Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 08 July 2010

To cite this Article Arafat, Hassan A. , Ahnert, Falk and Pinto, Neville G.(2005) 'On the Adsorption of Aromatics on Oxygenated Activated Carbon in Nonaqueous Adsorption Media', Separation Science and Technology, 39: 1, 43 — 62
To link to this Article: DOI: 10.1081/SS-120027400
URL: http://dx.doi.org/10.1081/SS-120027400

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 1, pp. 43–62, 2004

On the Adsorption of Aromatics on Oxygenated Activated Carbon in Nonaqueous Adsorption Media

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ABSTRACT

In a previous study, H-bonding was postulated as a mechanism of adsorption for aromatics on oxygen-containing activated carbon. To verify this, the adsorption of phenol, aniline, benzene, and nitrobenzene was studied as a function of surface oxygen groups. It was determined that there is a linear correlation between total surface acidity and adsorption capacity for H-bonding adsorbates in cyclohexane. Flow microcalorimetry (FMC) and ultrasonic desorption tests also indicate stronger and less reversible adsorption bonds for H-bonding adsorbates. Reversibility

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DOI: 10.1081/SS-120027400 0149-6395 (Print); 1520-5754 (Online)

of adsorption decreased with increasing surface oxygen concentration, indicating a strong relationship between the oxygen groups and adsorption mechanism.

Key Words: Activated carbon; Surface treatment; Oxidation; Microcalorimetry; Ultrasonic measurements.

INTRODUCTION

It is established[1–4] that surface heterogeneity of activated carbon plays a key role in the adsorption of many compounds. This is particularly true for dissolved aromatics. The presence of heterogeneous surface sites,[1,5] particularly oxygen-containing groups, have been shown to influence the adsorption capacity of many aromatics, causing order of magnitude differences in some cases. This happens in spite of the fact that oxygen groups constitute only a small portion of the total surface area, in most cases.

A few mechanisms have been reported in published research to explain the effects of heterogeneous surface groups on the adsorption of dissolved aromatics on activated carbon. The localization of π-electrons of carbon basal planes by oxygen groups was proposed to influence the adsorption capacity by affecting the dispersive/repulsive interactions between the adsorbate and carbon basal planes.[6] Water adsorption on surface oxygen groups, via H-bonding, is suspected to cause a reduction in adsorption capacity by reducing the accessibility of organic adsorbates to the micropores.[6–11] Donor-acceptor interactions between surface oxygen groups and the aromatic adsorbate have also been postulated to be important.[12,13]

In a recent study,[14] performed in our laboratory, the adsorption of phenol, aniline, nitrobenzene, and benzoic acid on activated carbon was studied. Adsorptions from both aqueous and organic (cyclohexane) media were performed, using three carbons with different amounts of surface oxygen groups. The data supported the influence of surface oxygen groups on dispersive/repulsive interactions between the basal planes and aromatic adsorbate. More significantly, opposite effects, with respect to the influence of surface oxygen content on capacity, were found in aqueous and nonaqueous solvents. In aqueous media, water adsorption reduced the adsorption capacity for all compounds studied. In cyclohexane, the adsorption capacity for phenol and aniline increased with surface oxygenation and this was proposed to be due to H-bonding.

In this study, additional evidence is provided to support the presence of H-bonding. The adsorption of both H-bonding and non-H-bonding aromatic compounds was studied using both aqueous and cyclohexane media. Nine

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carbons with different surface acidity and basicity characteristics were utilized. Flow microcalorimetry and ultrasonic desorption were used to investigate the effect of surface oxygen concentration on the reversibility of adsorption of both H-bonding and non-H-bonding compounds.

Flow microcalorimetry (FMC) has been used in many adsorption applications in the past.[15,16] One advantage of this technique is that it provides a convenient method to quantify the reversibility of adsorption through heats of adsorption and desorption.[15,16] Hence, the FMC technique can be used to compare the strength of surface–adsorbate interactions for different materials.

Desorption by ultrasound was investigated for the release of adsorbed materials from adsorbent surfaces. Applications of this method include the decontamination of soil and sediment for hazardous waste treatment.[17] Limited studies have also been conducted on using ultrasound in regenerating the surface of adsorbents, such as activated carbon and polymeric resins.[18,19]

The present study was undertaken to further investigate the influence of the heterogeneous surface oxygen groups on the adsorption mechanism, especially through H-bonding. Aromatic compounds with functional groups having different H-bonding characteristics were used, and adsorption from aqueous and nonaqueous solution on carbons with different amounts of oxygen groups was studied. Moreover, by utilizing FMC and ultrasonic desorption, information was gained on the strength and reversibility of H-bonding mechanism.

EXPERIMENTAL

Materials

Kureha BAC-G-70R spherical bead activated carbon (0.7 mm diameter), purchased from Kureha Chemical Industry Company (New York), was used in this study. This carbon, which is made from petroleum pitch, is ash free. Previous tests on this carbon[13] indicate that polymerization of aromatics, such as phenol and aniline, do not occur on the carbon surface, even under oxic solution conditions. The carbon was conditioned upon receiving by boiling in de-ionized water for 1 hour, then drying in an oven at 110°C for 24 hours. This carbon will be referred to as DI.

To study the influence of surface oxygen groups on adsorption, the DI carbon was oxygenated with air, 1-M nitric acid solution, 4-M nitric acid solution, or 12-M nitric acid solution. These oxygenated carbons will be referred to as AIR, 1M, 4M, and 12M, respectively. Oxygenation by air was achieved by placing a 3-g sample of DI in a quartz container, which was then

placed in a tubular furnace at 350°C for 60 minutes under a constant air flow of 100 L/hr. The sample was then cooled to room temperature in air. It was observed that oxygenation at temperatures below 300°C failed to produce significant amounts of oxygen groups, while oxygenation at temperatures higher than 400°C resulted in a significant net carbon loss. Carbon oxygenation by nitric acid was achieved by boiling 1-g DI in 10-mL nitric acid solution with the desired concentration (1M, 4M, or 12M HNO_3) for 1 hour. The solution was then cooled and decanted and the carbon was washed repeatedly with DI water to remove any acid residuals. Finally, the carbon was dried in a vacuum oven at 115°C for 24 hours.

Deoxygenated carbon was obtained by heating the DI carbon to 800 or 1000°C in a tubular furnace under a constant flow of nitrogen for 1 hour. This was followed by cooling to room temperature under a flow of nitrogen, and storage in a nitrogen atmosphere. These deoxygenated carbons will be referred to as N800 or N1000, depending on the temperature in the furnace (800°C and 1000°C, respectively). Two other forms of deoxygenated carbon were produced by deoxygenating the 4M carbon at 800°C or 1000°C, using the procedure just described, to give X800 and X1000, respectively.

All of the organic compounds used in this study were purchased from Fisher Scientific (Pittsburgh, PA) in the highest purity available, and no further purification was performed.

Characterization of Carbon Surface

Surface Area Measurements

A Micromeritics Gemini 2360 (Norcross, GA) BET apparatus (N_2 at 77 K) was used to measure the surface area of the carbons used. The surface area measurements were repeated twice for each carbon and the experimental error for these measurements was found to be in the range 2 to 5%. Measurements of cumulative micropore area (i.e., pores smaller than 20 Å) were performed with a Micromeritics ASAP 2010 machine with nitrogen, utilizing the Barrett, Joyner, and Halenda (BJH) method (ASTM D4641-94).

Characterization of Surface Groups

The amounts of acidic and basic surface groups were quantified using the Boehm titration method:[20] 0.25 g of carbon was placed in a bottle, to which 25 mL of 0.1-N solution of Na_2CO_3, $NaHCO_3$, or $NaCH_3CH_2O$ was added, and the bottles were sealed. After equilibration for 24 hours on a shaker, 20 mL of the solution were back-titrated using 0.05-N HCl. The amounts of

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$NaCH_3CH_2O$ and $NaHCO_3$ reacted were used to calculate the total number of acidic groups (phenol, lactone, and carboxylic) and the number of carboxylic groups, respectively. Na_2CO_3 consumption indicated the amount of both lactone and carboxylic groups. Consequently, the number of lactone groups was determined from the difference in Na_2CO_3 and $NaHCO_3$ consumption. The number of phenol groups was determined from the difference between $NaCH_3CH_2O$ and Na_2CO_3 consumption. The overall quantity of basic groups was determined by using 0.1-N HCl, back-titrated using 0.05-N NaOH.

Adsorption Isotherm Measurements

Equilibrium isotherms were determined using the bottle point method, following the ASTM standard procedure (ASTM D3860-89a). Adsorption isotherms were generated using either cyclohexane or water as the solvent. All aqueous isotherms were measured in controlled (buffered) pH solutions, at pH 7.0, to exclude any effects of pH variations on the solubility of the adsorbate or on the charge of the carbon surface. The buffer was prepared using 0.05-M Na_2HPO_4/H_3PO_4 in de-ionized water. A UV-spectrophotometer (Shimadzu, UV160U) was used to measure the adsorbate concentration in the solution. Control samples (with no carbon) were used for each set of adsorption isotherms to determine the amount of solute evaporated, if any, during the experiment. The concentration of the control samples was used as the initial concentration for the isotherm calculations.

Flow Microcalorimetry

A flow microcalorimeter (FMC), model 3vi (Microscal Ltd., London, UK), apparatus was used to obtain heats of adsorption and desorption of aniline and nitrobenzene on N800, DI, and AIR. A detailed description of the apparatus is given elsewhere.[15] The FMC cell was loaded with 10-mg carbon. Inert (nonadsorbing) sand was added to fill the cell volume (about 0.17 mL) to shorten the time needed to complete the adsorption/desorption cycle. A test was performed on a blank sample (sand only without carbon) to estimate the contribution of the heat of adsorption on sand to the total heat. This contribution was found to be negligible compared to the heat evolved from activated carbon. Vacuum was applied on the sample for 24 hours to remove any air from the pores. Cyclohexane was then introduced into the cell at a flow rate of 3.3 mL/hr, and enough time was allowed to establish thermal equilibrium. The flow was then switched to 0.2 g/L aniline or nitrobenzene in cyclohexane, and the heat of adsorption was monitored. When equilibrium

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was achieved, i.e., no further heat of adsorption was detected over an extended period, the flow was switched back to cyclohexane again. The heat of desorption of the adsorbate from the organic-loaded carbon to the carrier fluid was now monitored. Enough time was allowed for complete desorption, by monitoring the heat signal.

Ultrasonic Desorption Measurements

Activated carbon (75 to 120 mg) was placed in a glass tube, 25 mL of 100 mg/L phenol or benzene (in cyclohexane) solution was then added to the tube. The tube was covered with aluminum foil, securely capped, and placed on a shaker for 10 days until equilibrium was reached. The amount of phenol or benzene adsorbed on the carbon was measured as described previously. The tube was then placed on a holder and immersed in the center of a water bath, as shown in Fig. 1. At the base center of the water bath, an ultrasonic transducer was installed which operated at 1.6 MHz, with an instrument power of 75 W. The transducer was connected to an amplifier (Model 75A250, Amplifier Research Company, Souderton, PA), a 75 watts, 30 MHz synthesized function generator (Model DS345, Stanford Research Systems Inc., Sunnyvale, CA), and a four-channel digital delay/pulse generator (Model DG535, Stanford Research Systems, Inc., Sunnyvale, CA). The setup was operated with 50% delay factor, 100 Hz, and 5 msec for the pulse generator, and 0.4 V_{pp} for the amplifier. The system was turned on, with the tube immersed in the water bath,

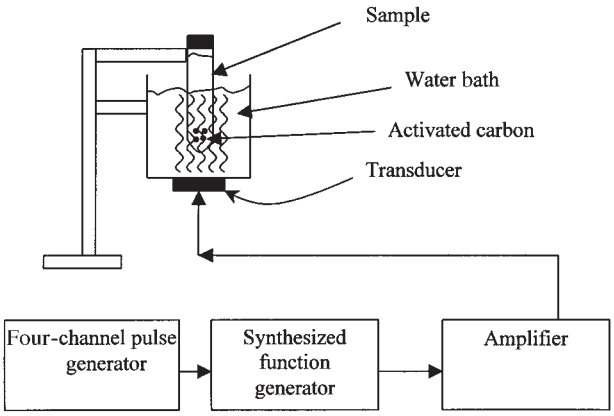

Figure 1. Ultrasonic desorption: experimental setup.

and timing was started simultaneously. Samples were taken from the tube at different time intervals and the concentration of the aromatic compound in the samples was measured. The amount of adsorbate that desorbed from the carbon surface during that time period was then calculated from a mass balance. The experiment was repeated using five samples for each carbon–adsorbate combination. Experimental error was found to be within 5%, and the average value for the five samples is reported.

RESULTS AND DISCUSSION

Surface Area and Pore Size Distribution

Shown in Table 1 are the total surface area and micropore area of all carbons used in this study, as obtained using N_2-BET measurements. Surface area measurements were repeated at least twice for each carbon, and the reproducibility of measurements was found to be very good, with less than 5% variation between measurements. Average surface area values are reported. It is recognized that the use of the BET method for obtaining micropore area is suspect.[21] This is due in part to the fact that nitrogen adsorption is much stronger in the micropores, compared to meso- or macropores, making its description by the capillary condensation theory debatable. Therefore, the micropore areas reported in Table 1 are used solely for qualitative comparison of the effect of different treatment methods, rather than to absolutely quantify the surface area.

The data shown in Table 1 suggest that for all carbons used the majority ($>$60%) of the surface area occurs in the microporous zone. This is expected

Table 1. Surface area and microporosity of carbons.

Carbon	BET total surface area (m^2/g)	Micropore area (m^2/g)	Microporosity (%)
DI	1,158	922	79.6
AIR	1,153	873	75.7
1M	1,010	808	80
4M	1,008	721	71.5
12M	594	391	65.8
N800	1,098	881	80.2
N1000	1,030	829	80.5
X800	1,119	693	61.9
X1000	987	618	62.6

for such a high surface area ($>950\,m^2/g$) activated carbon. Oxygenation of DI carbon had a pronounced effect on both total surface area and microporosity. While oxidation with air did not change the surface area or microporosity, oxidation with nitric acid had a more severe effect. As indicated by Table 1, both surface area and microporosity were decreased as the strength of oxidizing acid solution was increased. The strongest effect was observed for the 12 M carbon, where the strong acid solution was found to reduce the surface area by 50%. It is believed that oxidation with 12 M HNO_3 caused some carbon pores to collapse, especially in the microporous zone, resulting in the observed effects. This effect is described in more detail by other researchers.[22] To test for steric effects, due to surface oxygen groups affecting penetration of N_2 to the micropores,[23] surface area measurements were repeated for 4 M and 12 M carbons after deoxygenating these carbons in N_2 at 800°C. It was found that the surface area for 4 M increased by approximately 10% (X800), while the area of 12 M dropped by approximately 15%. Although this indicates some steric effect for the 4 M carbon as one possible explanation, it also indicates that the low surface area of 12 M is probably due to the destruction of micropores caused by the concentrated HNO_3 acid solution. Therefore, subsequent studies were not performed on the 12 M carbon.

Carbon deoxidation of DI was also found to influence surface area and microporosity. Deoxygenation of DI in N_2 at 800°C and 1000°C (N800 and N1000, respectively) resulted in 5 to 12% reduction in total surface area, but no apparent influence on the microporosity. This reduction in area can be attributed to the possible collapse of some of the pores due to the high temperature used. The large reduction in microporosity observed for X800 and X1000, in contrast, is attributed to the initial oxygenation step (DI to 4 M) rather than the subsequent deoxygenation.

Surface Groups

Shown in Table 2 are the concentrations of acidic oxygen groups, including carboxylic, phenol, and lactone groups, and basic surface groups for all the carbons used in this study. The amount of these groups, expressed in mmol per gram carbon, was obtained by Boehm titration.

From Table 2, the original carbon stock, DI, has a basic surface with a small amount of phenol acidic groups. As expected, oxygenation of DI was found to increase the amount of acidic oxygen groups, with stronger oxygenation resulting in a larger concentration of these groups. For example, 4 M has more carboxylic, phenol, and lactone groups than the 1M carbon, which, in turn, has more groups than AIR. Table 2 also shows that oxygenation

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Table 2. Boehm characterization of surface groups.

Carbon	Carboxyl groups (mmol/g)	Lactone groups (mmol/g)	Phenol groups (mmol/g)	Total acidic groups (mmol/g)	Basic groups (mmol/g)
DI	0	0	0.11	0.11	0.45
AIR	0.23	0.425	0.225	0.88	0.21
1M	0.46	0.55	0.27	1.28	0.13
4M	1.11	0.82	0.58	2.51	0.05
N800	0	0	0.11	0.11	0.5
N1000	0	0.05	0.15	0.2	0.5
X800	0	0.11	0.15	0.26	0.53
X1000	0	0.08	0.16	0.24	0.6

reduced the total amount of basic groups on the surface. Deoxygenation of DI to produce N800 and N1000, and of 4M to produce X800 and X1000, was found to increase the basic surface groups. This agrees with data reported by other researchers,[24,25] who attributed the increased basicity to the delocalization of the π-electrons of the basal planes. It is interesting to observe, however, that deoxygenation slightly increases the amount of some acidic groups, particularly the phenol and lactone groups. This could be due to the lack of stability of deoxygenated surface sites, which were apparently oxygenated despite storage under nitrogen; dissolved oxygen in the titration solution may be providing a source of oxygen for these active sites. Finally, deoxygenated X800 and X1000 have more acidic groups than the corresponding N800 and N1000 carbons, consistent with expectations, since the former are prepared from the more acidic (4M) starting material.

Adsorption Isotherms

To investigate the role of H-bonding in adsorption, the isotherms in Fig. 2 were measured. These were generated in aqueous medium at 23°C. It is observed that the adsorption capacity for phenol is inversely related to the concentration of surface acidic oxygen groups (see Table 2). DI, which has the minimum acidic groups concentration (0.11 mmol/g), showed the highest capacity for phenol. N800 and N1000 have slightly higher surface acid concentrations than DI, and a slightly lower adsorption capacity. The lowest capacity was observed for 4 M, which has the highest concentration of acidic groups (2.51 mmol/g). These results agree with the reported findings of other researchers.[6,26]

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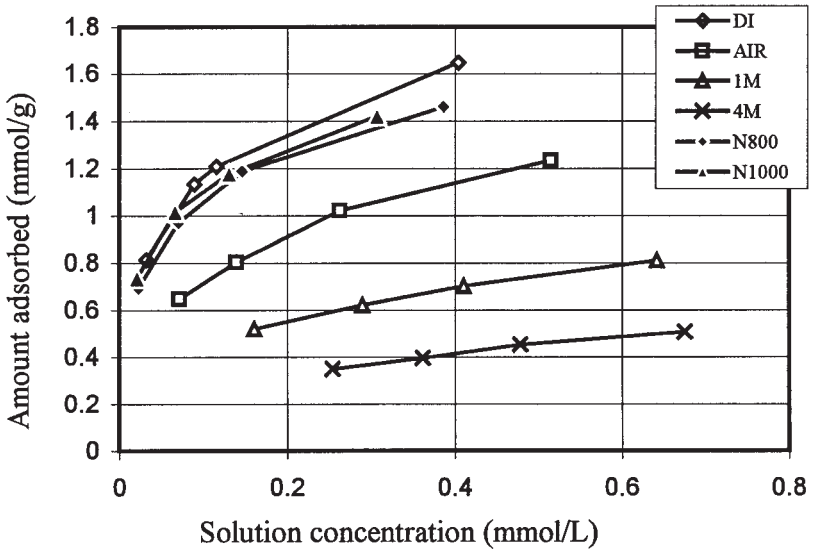

Figure 2. Phenol isotherms in aqueous solution.

To more clearly show the effect of acidic oxygen groups on capacity for phenol in aqueous solution, the adsorbed concentration at 0.4 mmol/L solution concentration was plotted vs. the total concentration of surface acidic oxygen groups in Fig. 3 (aqueous). Figure 3 includes the capacities for X800 and X1000, which are not shown in Fig. 2 for clarity. The total acidic groups concentration was obtained by summing the amounts of carboxylic, phenol, and lactone groups in Table 2; 0.4 mmol/L was picked because it is a concentration covered in all the isotherms. The data in Fig. 3 clearly indicate a linear decrease in capacity with increasing concentration of surface acidic groups. This behavior has been explained[8,9,11,14] by water adsorption. Acidic oxygen groups, generally located at the entrance of micropores in the carbon structure,[5] are involved in H-bonding with water molecules of the adsorption medium. This H-bonding involves polar oxygen from the surface acidic groups and the hydrogen of the water molecules. Further, water adsorption can proceed around this initially adsorbed water molecule, via H-bonding, to form water clusters surrounding the surface oxygen sites. These water clusters are postulated to reduce accessibility to the micropores, reducing the overall adsorption capacity.

In the absence of competitive water adsorption, the picture is quite different. Shown in Fig. 4 are adsorption isotherms for phenol in cyclohexane medium. In this case, the effect of acidic oxygen groups is the opposite, as can

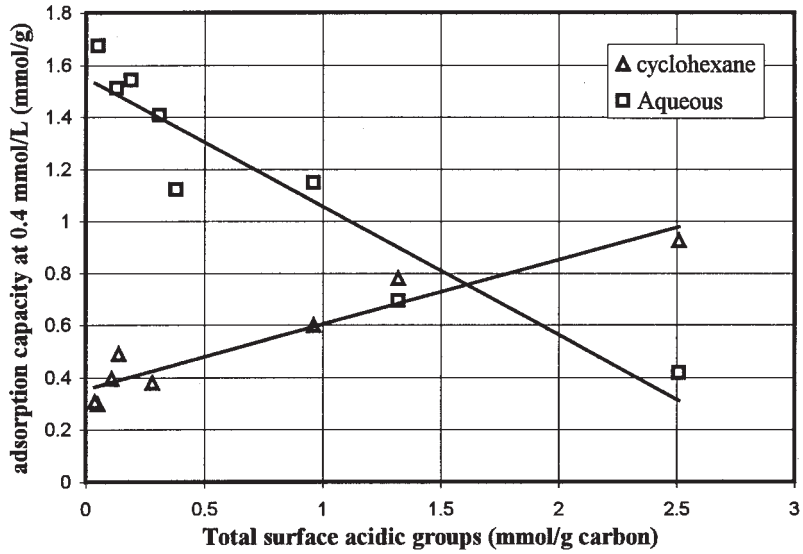

Figure 3. Effect of surface acidic groups on phenol adsorption.

be seen clearly in Fig. 3 (cyclohexane). There is a linear increase in capacity with increasing concentration of total surface acidic groups, and 4M has the highest capacity. In the absence of water adsorption, adsorption of phenol through H-bonding is postulated as the dominant influence. Hydrogens in the phenol hydroxyl group (—OH) are proposed to be involved in H-bonds with the polar oxygens on the surface. Increasing the amount of acidic surface oxygen groups, therefore, leads to the increase in capacity observed.

Two other observations can be drawn from Fig. 3. At the lower range of surface oxygen concentration (i.e., lower than 0.5 mmol/g), adsorption capacity for phenol is higher in aqueous solution than in cyclohexane. This is due to the fact that cyclohexane, a neutral and hydrophobic compound, effectively covers part of the basal plane system of the carbon, reducing phenol adsorption on these sites. Also, it is observed that the surface coverage does not exceed, at its highest value, 15% of the BET surface area. Surface coverage, in this case, was calculated assuming that phenol is adsorbed in a planar position on the carbon surface, with a phenol molecular diameter of 5.2 Å. Such a low surface coverage indicates that the majority of microporosity is not accessible to the phenol molecules, and the main adsorption is in meso- and macropores and on the oxygen groups. This conclusion is supported by data in Fig. 3. It is observed that increasing the concentration of surface oxygen groups from 0 to 2.5 mmol/g results in an adsorption capacity increase

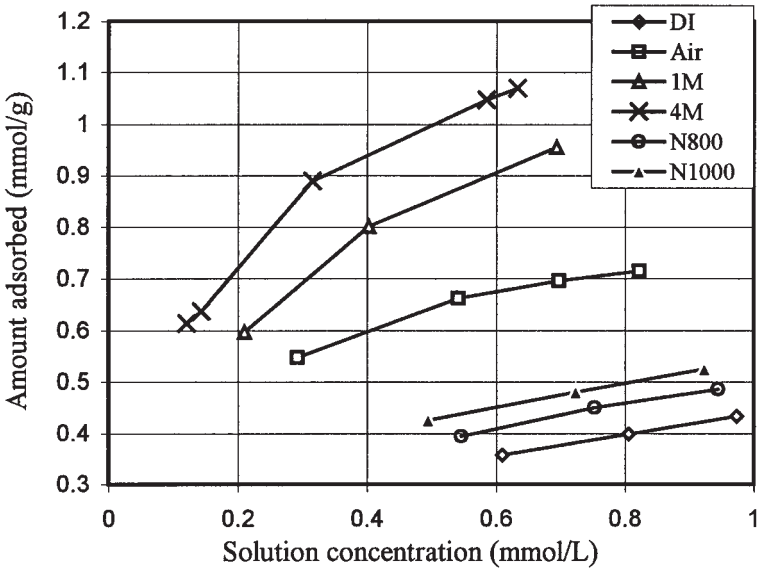

Figure 4. Adsorption isotherms for phenol in cyclohexane.

for phenol from 0.3 to 1.0 mmol/g, strongly suggesting that oxygen groups are primary sites for phenol adsorption.

Further support for H-bonding was obtained by studying the adsorption of aniline, which is also capable of H-bonding. Adsorption isotherms for aniline in cyclohexane on various carbons are shown in Fig. 5. It can be seen that the adsorption capacity trends for aniline are very similar to those for phenol. Increasing the amount of surface acidic oxygen groups was found to increase the adsorption capacity. The amine ($—NH_2$) functional group of aniline is postulated to be involved in a H-bond with surface oxygen, although the strength of aniline's H-bond is less than that for phenol. A plot of adsorption capacity at 0.4 mmol/L solution concentration vs. the amount of surface acidic groups (Fig. 6) shows a linear trend, similar to that obtained for phenol.

Finally, the adsorption of benzene, a molecule that cannot H-bond, was studied. Shown in Fig. 7 are adsorption isotherms for benzene in cyclohexane. With the exception of N800, which has a slightly higher capacity than DI, increasing the amount of acidic oxygen groups results in a reduced adsorption capacity. This is very clear for 4 M, which had a much lower capacity than the other carbons. For benzene adsorption in cyclohexane, both water adsorption and H-bonding mechanisms are eliminated. Other possible factors,[14] such as

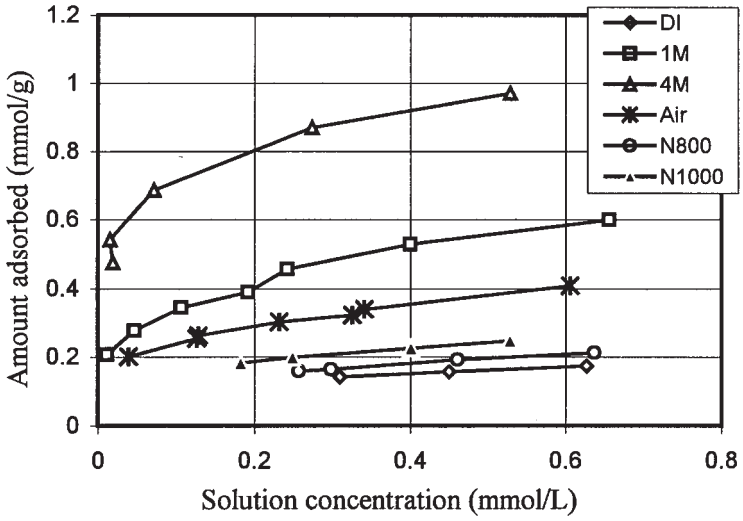

Figure 5. Adsorption isotherms for aniline in cyclohexane.

the effect of electron localization by surface groups on the dispersive interactions with the aromatic compound, can also be eliminated, since benzene is a neutral compound. The decrease in capacity with increasing surface acidity, observed in Fig. 7, can be explained on the basis of surface hydrophobicity. For a highly hydrophobic compound, such as benzene (octanol–water coefficient, $K_{ow} = 135$), it is to be expected that increasing the surface polarity with oxygen groups will reduce adsorption capacity. This phenomenon has been discussed in more detail elsewhere.[27] It is also observed in Fig. 7 that the adsorption capacity for benzene is an order of magnitude lower than that for phenol or aniline. This is also attributed to the lower affinity of benzene for the oxygenated carbon surface.

Flow Microcalorimetry and Ultrasonic Desorption

Both FMC and ultrasonic desorption techniques were utilized to further investigate H-bonding of aromatics on carbon. The basis is that compounds adsorbed via H-bonding will be more strongly (less reversibly) bound to the carbon surface than compounds adsorbed via dispersive forces.

Heat of adsorption and desorption of aniline and nitrobenzene were measured by FMC on N800, DI, and AIR, and the reversibility was quantified using Groszek's technique of dividing heat of desorption by heat of

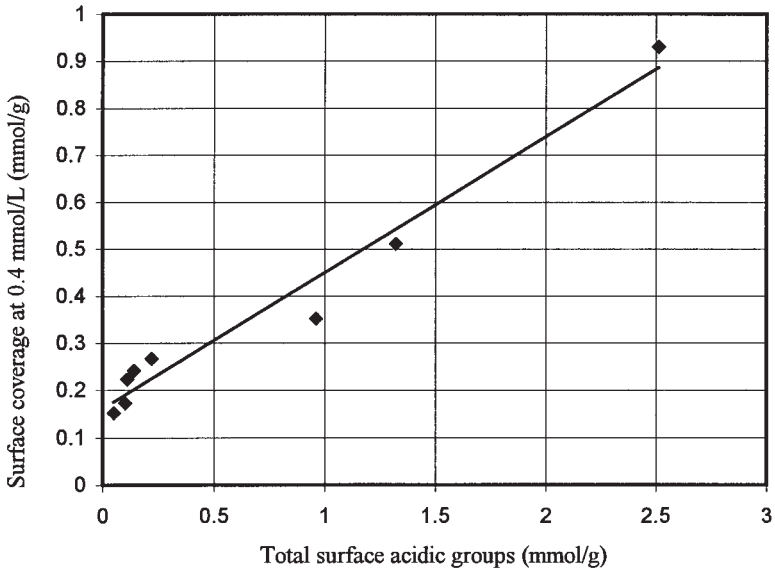

Figure 6. Effect of surface acidic groups on the adsorption of aniline in cyclohexane medium.

adsorption.[16] Nitrobenzene cannot hydrogen-bond with surface oxygen and is therefore expected to give a higher reversibility.

The heat obtained are shown in Table 3, and reversibility reported in Fig. 8. For both aniline and nitrobenzene, heats of adsorption are exothermic, and heats of desorption are endothermic, as expected. Franz et al.[14] showed that for nitrobenzene adsorption on activated carbon, repulsive interactions between nitrobenzene molecules (with a strong deactivating functional group) and the carbon basal planes increase with an increase in the amount of oxygen groups. This effect is caused by the localization of π-electrons of the basal planes by oxygen groups, which creates positive "islands" in the basal plane system. It is, therefore, anticipated that the heat of adsorption of nitrobenzene should decrease with increased surface oxygenation. Table 3 shows a lower heat of adsorption for nitrobenzene on DI, compared to N800, although these carbons have similar acidic and basic group concentrations (see Table 2). Also, the heat of adsorption on the more oxygenated carbon, AIR, is larger than that for DI, opposite to the expected trend. Boehm titration data alone appear to be inadequate to interpret these results. An explanation for the reduction in heat of adsorption for N800 and DI can be found in linear temperature

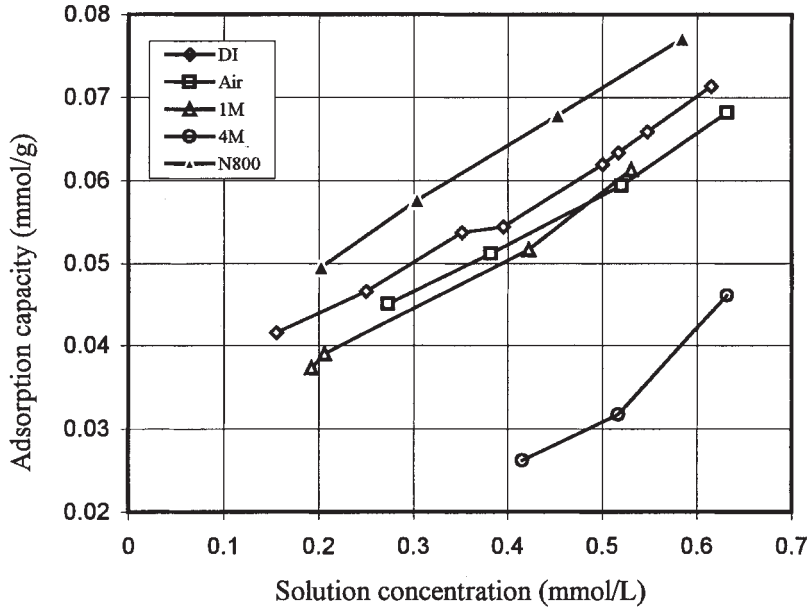

Figure 7. Adsorption isotherms for benzene in cyclohexane.

programmed desorption (LTPD) data reported earlier.[13] These data show a difference in total acidic oxygen concentration of 0.395 mmol/g between DI and N800, with DI having the higher concentration, consistent with the FMC data. It is postulated that this difference is due to carbonyl oxygen groups, which cannot be detected by the Boehm titration method.

Table 3. Heat of adsorption and desorption of aniline and nitrobenzene on N800, DI, and AIR carbons from cyclohexane solution.[a,b]

	Aniline		Nitrobenzene	
Carbon	Heat of adsorption (J/g adsorbed)	Heat of desorption (J/g adsorbed)	Heat of adsorption (J/g adsorbed)	Heat of desorption (J/g adsorbed)
N800	−50	39	−51	55
DI	−147	135	−41	41
AIR	−355	64	−111	108

[a]Exothermic heats are presented with a negative sign.
[b]Experimental error is ±5%.

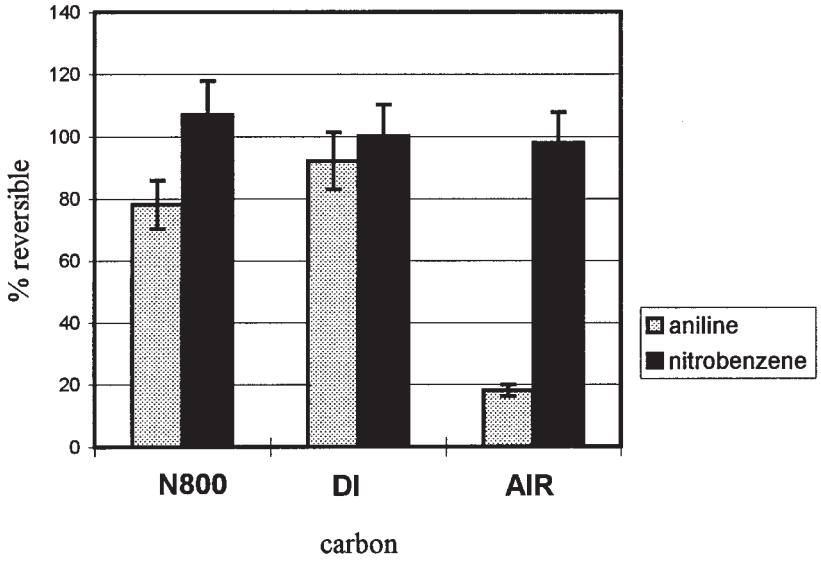

Figure 8. FMC reversibility test for aniline and nitrobenzene.

The reason for the increase in heat of adsorption from DI to AIR is not clear. It may be due to differences in microporosity of these carbons. It is possible that the lower microporosity (and, consequently, the higher meso- and macroporosity) of AIR (see Table 1) is the cause of this increase. A recent study[28] established a correlation between adsorption energy and carbon mesopore volume. It was found that adsorption energy increased with mesopore volume, which was argued to indicate that mesopores facilitate the adsorption of solute in the inner and narrow micropores, which contain adsorptive sites with higher adsorption energies.

For nitrobenzene, a non-H-bonding compound, the reversibility of adsorption was close to 100% for both DI and AIR, as observed in Fig. 8. For aniline, an H-bonding compound, reversibility was found to be less than 100%. Moreover, with significant amounts of acidic oxygen groups on the surface, as in AIR, the reversibility was only 18%. These results indicate that aniline adsorbs more strongly than nitrobenzene. Also, the strength of the adsorption bond increases by increasing surface oxygenation. These two observations suggest the existence of an H-bond for aniline, which is stronger than the dispersive interactions that are dominant for nitrobenzene.

Ultrasonic desorption of phenol and benzene from DI, AIR, and 4M carbons was also studied to determine the differences in adsorption strength. Figures 9 and 10 show, respectively, the percentage of phenol and benzene

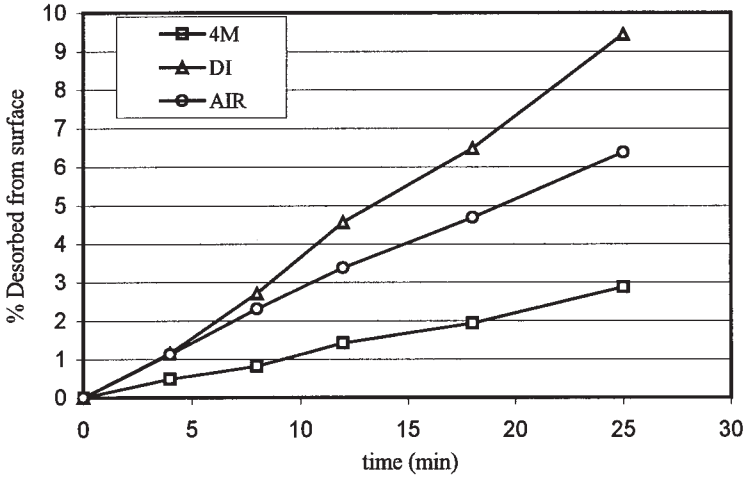

Figure 9. Ultrasonic desorption of phenol.

desorbed from the carbon surface over 25 minutes of exposure to ultrasonic waves. The different trends observed for these adsorbates are indicative of a fundamental difference. Phenol desorption is clearly dependent on the concentration of surface acidic oxygen groups, with less desorption observed for higher surface oxidation. Benzene, on the other hand, shows no dependence on surface oxygen concentration. Also, for all three carbons, and at any specific ultrasonic exposure time, the amount of phenol desorbed was found to be much lower than that of benzene. These observations are also consistent with the presence of H-bonding in phenol adsorption. The lower reversibility of phenol adsorption suggests a stronger adsorption bond for phenol compared to benzene. This stronger adsorption is proposed to be due to the H-bond between phenol molecules and surface oxygen groups.

CONCLUSION

Hydrogen bonding between functional groups on aromatic adsorbates and activated carbon surface oxygen groups was investigated. Adsorption of compounds with H-bonding groups, phenol and aniline, and non-H-bonding groups, nitrobenzene and benzene, was studied on carbons with different surface oxygen concentrations. It was found that in an aqueous medium, H-bonding of aromatic adsorbates was ineffective due to competitive water

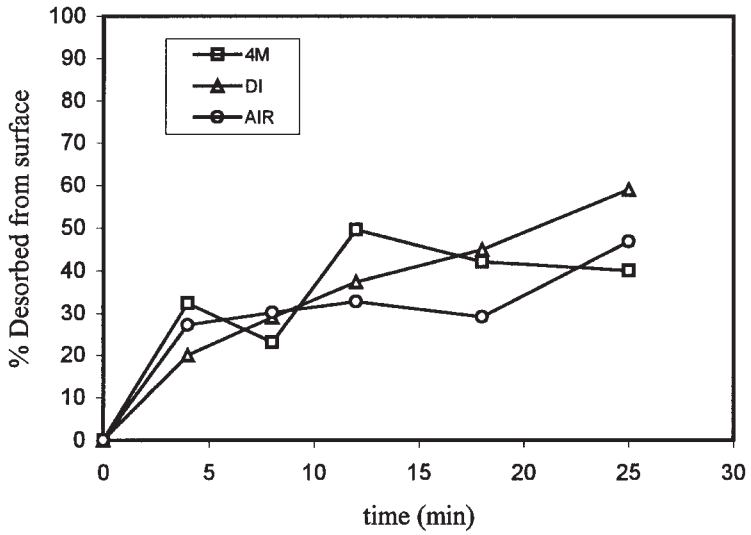

Figure 10. Ultrasonic desorption of benzene.

adsorption, which caused a reduction in adsorption capacity as the concentration of acidic surface oxygen groups was increased. In cyclohexane medium, on the other hand, the adsorption capacity for H-bonding compounds increased linearly with the concentration of surface acidic groups. This was not observed for non-H-bonding compounds. The influence of H-bonding is further supported with calorimetric and ultrasonic desorption data. These techniques have shown that adsorption reversibility is lower for aromatics that can H-bond and is reduced as surface acidic groups are increased.

ACKNOWLEDGMENTS

The authors are grateful to Professor Peter Nagy, from the Aerospace Engineering Department, University of Cincinnati, for providing the experimental setup for the ultrasonic desorption experiments. This work was supported by the National Science Foundation GOALI Grant No. BES 9930739, co-sponsored by Calgon Carbon Corporation and E.I. DuPont deNemours. This support is gratefully acknowledged.

REFERENCES

1. Radovic, L.; Moreno-Castilla, C.; Rivera-Utrilla, J. Carbon materials as adsorbents in aqueous solutions. In *Chemistry and Physics of Carbon*; Radovic, L., Ed.; Marcel Dekker: New York, 2001; Vol. 27.
2. Martin, R.J.; Ng, W.J. Chemical regeneration of exhausted activated carbon—I. Wat. Res. **1984**, *18* (1), 59–73.
3. Sontheimer, H.; Crittenden, J.; Summers, R.S. The production and physical-chemical evaluation of activated carbon. In *Activated Carbon for Water Treatment*; DVGW-Forschungsstelle: Germany, 1988.
4. Weber, W.J.; McGinley, P.; Katz, L. Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport. Wat. Res. **1991**, *25* (5), 499–528.
5. Puri, B.R. Surface complexes on carbon. In *Chemistry and Physics of Carbon*; Walker, P.L., Ed.; Marcel Dekker: New York, 1993; Vol. 6, 191–282.
6. Coughlin, R.W.; Ezra, F. Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. Environ. Sci. Technol. **1968**, *2* (4), 292–297.
7. Dubinin, M.M. Porous structures and adsorption properties of active carbon. In *Chemistry and Physics of Carbon*; Walker, P.L., Ed.; Marcel Dekker: New York, 1966; Vol. 2.
8. Mahajan, O.; Moreno-Castilla, C.; Walker, P.L. Surface-treated activated carbon for removal of phenol from water. Sep. Sci. Technol. **1980**, *15* (10), 1733–1752.
9. Arafat, H.A.; Franz, M.; Pinto, N.G. Effect of salt on the mechanism of adsorption of aromatics on activated carbon. Langmuir **1999**, *15* (18), 5997–6003.
10. Lee, W.H.; Reucroft, P.J. Vapor adsorption on coal- and wood-based chemically activated carbons (I) surface oxidation states and adsorption of H_2O. Carbon **1999**, *37* (1), 7–14.
11. Muller, E.A.; Gubbins, K.E. Molecular simulation study of hydrophilic and hydrophobic behavior of activated carbon surface. Carbon **1998**, *36* (10), 1433–1438.
12. Mattson, J.S.; Mark, H.B.; Malbin, M.D.; Weber, W.J.; Crittenden, J.C. Surface chemistry of active carbon: specific adsorption of phenol. J. Col. Interface Sci. **1969**, *3* (1), 116–130.
13. Leng, C.C. Mechanism of adsorption and desorption of oxygen and nitrogen containing aromatics on activated carbon. University of Cincinnati: Cincinnati, OH, USA, 1996; Ph.D. Dissertation.
14. Franz, M.; Arafat, H.A.; Pinto, N.G. Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon. Carbon **2000**, *38* (13), 1807–1819.

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15. Groszek, A.J.; Partyka, S. Measurements of hydrophobic and hydrophilic surface sites by flow microcalorimetry. Langmuir **1993**, *9* (10), 2721–2725.
16. Groszek, A.J. Irreversible and reversible adsorption of some heavy transition metals on graphitic carbons from dilute aqueous solutions. Carbon **1997**, *35* (9), 1329–1337.
17. Liu, D.; Aoyama, I.; Okamura, H.; Dutka, D. Enhancement of toxicant release from sediment by sonication and sodium ligninsulfonate. Environ. Toxicol. Water Qual. **1996**, *11* (3), 195–203.
18. Rege, S.U.; Yang, R.T.; Cain, C.A. Desorption by ultrasound: phenol on activated carbon and polymeric resin. AIChE J. **1998**, *44* (7), 1519–1528.
19. Qin, W.; Yuan, Y.; Dai, Y. Studies on the "spot energy effect" of ultrasound, Proc. China/USA Chem. Eng. Conf. Vol. II, Chem. Ind. Eng. Soc. (China), Beijing, 1997; 666.
20. Boehm, H.P. Chemical identification of surface groups. In *Advances in Catalysis*; Academic Press: New York, 1966; Vol. 16, 179–374.
21. Stoeckli, H.F. Microporous carbons and their characterization—the present state-of-the-art. Carbon **1990**, *28* (1), 1–6.
22. Moreno-Castilla, C.; Carrasco-Marin, F.; Maldonado-Hodar, F.J.; Rivera-Utrilla, J. Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content. Carbon **1998**, *36* (1–2), 145–151.
23. Rodriguez-Reinoso, F.; Molina-Sabio, M.; Munecas, M.A. Effect of microporosity and oxygen-surface groups of activated carbon in the adsorption of molecules of different polarity. J. Phys. Chem. **1992**, *96* (6), 2707–2713.
24. Barton, S.S.; Evans, M.J.; Halliop, E.; MacDonald, J.A. Acidic and basic sites on the surface of porous carbon. Carbon **1997**, *35* (9), 1361–1366.
25. Lopez-Ramon, M.V.; Stoeckli, F.; Moreno-Castilla, C.; Carrasco-Marin, F. On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon **1999**, *37* (8), 1215–1221.
26. Nevskaia, D.M.; Santianes, A.; Munoz, V.; Guerrero-Ruiz, A. Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study. Carbon **1999**, *37* (7), 1065–1074.
27. Ahnert, F.; Arafat, H.A.; Pinto, N.G. Effects of hydrophobicity on the adsorption of aromatics on activated carbon in non-aqueous medium. Adsorption J **2003**, *9* (4), 311–319.
28. Hsieh, C.T.; Teng, H. Influence of mesopore volume and adsorbate size on adsorption capacities of activated carbons in aqueous solutions. Carbon **2000**, *38* (6), 863–869.

Received October 2002
Revised July 2003