

EFFECTS OF SURFACE CHEMISTRY OF ACTIVATED CARBON ON THE ADSORPTION OF AROMATICS CONTAINING ELECTRON-WITHDRAWING AND ELECTRON-DONATING FUNCTIONAL GROUPS

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INTRODUCTION

Adsorption of organic water pollutants onto activated carbon surfaces has been studied extensively and a voluminous literature is available on this increasingly important practical problem [1,2]. There are many well established facts; there are also some conflicting data. More importantly, conflicting interpretations have been offered and no attempt seems to have been made to reconcile them. Because many of the pollutants are weak electrolytes, the central fundamental issue is how to account for the well documented importance of (a) the pH of the aqueous solution, and (b) the surface chemistry of the adsorbent.

In an early study, Getzen and Ward [3,4] presented a Langmuirian theoretical framework for the adsorption of both ionic and molecular species as a function of pH. Their approach provided an explanation for the often observed maximum in adsorbate uptake at $\text{pH} = \text{pK}_a$, without explicitly taking into account the changes in the surface chemistry with pH. The explanation for an acid adsorbate is as follows: as pH decreases toward the pK_a value, H^+ ions as well as organic anions are adsorbed on the surface. Since the concentration of H^+ rapidly exceeds that of the weak electrolyte anions, the former adsorb on the carbon surface far in excess of the anions and subsequently enhance anion adsorption. However, because the concentration of anions decreases as pH increases, a point of diminishing returns is eventually reached and a maximum in adsorption uptake is observed.

In another milestone study, Müller et al. [5-7] used the same approach based on Langmuirian competitive adsorption of ionic and molecular species, but accounted explicitly for the pH-induced variations in the adsorbent surface charge. This allowed them to provide a more rigorous explanation of the adsorption maximum at $\text{pH} = \text{pK}_a$ in terms of both adsorbate and adsorbent properties. It is necessary that considerable ionization of the adsorbate (solute) take place while the surface still possesses a charge that is opposite to that of the ionic solute. In particular, for an acidic solute, it is necessary that, for a given pH increment, the magnitude of the slope of the solute dissociation curve be larger than that of the surface potential curve.

Our interest in this topic [8,9,10] stems from the realization [11,12] that the lack of understanding of adsorption of inorganic solutes on carbons has suffered for many years from a lack of appreciation of the amphoteric nature [13] of carbon surfaces. Based on intriguing results for adsorption of benzoate, oxalate and fumarate anions on chemically modified (oxidized vs. nitrated) activated carbons [14], we proposed the following mechanisms of adsorption: (a) adsorption of benzoate (aromatic) anions occurs primarily on the basal plane of carbon and the electron-withdrawing effects of nitrogen and carboxyl functional groups suppress the interaction of the basal planes with the adsorbate's aromatic rings; (b) adsorption of aliphatic anions occurs also predominantly on the basal plane and the same electron-withdrawing effects enhance its interaction with the carboxyl anions. More recently, we have begun to study in some detail the relative importance of dispersion and electrostatic adsorbate/adsorbent interactions as we examined the uptake of methylene blue and p-nitrophenol, as well as benzoic acid and oxalic and fumaric acids [15]. We concluded that, while electrostatic interactions are important, π - π dispersion interactions appear to be dominant in the adsorption of aromatic solutes. On the other hand, electrostatic repulsion appears to be much more important for the adsorption of aliphatic anions. These are important and arguably novel findings, and their further investigation (and substantiation) is of interest.

In the present study, we contrast the behavior of chemically different carbons in adsorbing two vastly different aromatic solutes: nitrobenzene is a very weak Lewis acid that possesses the electron-withdrawing NO_2 group, while aniline is a predominantly cationic species at $\text{pH} < 4.6$ which also possesses the electron-donating NH_2 group.

EXPERIMENTAL SECTION

Two commercial granular carbons, NORIT GCW and Calgon BPL, were used as the adsorbents. Oxidation of GCW was performed by contacting the sample with concentrated HNO_3 at 363 K for 6 h. The sample was washed until neutral pH was achieved, and dried at 380 K before use. The reaction with NH_3 (nitriding) was carried out in a tubular furnace flushed at a flow rate of 30 cc/min. The temperature was kept constant for 3 h. Prior to use, the sample was washed and dried. Devolatilization of the carbon was achieved by heat treatment in inert atmosphere at 1173 K. Elemental analysis of the samples was performed using LECO CHN-600. Maximum nitrogen incorporation was observed at 673 K.

The isoelectric point (IEP) and the point of zero charge (PZC) were measured by electrophoresis and mass titration, respectively. The IEP was determined with a Zeta-Meter System 3.0+ apparatus, using 10^{-3} M KNO_3 as the indifferent electrolyte; the plateau in the plot of equilibrium pH of the slurry vs. solid weight fraction identified the PZC of a carbon. Additional chemical surface characterization of the as-received and modified carbons was attempted briefly using XPS (ESCALAB 200A-VG). Physical surface properties of the carbons were determined using an Autosorb adsorption apparatus (Quantachrome).

Adsorption isotherms were obtained by adding different amounts of carbon to Nalgene flasks containing 0.1 g/L of aniline or nitrobenzene. The pH was adjusted with NaOH or HCl. The suspensions were shaken until equilibrium was reached (ca. 24 h), and the residual adsorbate concentrations were measured by uv spectroscopy.

RESULTS AND DISCUSSION

Table 1 summarizes the physical and chemical characteristics of the GCW samples used. For both nitrated and oxidized samples no drastic changes in surface area or micropore volume were observed, in agreement with our previous studies [12,14]. Curiously, for a nitrated sample that had been oxidized previously, a higher N incorporation (~7 wt%) was achieved (at 658 K for 3 h) at the expense of a drastic decrease in BET surface area (~300 m^2/g).

The values of PZC were consistently higher than those of IEP, in agreement with previous studies [12,14]. They indicate surface charge inhomogeneities within the carbon particles [12,14]. More recently, this difference between IEP and PZC values, i.e., the combination of electrophoresis and mass titration, was shown to be a powerful tool for the analysis and design of surface chemistry of active carbons, especially for determining the spatial (radial) distribution of the acidic oxygen functional groups within carbon particles [16].

Deconvolution of the broad and complex N1s XPS peaks of nitrated carbon [10] suggests the presence of pyridine (or nitrile groups), as well as amide, amine and pyrrole groups.

Figures 1-3 show the behavior of the different carbons in adsorbing aniline under widely varying solution chemistry conditions. A significant effect of solution chemistry (pH) on the uptake is observed for both as-received and modified carbons. The effect of carbon surface chemistry is seen to depend on pH. The uptakes at $\text{pH} \leq \text{PZC}$ are enhanced by surface oxidation; at $\text{pH} = 11$ the effect is much less pronounced.

Figures 4-6 show the behavior of the different carbons in adsorbing nitrobenzene. In contrast to the findings for aniline, solution chemistry (pH) had little effect on the equilibrium uptakes. The effect of surface chemistry is seen to be much more important. The as-received and devolatilized carbons had the highest uptakes, while adsorption was suppressed for both nitrated and oxidized carbons.

Some of the phenomena observed in the present work were observed in the published literature. Some of them were also misinterpreted, as argued in more detail elsewhere [2,10]. The principal reason for these misinterpretations is the failure to recognize the amphoteric nature of carbon surfaces and its effects on electrostatic adsorbate/adsorbent interactions. For example, in a large number of studies it is assumed that the carbon surface acquires a net negative charge over a very wide range of pH conditions [17]. A typical example of the resulting inconsistencies is a discussion of phenol adsorption by Grant and King [18]. They observed a significant increase in reversible phenol uptake as the pH was reduced from 12.1 to 8.0, and then to 1.8. This was tentatively attributed to changes in phenol activity with decreasing pH. A more straightforward explanation (apparently discarded by the authors) - which is thought to explain the vast majority of phenol adsorption data [2] - is the one based on the work of Müller et al. [5-7]. At the high pH of 12.1 ($\text{pH} > \text{pK}_a$, $\text{pH} > \text{PZC}$), the low uptake is due to the electrostatic repulsion between the negatively charged carbon surface and phenolate anions. At $\text{pH} = 8.0$

($\text{pH} < \text{pK}_a$), 99% of the adsorbate exists as phenol molecules, and 1% as phenolate anions; at the same time, the degree of dissociation of acidic groups decreases and there is a better balance between positively and negatively charged sites on the surface. At low pH (e.g., $\text{pH} < 3$), most carbons are positively charged, at least in part as a consequence of donor/acceptor interactions between the graphene layers and the hydronium ions [19]. In agreement with these arguments, for BPL carbon we observed similar uptakes of aniline at $\text{pH} > \text{PZC}$ ($\text{pH} = 6.0\text{--}10.8$) and a drastic decrease at $\text{pH} = 1.5$.

The importance of dispersive interactions is also apparent in Figures 1-6. For example, aniline is much more soluble in water than nitrobenzene (35 vs. 2 g/L at 25 °C); yet its uptake does not reflect this. This is attributed to the beneficial effect of the electron-donating NH_2 group. Enhanced adsorption of aniline is due to the resulting increase in the negative charge density on the graphene layers of the adsorbent. Similarly, both oxidation and nitriding of the carbon (which have opposite electrostatic effects) reduce the π electron density on the graphene layers and have a negative effect on the uptake of nitrobenzene, in agreement with our results with benzoic acid [14]. Furthermore, neutralization of oxygen functional groups produced no significant effect on the uptake of nitrobenzene [10].

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REFERENCES

1. A. Derylo-Marczewska and M. Jaroniec, *Surf. Colloid Sci.* **14**, 301 (1987).
2. L. R. Radovic, C. Moreno-Castilla and J. Rivera-Utrilla, in preparation.
3. T. M. Ward and F. W. Getzen, *Environ. Sci. Technol.* **4**(1), 64 (1970).
4. F. W. Getzen and T. M. Ward, *J. Colloid Interf. Sci.* **31**, 441 (1969).
5. G. Müller, C. J. Radke and J. M. Prausnitz, *J. Phys. Chem.* **84**, 369 (1980).
6. G. Müller, C. J. Radke and J. M. Prausnitz, *J. Colloid Interf. Sci.* **103**, 466 (1985).
7. G. Müller, C. J. Radke and J. M. Prausnitz, *J. Colloid Interf. Sci.* **103**, 484 (1985).
8. J. M. Solar, Ph.D. Thesis, The Pennsylvania State University, 1991.
9. G. M. K. Abotsi, Ph.D. Thesis, The Pennsylvania State University, 1990.
10. I. F. Silva and L. R. Radovic, in preparation.
11. J. M. Solar, C. A. Leon y Leon, K. Osseo-Asare and L. R. Radovic, *Carbon* **28**, 369 (1990).
12. C. A. Leon y Leon, Ph.D. Thesis, The Pennsylvania State University, 1992.
13. C. A. Leon y Leon and L. R. Radovic, in *Chem. Phys. Carbon* (P. A. Thrower, Ed.), Vol. 24, 1994, p. 213.
14. J. I. Ume, A. W. Scaroni and L. R. Radovic, Proc. 21st Biennial Conf. Carbon (Buffalo, NY), July 1993, p. 468.
15. L. R. Radovic, J. I. Ume and A. W. Scaroni, in "Fundamentals of Adsorption" (D. M. LeVan, Ed.), Elsevier, Amsterdam, in press (1996).
16. J. A. Menendez, M. J. Illan-Gomez, C. A. Leon y Leon and L. R. Radovic, *Carbon* **33**, 1655 (1995).
17. K.-S. Ha, H. Hinago, A. Sakoda and M. Suzuki, in "Fundamentals of Adsorption" (M. Suzuki, Ed.), International Adsorption Society, 1993, p. 251.
18. T. M. Grant and C. J. King, *Ind. Eng. Chem. Res.* **29**, 264 (1990).
19. C. A. Leon y Leon, J. M. Solar, V. Calemma and L. R. Radovic, *Carbon* **30**, 797 (1992).

Table 1
Characteristics of GCW Carbons Used

Sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	$S_{\text{N}_2}^*$ (m^2/g)	V_{mi}^{**} (cc/g)	IEP	PZC
As received	96.5	0.57	1.29	1.64	859	0.62	4.0	8.0
Devolatilized	98.0	0.41	1.46	0.13	858	0.58	5.5	10
Oxidized	82.9	1.30	1.60	14.2	807	0.55	1.5	2.6
Nitrided	90.5	0.47	5.81	3.22	869	0.59	5.2	8.9

*BET surface area;

**micropore volume obtained from the Dubinin-Radushkevich equation applied to the N_2 adsorption isotherm.

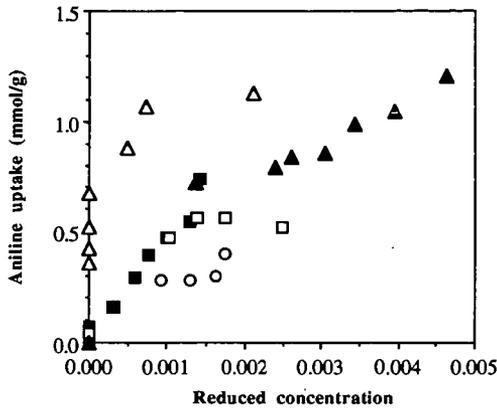


Figure 1. Aniline adsorption isotherms at pH=2 for different carbons: ■, as-received(1); □, as-received(2); ▲, devolatilized; ○, nitrided; △, oxidized.

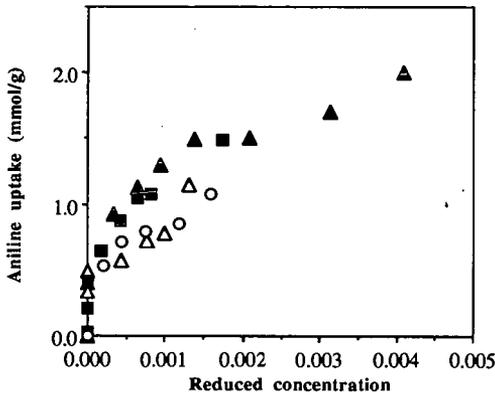


Figure 2. Aniline adsorption isotherms at pH=11 for different carbons: ■, as-received; ▲, devolatilized; ○, nitrided; △, oxidized.

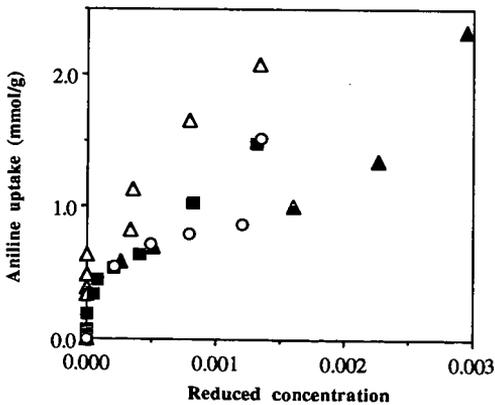


Figure 3. Aniline adsorption isotherms at pH=PZC for different carbons: ■, as-received; ▲, devolatilized; ○, nitrided; △, oxidized.

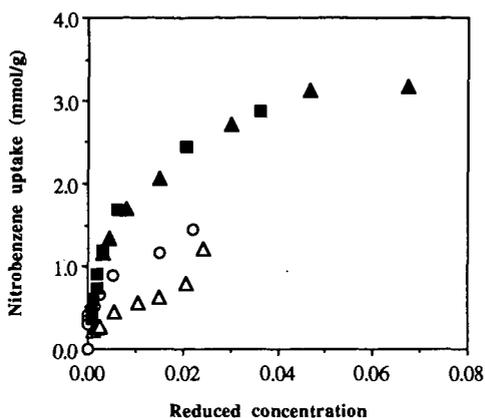


Figure 4. Nitrobenzene adsorption isotherms at pH=2 for different carbons: ■, as-received; ▲, devolatilized; ○, nitrified; Δ, oxidized.

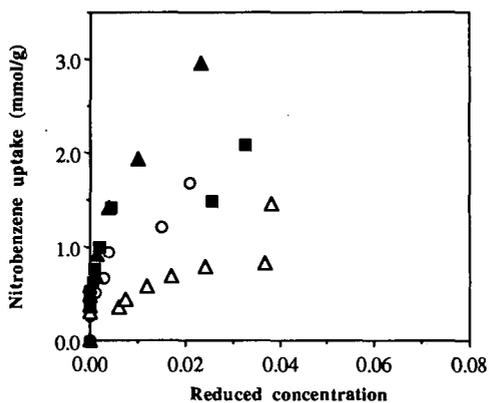


Figure 5. Nitrobenzene adsorption isotherms at pH=11 for different carbons: ■, as-received; ▲, devolatilized; ○, nitrified; Δ, oxidized.

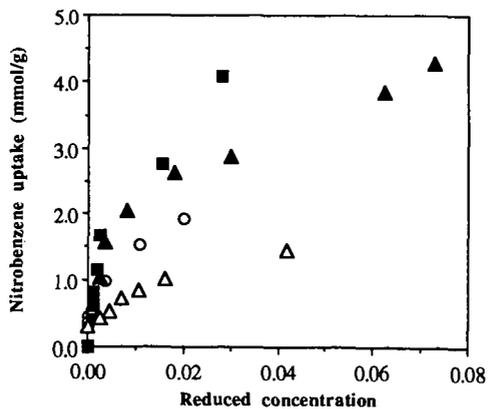


Figure 6. Nitrobenzene adsorption isotherms at pH=PZC for different carbons: ■, as-received; ▲, devolatilized; ○, nitrified; Δ, oxidized.