PORE STRUCTURE AND ADSORPTION AFFINITY OF ACTIVATED CARBONS

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Introduction

Activated carbons (ACs) and activated carbon fibers (ACFs) have been extensively used for the removal of synthetic organic compounds (SOCs) that have been produced for the purpose of industrial and domestic uses for decades. Adsorption of SOCs on ACs and ACFs are affected by both physical and chemical factors such as the characteristics of adsorbent (surface area, pore size distribution (PSD), and surface chemistry) and adsorbate (molecular weight, size, functional groups present, polarity, hydrophobicity, solubility), and the background solution conditions (pH, temperature, presence of competitive solutes, ionic strength) [1-5].

In this study, the role of pore structure of the adsorbents in adsorption was examined and the accessible pore size regions for the selected SOCs were determined by excluding the chemical interactions. In order to minimize the effect of chemical interactions, carbons which have similar surface chemistries were used for comparison. For this purpose, adsorption of three SOCs on the heat-treated ACFs and heat-treated granular activated carbons (GACs) were investigated.

Experimental

Materials. Three phenol formaldehyde-based ACFs (ACF10, ACF15 and ACF20 (from American Kynol Inc.)) and three GACs (a coconut shell-based: OLC (from Calgon Carbon Corporation); two coal-based: F400 (from Calgon Carbon Corporation) and HD4000 (from Norit Inc.)) were used in this study. Carbons were heat-treated at 1173 K for 2 hours under hydrogen flow to remove surface functional groups and decrease the acidity. Benzene (BNZ, 99.8+%, 7.4Å×6.7Å×3.4Å), biphenyl (BP, 99.5+%, 11.8Å×6.8Å× 4.7Å), and phenanthrene (PHE, 97+% 11.7Å×8.0Å× 3.4Å) were obtained from Sigma-Aldrich Chemical Co.

Characterization of Carbons. Surface areas, pore volumes and surface polarities were determined from nitrogen adsorption at 77K and water vapor adsorption at 273K with a Micromeritics ASAP 2010 instrument. 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), respectively. BET method was employed to obtain pore diameters of the carbons. Elemental analysis was performed with an EA1112 elemental analyzer (Thermo Electron Co.) to determine the oxygen contents of the adsorbents.

Isotherm Experiments. Constant dose bottle point technique was used for the single solute isotherm experiments. Experiments were performed in 255 ml amber glass bottles with Teflon-lined screw caps. One mg of ACFs and 1 mg of GACs were equilibrated in solutions with different concentrations of BNZ and BP, whereas 0.5 mg of carbons was equilibrated in solutions of PHE. 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. Remaining liquid phase concentrations were analyzed using both UV-Vis spectrophotometer and a high performance liquid chromatography (HPLC). Linear form of Freundlich Model (FM) was employed to the experimental data.

Results and Discussion

Characterization Results. According to the nitrogen adsorption data, ACFs were more microporous than GACs, and their microporosity increased with increasing level of activation. Among all carbons, only F400 and HD4000 showed desorption hysteresis, which were related to mesopore structure of these carbons. HD4000 was more mesoporous than F400 and had some degree of macropores. Pore volumes less than 2 nm were the adsorption sites for our compounds and comprised a large portion of the carbons, except that of HD4000. Pore diameters were larger for the GACs and smaller for the ACFs, and they increased with increasing level of activation (Table 1). Both elemental analysis and water vapor adsorption experiments demonstrated that the six carbons had similar amounts of oxygen contents and low polarity.

Table 1. Surface and pore structures of the adsorbents.

Adsorbents	S_{BET}[a] (m²/g)	S_{mic}[b] (m²/g)	V_t[c] (cm³/g)	V_{mic}[d] (cm³/g)	D_{BET}[e] (nm)
ACF10	1066	971	0.445	0.381	0.56
ACF15	1512	1353	0.624	0.533	0.61
ACF20	1978	1483	0.900	0.608	0.74
OLC	1080	883	0.484	0.353	1.79
F400	1075	662	0.596	0.277	2.22
HD4000	838	355	0.875	0.155	4.18

[a] BET surface areas of adsorbents; [b] Microporous surface areas of adsorbents; [c] Total pore volumes of adsorbents; [d] Microporous pore volumes of adsorbents; [e] Pore diameters obtained from BET method.

Adsorption Isotherms. FM isotherm parameters are given in Table 2. In order to explain the adsorption phenomena, mass-basis, solubility normalized and surface area normalized adsorption capacities of the adsorbates are used. Capacities are represented by K_F, K_{FS}, and Q, respectively. Since the molecular dimensions of selected adsorbates are smaller than 2 nm, micropores and available surface areas play an important role on the adsorption. K_F values demonstrate that ACFs have higher adsorption capacities than GACs, which is consistent with the higher specific surface areas and microporosity ratios of ACFs (more than 75% of the pores in ACFs are microporous,

whereas this ratio is 40, 60, and 80% for HD4000, F400, and OLC, respectively).

Table 2. Freundlich isotherm parameters of BNZ, BP and PHE.

SOC	Adsorbent	$K_F{}^a$ [(mg/g)/(µg/L)^n]	$K_{FS}{}^b$ (mg/g)	Q^c (mg/m^2)	n	r^2
BNZ	ACF10	1.80	290	0.272	0.52	0.976
	ACF15	2.91	318	0.210	0.48	0.972
	ACF20	3.11	382	0.193	0.49	0.971
	OLC	1.39	245	0.227	0.53	0.979
	F400	0.95	212	0.197	0.55	0.972
	HD4000	0.72	152	0.181	0.55	0.950
BP	ACF10	13.99	565	0.530	0.42	0.954
	ACF15	17.02	976	0.646	0.46	0.949
	ACF20	19.45	1825	0.923	0.52	0.946
	OLC	9.98	870	0.806	0.51	0.905
	F400	12.87	656	0.610	0.45	0.894
	HD4000	13.04	578	0.690	0.44	0.897
PHE	ACF10	2.84	209	0.196	0.61	0.960
	ACF15	7.41	427	0.282	0.58	0.957
	ACF20	13.65	604	0.305	0.54	0.886
	OLC	0.67	419	0.388	0.92	0.989
	F400	2.12	255	0.237	0.68	0.982
	HD4000	1.86	325	0.388	0.74	0.898

[a] Adsorption capacity; [b] Solubility normalized adsorption capacity (K_F values at saturated concentrations of SOCs). Due to its high solubility, BNZ was simulated with 1% of its water solubility; [c] Surface area normalized adsorption capacity.

Since the size of the BNZ molecule is smaller than 1 nm, both PSD and pore volume in pores less than 1 nm are important for the adsorption. Moreover, BNZ is a liquid compound and can access and fill the pores easily. As a result, pore filling is expected to be the main mechanism on the adsorption of BNZ. In fact, BNZ adsorption was found correlated with not only S_{BET} but also S_{mic} and V_{mic} of the carbons, especially surface areas and pore volumes that come from pores smaller than 1 nm. Adsorption capacities of the carbons for BNZ followed the order of ACF20 > ACF15 > ACF10 > OLC > F400 > HD4000. The reason for this order can be attributed to the order of S_{mic} and V_{mic} of the carbons. While the solubility normalized adsorption capacities followed the same order with mass-basis ones, surface area normalized adsorption capacities showed a different trend. Solubility normalization gives overall adsorption capacity, and it is related to available adsorption sites. It appears that there was no restriction for BNZ molecules to access to the pores; and thus, adsorption increased with increasing specific surface areas. Surface area normalization is related to adsorption potential which is important for adsorption at low concentrations, and gives information about the effect of carbon pore structure on the adsorption. Carbons which have higher adsorption affinities at low concentrations showed lower adsorptions at saturated concentration probably due to the less available adsorption sites remaining for the adsorption [6].

BP uptake was in the order of ACF20 > ACF15 > ACF10 > HD4000 > F400 > OLC, whereas PHE uptake followed the order of ACF20 > ACF15 > ACF10 > F400 > HD4000 > OLC. Neither solubility nor surface area normalized adsorption capacities of BP and PHE reflected this order. Among the six carbons, ACF10 has the least amount of pores distributed between 1-2 nm, which provide the dominant adsorption sites for BP and PHE. More than 70% of the pores in ACF10 are smaller than 1 nm. Therefore, the uptakes of ACF10 on BP and PHE were the lowest at both saturated concentrations and low concentrations, which indicated that molecular sieving effect occurred on the adsorption of ACF10. Unlike BNZ, adsorption of BP and PHE was found correlated only with S_{BET}, indicating that their adsorptions were controlled by the surface areas of carbons. PHE is a large planar compound and its molecules can only attach to the carbon surface and cannot fill the pores. As a result, adsorption capacities of PHE were lower than those of nonplanar BP, which can change its molecular configuration and has more access to the small pores. Among the GACs, OLC had higher solubility normalized and surface area normalized adsorption capacities than those of F400 and HD4000. Coconut-based carbons exhibit better adsorptive capacities for small compounds than the coal-based carbons [7]. Overall, microporosity and molecular sieving played important roles on the adsorption of BP and PHE.

Conclusions

Results indicate that ACFs exhibited higher adsorption capacities for adsorbates with low-molecular sizes than those of GACs, because of their higher specific surface areas and microporous structures. Pore filling played an important role on the adsorption of BNZ, whereas molecular sieving and micropore effects were the main mechanisms on the adsorption of BP and PHE as a result of their molecular sizes.

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