

ADSORPTION SITE ANALYSIS FOR CARBONACEOUS ADSORBENTS

S.J. Zhang, T. Shao, S. Kose and T. Karanfil

Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625

Introduction

Adsorption is one of the most powerful techniques in water treatment. Carbonaceous adsorbents, as the main type of adsorbents, play a significant role in removal of hydrophobic contaminants from water. Besides the conventional granular activated carbons (GACs) and activated carbon fibers (ACFs), the newly emerged carbon nanotubes (CNTs) have attracted extensive attention for their potential use in water treatment [1]. In order to make a conclusive comparison between the adsorption behaviors of the various types of carbonaceous adsorbents, a systematic investigation was performed to elucidate the adsorption sites for two aromatic organic chemicals (AOCs) on a set of carbons (CNTs, GAC, ACF). The present work is expected to help us answer the following two questions: (i) Are the newly emerged CNTs promising substitutes for the conventional GACs and ACFs? (ii) What is the criterion for the selection of a suitable carbonaceous adsorbent in water treatment for a specific point-of-use?

Experimental

A coal-based GAC (HD4000, from Norit Inc.), a phenol formaldehyde-based ACF (ACF10, from American Kynol Co.), a SWNT (outer diameter: 1-2 nm, length: 5-30 μm , purity > 90%, from Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences), and a MWNT (inner diameter: 3-5 nm, outer diameter: 8-15 nm, length: 10-50 μm , purity > 95%, from Nanostructured & Amorphous Materials, Inc., USA) were used as received.

The two AOCs, phenanthrene (PNT, 99.5+%) and biphenyl (BP, 99+%), were obtained from Sigma-Aldrich Chemical Co. The molecular properties of the two AOCs are provided in Fig. 1.

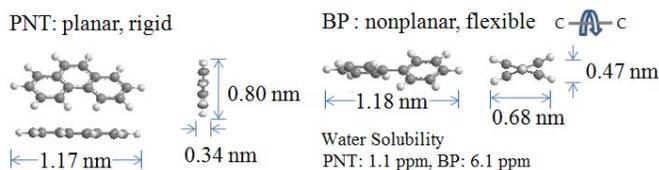


Fig. 1 Molecular properties of adsorbates.

The structural characteristics of the carbons were determined by low temperature nitrogen gas adsorption at 77K. The Brunauer-Emmett-Teller (BET) equation, t -plot method, and density functional theory (DFT) were used to calculate BET specific surface area (S_{BET}), total pore volume (V_t), and pore size distribution

Aqueous phase isotherm experiments were conducted to elucidate the adsorption sites for AOCs on different carbons. Detailed experiment process was given elsewhere [2].

Results and Discussion

The surface area, pore volume, and pore size distribution of the adsorbents are summarized in Table 1. The four carbons differ significantly in structural characteristics: ACF10 is nearly 100% microporous; SWNTs are hybrid in mesopores and micropores; MWNT is dominated with mesopores and macropores; and HD4000 has the highest heterogeneity in pore structure with a wide distribution of pore sizes.

Table 1. Structural parameters of adsorbents.

Carbon	S_{BET} (m^2/g)	Surface area distribution*				V_t (cm^3/g)
		< 1	< 2	2-50	> 50	
ACF10	949	0.73	1.00	0.00	0.00	0.381
HD4000	706	0.66	0.81	0.12	0.06	0.711
SWNT	486	0.12	0.44	0.56	0.00	0.722
MWNT	164	0.00	0.13	0.31	0.56	0.664

* The surface area fraction in each pore size range (pore size in nm).

All liquid phase adsorption isotherms of the two AOCs on the four adsorbents were nonlinear when the q_e vs C_e values were plotted on linear coordinates. A modified Freundlich equation was employed to describe the adsorption isotherms by normalizing the C_e with the water solubility (S_w) of the adsorbate.

$$q_e = K_{\text{FS}} (C_e / S_w)^n \quad (1)$$

where K_{FS} is a parameter independent of the concentration units and represents the effective adsorption capacity of the adsorbent.

After surface area normalization, the isotherms of PNT on the three adsorbents with the majority of their pores larger than 1 nm converged, while that of PNT on the microporous ACF10 was significantly lower than the others. As for BP, the adsorption isotherms were still scattered after surface area normalization, especially at low concentrations.

As shown in Fig. 1, the molecular dimensions of the two AOCs are smaller than 2 nm. Therefore, micropores and available contact surfaces in the adsorbents should play dominant role in the adsorption. The lower surface heterogeneities (larger slopes of isotherms, data not shown) of ACF10 for the two AOCs than those of SWNT and HD4000 suggest that the surface heterogeneity was positively related with the pore size distributions of the adsorbents.

To examine possible relationships between the adsorbed amounts of AOCs and the structural parameters of carbons, some quantitative analyses were performed. The volumes occupied by adsorbed AOCs (V_{AOC}) were calculated by dividing the K_{FS} values with the bulk densities of the AOCs.

The monolayer nitrogen adsorption volume capacities (V_{N_2}) of the carbons were calculated from the S_{BET} and the thermal transition hard-sphere diameter of nitrogen (0.386 nm). Ratios of V_{AOC} to V_{N_2} were calculated to show the surface coverage of the carbons by the two AOCs, whereas ratios of V_{AOC} to V_t were employed to reflect the pore volume occupancy.

As indicated by the V_{AOC}/V_t values in Table 2, the order of pore volume occupancies was consistent with the order of micropore fractions of the carbons. The carbons with higher micropore fractions had higher pore volume occupancies. In liquid phase adsorption of low molecular weight chemicals, macropores and mesopores usually act as diffusion channels, and micropores play the key role in adsorption, because overlapping adsorption potentials of opposite walls make the adsorption energies much stronger in micropores than those in meso- and macro- pores, i.e., micropore effect [3].

Table 2. Adsorption parameters of AOCs on the CNTs, GAC, and ACF

AOC	Carbon	K_{FS} (mg/g)	V_{AOC} (mL/g)	V_{AOC}/V_{N_2} (-)	V_{AOC}/V_t (-)
PNT	ACF10	248	0.233	0.64	0.61
	HD4000	414	0.389	1.43	0.55
	SWNT	314	0.296	1.58	0.41
	MWNT	60	0.057	0.90	0.09
BP	ACF10	553	0.558	1.52	1.46
	HD4000	428	0.431	1.58	0.61
	SWNT	254	0.256	1.36	0.35
	MWNT	90	0.091	1.43	0.14

As illustrated in Fig. 2, the ellipsoidal micropores in ACF10 and the slit-shaped micropores in HD4000 could provide more contact sites for adsorbates than the larger pores in the CNTs. With increasing distance to the graphitic wall, the adsorption potential reduced rapidly. As a result, the inner cavities of the MWNT could not be completely filled by the AOCs, as did in the other three types of carbons, which explained the micropore effect.

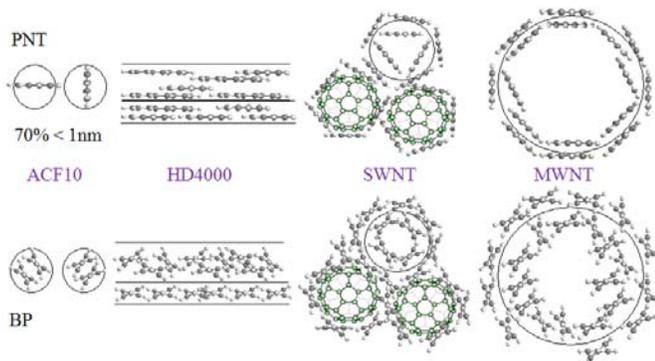


Fig. 2 Adsorption sites of AOCs on the carbons.

The V_{AOC}/V_{N_2} values demonstrate that complete monolayer coverage of MWNT and ACF10 was not formed by PNT (values less than 1), which could be attributed to the molecular sieving effect in PNT adsorption on ACF10 and the low adsorption affinity of MWNT to PNT. The adsorbed volumes of PNT on the SWNTs and HD4000 and those of BP on all carbons were higher than the monolayer nitrogen adsorption volume capacities, indicating the occurrence of multilayer adsorption and pore filling in the adsorption of AOCs by these carbons.

As illustrated in Fig. 3, a linear relationship between K_{FS} and S_{BET} was observed, exclusive of the case with molecular sieving effect, i.e., the adsorption of PNT on ACF10, indicating that in the absence of molecular sieving effect, the adsorption capacities of AOCs by the carbonaceous adsorbents is controlled and can be estimated by the surface areas of these carbons, independent of their types.

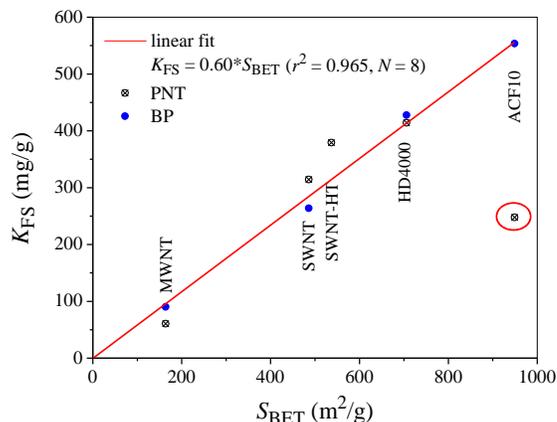


Fig. 3 K_{FS} of AOCs vs S_{BET} of carbons. The circled data point was excluded from linear fitting.

Conclusions

Adsorption of AOCs on porous carbonaceous adsorbents may be subjected to micropore effect and molecular sieving effect. Almost all the adsorption sites in ACF10 and HD4000 are derived from their abundant pores, whereas the available adsorption sites on the SWNTs for AOCs are likely to be the external surfaces and interstitial channels trapped in the aggregates (most of the SWNTs are close-ended), and those of the MWNTs are mainly the external surface and inner cavities. Due to their larger pore sizes, SWNTs and MWNTs are expected to be more efficient in adsorption of large size molecules than ACF10 and HD4000. Since the inter-wall cavities of MWNTs are not accessible to adsorbates, their adsorption capacities on mass basis are usually low. Furthermore, due to their small particle sizes and dispersibility in water, the removal of MWNTs after use is also a challenge. Even in some cases the CNTs showed higher adsorption capacities and/or faster kinetics than ACs, their use as substitutes for ACs warrants more research.

Acknowledgment. This work was partly supported by a research grant from National Science Foundation (CBET 0730694).

References

- [1] Mauter MS, Elimelech M. Environmental applications of carbon-based nanomaterials. *Environ. Sci. Technol.* 2008;42(16):5843-5859.
- [2] Zhang SJ, Shao T, Bekaroglu SSK, Karanfil T. The impacts of aggregation and surface chemistry of carbon nanotubes on the adsorption of synthetic organic compounds. *Environ. Sci. Technol.* 2009;43:5719-5725.
- [3] Dubinin MM. Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characterization properties and micropore structures. *Carbon* 1989;27:457-467.