ACFs was investigated to elucidate the effect of adsorbent surface chemistry and hydrophobic interactions.

Experimental

Materials. Three phenol formaldehyde-based ACFs (ACF10, ACF15 and ACF20 (from American Kynol Inc.)) were selected for this study. Carbons were modified by heat treatment and oxidation. Heat treatment was performed under the flow of hydrogen at 1173 K for 2 hours to remove surface functional groups and decrease the acidity. In order to add more surface functional groups, carbons were oxidized by 4 M nitric acid for 1 h at 363 K. While heat-treated samples were labeled as ACF10-H_2, ACF15-H_2, ACF20-H_2, oxidized ACFs were labeled as ACF10-NO, ACF15-NO, and ACF20-NO. Selected SOCs, BP (99.5+%) and 2HB (99+%), were obtained from Sigma-Aldrich Chemical Co.

Characterization of Carbons. Nitrogen adsorption at 77 K and water vapor adsorption at 273 K with a Micromeritics ASAP 2010 instrument were performed to determine surface areas, pore volumes and surface polarities of the carbons. Brunauer-Emmett-Teller (BET) equation, *t*-plot method, and density functional theory (DFT) model for slit-shaped pores were used to calculate surface areas, pore volumes, and pore size distributions (PSDs). Pore diameters of the carbons were obtained by BET method. The pH of the point of zero charge (pH_{pzc}) was determined by employing batch equilibrium experiments. In order to determine the oxygen contents, elemental analysis was performed with an EA1112 elemental analyzer (Thermo Electron Co.)

Isotherm Experiments. Constant dose bottle point technique was employed for the single solute isotherm experiments by using 255 mL amber glass bottles with Teflon-lined screw caps. One mg of ACFs was equilibrated in solutions with different concentrations of BP and 2HB. The bottles were first filled with distilled and deionized water to nearly full, and then were spiked into predetermined volumes of stock adsorbate solutions. The bottles were then placed into a tumbler for one week at room temperature. UV-Vis spectrophotometer and a high performance liquid chromatography (HPLC) were used to analyze remaining liquid phase concentrations. Linear form of Freundlich Model was employed to the experimental data.

Results and Discussion

Characterization Results. According to the nitrogen adsorption isotherms, the selected ACFs were highly microporous with a ratio more than 75%, and regardless of the surface modification characteristics, the BET surface area increased and PSD broadened in the order of ACF10 < ACF15 < ACF20, which is consistent with the increasing level of activation. The surface areas of heat-treated ACFs were slightly higher than those of oxidized ACFs. Heat treatment increased the microporous surface areas (S_{mic}) by 2 to 13% compared to the oxidation of ACF samples. Pore volumes less than 2 nm were the adsorption sites for selected SOCs and comprised a large portion of the carbons. The results also indicated that modification of the ACFs by either heat-treatment or oxidation did not change the pore diameters, which ranged from 0.56 to 0.74 nm. According to the water vapor adsorption isotherms, the oxidized ACFs demonstrated higher affinities for water than the heat-treated ones at the low P/P_0 range. This confirms that the oxidized carbons were more hydrophilic, while the heat-treated carbons were more hydrophobic. In fact, oxidized carbons had lower pH_{pzc} values than heat-treated ones, indicating higher acidity of these carbons. As shown in Table 1, the increased functional groups, especially oxygen containing ones, by oxidation enhanced the acidity of the ACFs, and thereby increased the hydrophilic character of the ACFs without affecting the overall porosity [9, 10].

BP and 2HB were selected as adsorbates, because they are very similar in terms of molecular size and configuration, whereas their hydrophobicities are quite different (Table 2).

Table 1. Chemical characteristics of the adsorbents.

Adsorbents	pH_{PZC}	Elemental Analyses (%)			
		C	H	N	O
ACF10-H_2	9.94	95.46	0.87	0.00	0.15
ACF15-H_2	10.08	96.11	0.64	0.00	0.10
ACF20-H_2	10.13	96.67	0.64	0.07	0.07
ACF10-NO	3.15	75.79	1.79	0.68	16.62
ACF15-NO	3.08	70.11	1.60	0.77	15.82
ACF20-NO	3.15	75.09	0.72	0.87	10.61

Table 2. Physicochemical properties of the adsorbates.

Adsorbates	BP[*]	2HB
Molecular Configuration	Nonplanar	Nonplanar
Molecular Size[a] (Å×Å×Å)	11.8×6.8×4.7	11.8×7.8×5.4
MW^b (g/mol)	154.21	170.21
Density (g/cm³)	0.992	1.213
S_w^c (mg/L)	6.1	700
Dihedral (θ)	37	52

[*]Nonplanar in water, planar in adsorbed state; [a] Simulated with ACDLABS11.0 (ChemSketch and ACD/3D Viewer); [b] Molecular weight; [c] Water solubility at 25 °C.

Adsorption Isotherms. BP and 2HB adsorptions on the heat-treated and oxidized ACFs are illustrated in Figure 1. Both BP and 2HB adsorptions on the heat-treated ACFs are higher than that of oxidized ones, and their uptakes were in the order of ACF20-H_2 > ACF15-H_2 > ACF10-H_2 > ACF20-NO > ACF15-NO > ACF10-NO.
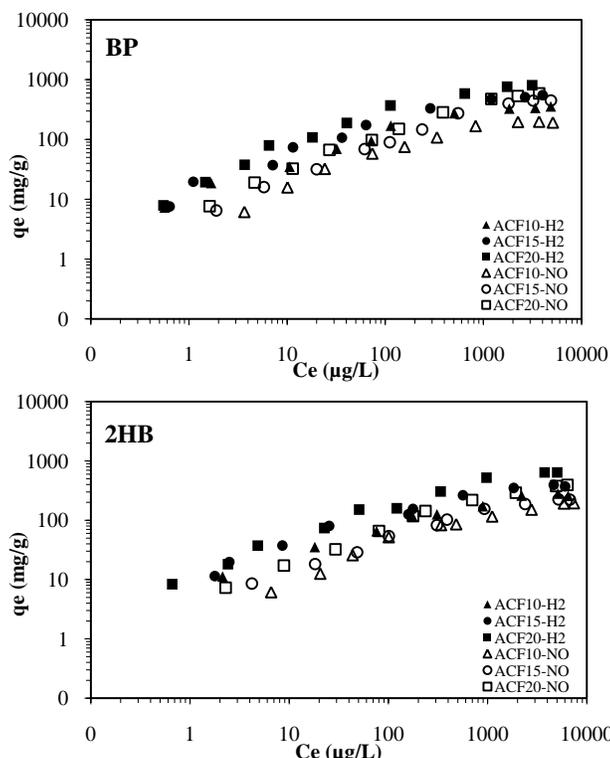

Fig. 1 Adsorption isotherms of BP and 2HB.

Table 3. Freundlich isotherm parameters of BP and 2HB.

SOC	Adsorbent	K_F^a [(mg/g)/Ce^n] (μg/L)	(mg/L)	n	r^2
BP	ACF10-H_2	13.99	262	0.42	0.954
	ACF15-H_2	17.02	421	0.46	0.949
	ACF20-H_2	19.45	711	0.52	0.946
	ACF10-NO	5.92	142	0.46	0.907
	ACF15-NO	6.12	273	0.55	0.979
	ACF20-NO	7.83	377	0.56	0.981
2HB	ACF10-H_2	11.18	173	0.40	0.964
	ACF15-H_2	14.35	254	0.42	0.954
	ACF20-H_2	14.84	383	0.47	0.958
	ACF10-NO	4.22	102	0.46	0.956
	ACF15-NO	4.92	120	0.46	0.963
	ACF20-NO	6.76	213	0.50	0.959

[a] Adsorption capacities expressed in different units.

Since the heat-treated ACFs and oxidized counterparts of ACFs had almost identical surface areas and pore volumes, their physical structural parameters cannot explain their differences in adsorption behavior to BP and 2HB. The major differences between these two groups of ACFs are their oxygen and nitrogen contents, which are higher for the oxidized ACFs and lower for the heat-treated ACFs. These functional groups can serve as hydrogen-bond donor and/or acceptor sites which interact with water molecules more than they interact with organic compounds. Consequently, water clusters are built up and prevent organic compounds to access the basal planes of adsorbent and/or reduce the interaction energy between the compounds and the adsorbent surface, especially at low concentrations [11]. As shown in Figure 1, the isotherm differences between the oxidized and heat-treated ACFs were larger at low concentrations, whereas the isotherms converged at high concentrations. The heat-treated carbons with their low oxygen and nitrogen contents are more hydrophobic. As a consequence, their affinities for organic compounds are higher; and thus, they showed better adsorption potentials.

To further investigate the hydrophobic interactions, BP and 2HB adsorptions were compared (Table 3). At the same concentration levels, 2HB had lower adsorption capacities than BP. Since they are very similar in molecular size and configuration, the differences in their uptakes can be attributed to their difference in solubility. The substitution of a hydroxyl group in the 2HB is the only difference between the molecular structures of BP and 2HB. This hydroxyl group provides enhanced interactions with water via hydrogen-bonding and increased in water solubility, which in turn decreased the adsorption capacity.

Conclusions

Oxygen and nitrogen containing groups reduced the adsorption capacities of ACFs to aromatic compounds. Hydrophobic carbons are more effective for the removal of both hydrophilic and hydrophobic adsorbates from aqueous solutions. In addition, adsorbates that are more hydrophobic have higher adsorption capacities.

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