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A Study of the Influence of Hydrophobicity of Activated Carbon on the Adsorption Equilibrium of Aromatics in Non-Aqueous Media

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Abstract. The effect of hydrophobicity on the adsorption of aromatics on metal-free activated carbons was studied. Adsorption isotherms for phenol, aniline, benzene, and xylene were generated in cyclohexane and heptane media, using seven carbons with different surface heterogeneity. The hydrophobicity of these carbons was probed using flow microcalorimetry (FMC). Surface polarity and solvent and adsorbate hydrophobicity were found to influence the adsorption capacity. For adsorbates that do not form hydrogen bonds with oxygen on the carbon surface, higher surface acidity lowers adsorption capacity due to increased polarity. In contrast, for adsorbates that can form hydrogen bonds with surface oxygen, the capacity is enhanced at higher surface acidities. A higher solvent hydrophobicity was found to decrease capacity for all the aromatic adsorbates studied, except at high surface polarity, where the effect of the solvent was found to be minimal.

Keywords: activated carbon, adsorption, aromatics, isotherms

Introduction

Activated carbon has been used as an adsorbent for a very long time. Despite its wide use, the adsorption mechanisms of organics on carbon, and the effects of surface properties on these mechanisms, are not sufficiently understood. It is generally believed (Puri, 1970; Leon y Leon and Radovic, 1994; Radovic et al., 2001) that the heterogeneity of the activated carbon surface, particularly the surface oxygen groups, contributes significantly to its adsorption capacity. These groups, although present in relatively small amounts, affect many surface properties. These include surface acidity (Menendez et al., 1999; Leon y Leon et al., 1992; Boehm, 1994), polarity or hydrophobicity (Groszek and Partyka, 1993; Groszek, 1997), and surface charge (Arafat et al., 1999).

In an aqueous adsorption medium, the presence of heterogeneous oxygen groups on the carbon surface was found to reduce the adsorption capacity (Franz et al., 2000; Nevskaia et al., 1999; Coughlin and Ezra, 1968). This effect is attributed to water adsorption on these groups via H-bonding. In an organic adsorption medium, other mechanisms become dominant. These include H-bonding between the functional group of the aromatic adsorbate and surface groups (Arafat et al., 2003; Franz et al., 2000). Other mechanisms, such as dispersive/repulsive interactions, and the effects of

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surface oxygen groups on these interactions, have also been investigated (Franz et al., 2000). Additional mechanisms such as the donor-acceptor interactions between the adsorbate and surface oxygen groups have been suggested (Mattson et al., 1969).

In this study, the effect of hydrophobicity on the adsorption of aromatics on oxygenated and deoxygenated activated carbons is reported. Using combinations of organic solvents and solutes and carbons with different amounts of surface oxygen groups, the effects of carbon surface polarity on the adsorption capacity for aromatic compounds with different degrees of polarity was determined.

Experimental

Surface Treatment of Activated Carbon

In this study, Kureha G-70R spherical Bead Activated Carbon (0.7 mm diameter) was used. This carbon was purchased from Kureha Chemical Industry Company (NY, USA). The G-70R carbon, which is made from petroleum pitch, is metal-free. Previous tests on these carbons (Leng, 1996) have indicated that polymerization of aromatics such as phenol and aniline does not occur on the carbon surface, even under oxic solution conditions. The G-70R carbon was conditioned upon receiving by boiling in de-ionized water for one hour, then drying in an oven at 110°C for 24 hours. This carbon is referred to as G-70R-DI.

To study the influence of surface oxygen groups on adsorption, G-70R-DI was oxygenated with air in a tubular furnace (model 55035, Lindberg Co., Watertown, WI) at 350°C under a constant air flow of 100 L/h. A 3 g sample was placed in a quartz container, which was then placed in the furnace for 60 minutes under a constant flow of air. The sample was then cooled to room temperature in air. This oxygenated carbon will be referred to as G-70R-AIR. It was observed that air 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 net carbon loss.

The G-70R-DI carbon was also oxygenated with 1M and 4M nitric acid solutions. These oxygenated carbons are referred to as G-70R-1M and G-70R-4M, respectively. Carbon oxygenation by HNO_3 was achieved by boiling 1 g G-70R-DI in 10 ml acid solution of the desired concentration (1 M or 4 M) for 1 hour. The solution was then cooled and decanted, and the carbon was washed repeatedly with DI water to remove any acid residuals. After each wash with DI water, the water pH was measured to check for HNO_3 residuals. When a neutral, constant pH was achieved, the washing was stopped and the carbon was dried in a vacuum oven at 115°C for 24 hours.

Deoxygenated carbon was obtained by heating the G-70R-DI carbon to 800°C in a tubular furnace under a constant flow of nitrogen (100 L/h) for one hour. This was followed by cooling to room temperature under a flow of nitrogen, and storage in a nitrogen atmosphere. This deoxygenated carbon is referred to as G-70R-N800. Two other deoxygenated carbons were produced by deoxygenating the G-70R-4M carbon at 800°C and 1000°C, using the procedure described above, to give G-70R-X800 and G-70R-X1000, respectively.

Characterization of Surface Groups

The amounts of acidic and basic surface groups were quantified using the Boehm titration method (Boehm, 1966). 0.25 g of dry 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 shaking for 24 hours on a G24 Environmental Incubator shaker (280 rpm under 23°C), 20 ml of the solution were back-titrated using 0.05 N HCl. The amounts of $NaCH_3CH_2O$ and $NaHCO_3$ reacted were used to calculate the total number of acidic groups (phenol, lactone, and carboxylic groups) 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 titration with 0.1 N HCl, back-titrated with 0.05 N NaOH. Despite following the standard procedure (Boehm, 1966) for surface group characterization, it should be kept in mind that the molecular size and diffusivity of the aromatic molecules are likely to be different from those of the reagents used in the Boehm characterizations. Nonetheless, since most heterogeneous surface groups are located at the external edges (mouths) of the micropores (due to the presence of free-valence carbon atom at these edges), the interaction of the aromatic molecule with the carbon surface is strongly related to the amount of heterogeneous groups, as characterized in this work.

Effects of Aging

These tests were performed to examine the stability of both acidic and basic surface groups of the deoxygenated carbons, under atmospheric conditions. After preparing the carbons, 3 g of dry G-70R-DI, G-70R-N800, G-70R-X800, and G-70R-X1000 were placed in separate open bottles and exposed to air at 23°C. After 3 weeks of exposure, samples were dried at 115°C in a vacuum oven (26″Hg) for one hour to remove any adsorbed moisture. Boehm titrations were then performed on the samples, as described earlier.

Surface Area Measurement

The BET surface area was measured with an ASAP 2010 Micromeritics apparatus using nitrogen at 77.3 K. 0.05 g of carbon were degassed at 200°C and a pressure of 2 mm Hg prior to nitrogen adsorption. The pore size distribution was calculated using the Barrett, Joyner and Halenda (BJH) method (ASTM D4641-94).

Measurements of Carbon Surface Polarity

Surface polarity (or hydrophilicity) was estimated using a technique that was introduced by Groszek and Partyka (1993). They proposed that the fraction of the area occupied by hydrophobic sites is correlated to the heat of adsorption of n-butanol on the carbon surface initially covered with water. Similarly, the area of hydrophilic sites can be estimated from the heat of n-butanol adsorption on a surface that is initially immersed in heptane, a highly hydrophobic adsorbate.

A flow microcalorimeter (FMC), model 3vi (Microscal Ltd., London, UK), was used to obtain heats of adsorption. A detailed description of the apparatus is given by Groszek (1997) and Groszek and Partyka (1993). The FMC cell was filled with 10 mg of carbon. The dry adsorbent in the cell was evacuated to 0.2 mm Hg at 25°C for a period of 12 hours to ensure the removal of any air or moisture from the carbon pores. The point of complete moisture removal was detected by the attainment of a steady thermal signal by the FMC detector. This was further confirmed by introducing a thermal pulse in the adsorbent compartment, after which the original thermal baseline was re-attained, indicating complete moisture removal. Heptane or DI water was then introduced into the cell. The solvent (water or heptane) was percolated through the sample at the rate of 3.3 ml per hour. After the attainment of thermal equilibrium, the flow was switched from solvent (water or heptane) to a solution of 2 g/l 1-butanol in the same solvent. The thermal signal due to the adsorption of butanol was measured.

Adsorption Isotherm Measurements

Equilibrium adsorption isotherms were determined using the bottle point method, following the ASTM standard procedure (ASTM D3860-89a). Adsorption isotherms were generated at room temperature (23°C) using cyclohexane or heptane as the adsorption solvent. Pre-weighed amounts of carbon were placed in 50-ml bottles with two blank solution bottles (no carbon) to test for evaporation. Each point on the isotherm is the average of three bottle measurements. Variation between the data points generated from the three bottles was found to be within ±5%. The adsorption solutions were prepared by dissolving the adsorbate in the organic solvent, with initial adsorbate concentration ranging from 50 to 200 mg/L. The bottles were then filled with 50 ml of solution, leaving no headspace to minimize evaporation, and covered with aluminum foil and caps, and then placed in a mechanical shaker for a period of seven days. This time was found to be adequate for equilibration based on preliminary kinetic studies. After equilibration, a UV-spectrophotometer (Shimadzu, UV160U) was used to measure the adsorbate concentration in the solution. The equilibrium amount adsorbed on the carbon was then calculated with a mass balance.

Results and Discussion

Heterogeneous Surface Groups and Aging Effects

Shown in Table 1 are the concentrations of acidic oxygen groups, including carboxylic, phenol, and lactone groups, and basic surface groups for all the G-70R carbons used. The original carbon stock, G-70R-DI, has a predominantly basic surface with only a small amount of acidic groups. As expected, oxygenation of G-70R-DI increased the amount of acidic oxygen groups, with stronger oxygenation resulting in a larger

Table 1. Quantification of surface oxygen groups on G-70R carbons.

Carbon	Carboxyl groups (mmol/g)	Lactone groups (mmol/g)	Phenol groups (mmol/g)	Total acidic groups (mmol/g)	Total acidic groups (mmol/m^2) × 10^4	Basic groups (mmol/g)	Summation of acidic and basic groups (mmol/g)
G-70R-DI	0	0	0.11	0.11	1.0	0.45	0.56
G-70R-N800	0	0	0.11	0.11	1.0	0.5	0.61
G-70R-X800	0	0.11	0.15	0.26	2.3	0.53	0.79
G-70R-X1000	0	0.08	0.16	0.24	2.4	0.6	0.84
G-70R-AIR	0.23	0.43	0.23	0.88	7.7	0.21	1.09
G-70R-1M	0.46	0.55	0.27	1.28	12.7	0.13	1.42
G-70R-4M	1.11	0.82	0.58	2.51	24.9	0.05	2.56

concentration of these groups. For example, G-70R-4M has more carboxylic, phenol, and lactone groups than the G-70R-1M carbon, which, in turn, has more of these groups than G-70R-AIR. Oxygenation was also found to remove basic groups from the surface.

Deoxidation of G-70R-DI to produce G-70R-N800, and of G-70R-4M to produce G-70R-X800 and G-70R-X1000, was found to increase the basic surface groups, which is mainly due to the nitrogen added to the surface. It is interesting to observe, however, that deoxidation slightly increases the amount of some acidic groups, particularly the phenol and lactone groups. This increase in phenol and lactone groups in the deoxygenated carbon is the subject of further investigation, which will be presented in a future publication. Finally, deoxygenated G-70R-X800 has more acidic groups than G-70R-N800, consistent with expectations, since the former is prepared from the more acidic (G-70R-4M) starting material.

Table 2 summarizes the effects of aging on surface groups. Shown in Table 2 are the differences, before and after aging, in the total amounts of acidic and basic groups, and in the amounts of both lactone and carboxylic groups, for the three-week-aged deoxygenated carbons. For all carbons, no significant difference in the amount of carboxylic groups could be detected upon aging. Therefore, these amounts are not included in Table 2. This indicates that carboxylic groups were highly stable and do not increase with air exposure at room temperature. In fact, a strong oxidizer, such as nitric acid, is needed to create surface carboxylic groups.

Table 2. Effects of aging on the amounts of surface groups.

Carbon	Change in amount of lactone and carboxylic groups after aging (%)	Change in amount of total acidic groups after aging (%)	Change in amount of total basic groups after aging (%)
G-70R-DI	NA	80	2
G-70R-N800	50	10	2
G-70R-X800	18	73	−4
G-70R-X1000	38	121	−8

Table 2 shows that aging caused the total basic groups concentration to decrease, except for G-70R-DI and G-70R-N800, for which an increase of 2% was observed. Since 2% is close to the experimental error of the Boehm titration method, one can generalize that aging causes either no change or a slight decrease (up to 8%, for G-70R-X1000) in the total amount of surface basic groups, indicating that these groups are relatively stable under atmospheric conditions.

It is also observed in Table 2 that the total amount of acidic groups increases for all carbons by at least 10%, and up to 120% in some cases. A significant portion of this increment is believed to be due to lactone and phenolic groups, based on the data in Table 2.

Since the reduction in the amount of basic groups is smaller than the corresponding increase in acidic groups, it can be concluded that new acidic groups are created on the surface (not necessarily from existing basic groups).

Surface Area

Shown in Table 3 are the surface areas of the carbons studied. It was observed that oxidizing with HNO_3 and treatment with nitrogen at 1000°C reduced the surface area to approximately 1000 m^2/g. All other treatments resulted in carbons with surface areas very similar to that of the source (DI) with values between 1100 and 1150 m^2/g.

Table 3. Surface area, microporosity, and surface polarity for G-70R carbons.

Carbon	Total BET surface area (m^2/g)	Micropore area (m^2/g)	Microporosity (%)	Heat of butanol adsorption from water (mJ/g)	Heat of butanol adsorption from heptane (mJ/g)	Non-polar surface area (% of total area)
G-70R-DI	1160	922	79.6	41060	3652	99
G-70R-N800	1100	881	80.2	36754	5704	98
G-70R-X800	1120	693	61.9	23464	13365	93
G-70R-X1000	990	618	62.6	25537	8899	96
G-70R-AIR	1150	873	75.7	24236	10185	95
G-70R-1M	1010	808	80.0	10356	17836	81
G-70R-4M	1010	721	71.5	2247	37554	31

Eighty percent of the surface of the G-70R-DI carbon is in micropores. Oxidation generally reduced the fraction of micropore area (possibly due to partial condensation of the micropores), and G-70R-X800 and G-70R-X1000 were observed to have the lowest microporous surface area. It is worth mentioning, however, that the total surface area, as measured using the BET technique, does not necessarily present the area accessible to the adsorbate molecules used in this study. This is due to a number of factors including molecular size and diffusivity of the adsorbate molecules.

Effect of Heterogeneous Groups on Surface Polarity

Heats of adsorption of 1-butanol from water and n-heptane were measured using FMC for all seven G-70R carbons used in this study, and are listed in Table 3. These data were used to calculate the fraction of polar area on the carbon surface shown in Table 3.

With the exception of G-70R-4M, the FMC characterization indicates that the majority of the carbon surface for all the carbons studied is composed of non-polar sites, or basal planes sites. In general, the degree of polarity corresponds to the total acidic groups concentration on the surface (Table 1). G-70R-DI and G-70R-N800 have the lowest polar surface fraction and the lowest acidity per unit area ($\approx$1E-4 mmol/m^2). G-70R-X1000 and G-70R-X800 have similar polarity and surface acidity. Also, G-70R-AIR, G-70R-1M, and G-70R-4M have progressively higher polarity, consistent with increasing surface acidity. The one exception to this general pattern is the relative polarity of G-70R-AIR to that of G-70R-X800. Based on surface acidity, it is expected that G-70R-AIR have a higher polar surface fraction than indicated by FMC measurements.

Effects of Hydrophobicity on Adsorption Capacity

In order to investigate the effects of hydrophobicity on adsorption capacity, studies were performed using adsorbates and solvents with different hydrophobic characteristics. Cyclohexane and heptane were utilized as solvents. Phenol, aniline, benzene, and xylene were used as adsorbates. The octanol-water distribution coefficient (K_{ow}) was used as a quantitative measure of hydrophobicity. K_{ow} values for the six organic compounds used in this study are listed in Table 4. A higher K_{ow} value indicates a more hydrophobic material.

Shown in Fig. 1 are adsorption isotherms for benzene from cyclohexane on five carbons. These indicate an inverse relationship between adsorption capacity and the surface acidity or, equivalently, polarity. Previous studies (Franz et al., 2000; Arafat et al., 2003) have suggested that H-bonding between aromatic adsorbates and surface groups, as well as dispersive/repulsive interactions between functional groups on the aromatic adsorbate and the carbon surface, are key factors that influence capacity variations. However, the trend in Fig. 1 cannot be explained on this basis, since benzene

Table 4. Octanol-Water coefficient for solutes and solvents studied (CRC, 1991).

Compound	Octanol-Water distribution coefficient (K_{ow})
Aniline	8
Phenol	32
Benzene	135
Xylene	1,413
Cyclohexane	2,754
Heptane	31,623

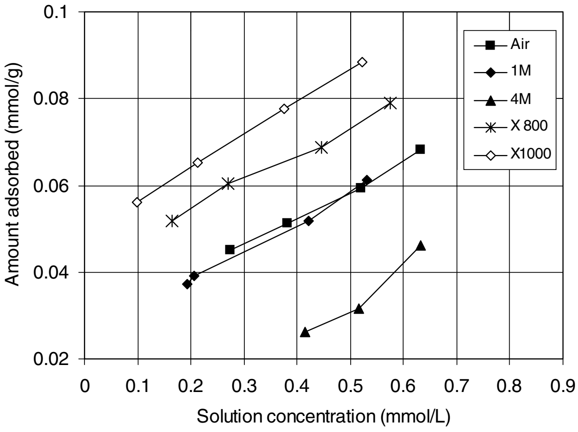

Figure 1. Adsorption isotherms for benzene in cyclohexane on G-70R carbons.

cannot H-bond and has no functional group. Furthermore, there is no correlation between the variations in capacity observed and the variations in the BET surface area (Table 3). The observed trend is due to the changes in the hydrophobicity of the surface. The strongly hydrophobic benzene ($K_{\mathrm{ow}} = 135$) has a lower affinity for adsorption when the polarity of the surface is increased. Since, as was discussed earlier, the polarity generally correlates to the number of acid groups, it is expected that the capacity of benzene will, at least roughly, correlate with the surface acid concentration. This is found to be the case as shown in Fig. 2, which shows a plot of the normalized adsorption capacity (defined as the amount adsorbed at 0.4 mmol/L divided by the BET surface area) versus total acid group concentration. Figure 2 shows an inverse, linear relation between total surface acidity and the amount adsorbed per unit area. This shows a strong effect of surface acidity on benzene adsorption.

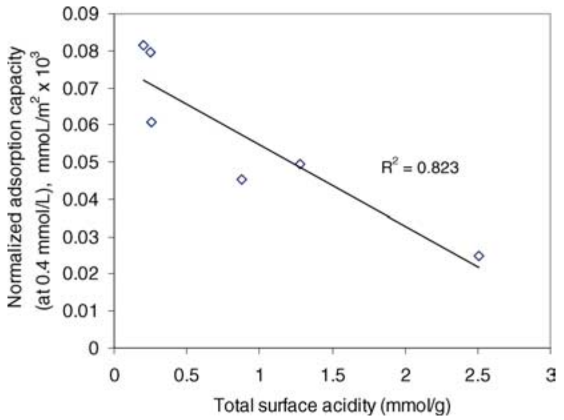

Figure 2. Relation between surface acidity and adsorption capacity of benzene from cyclohexane.

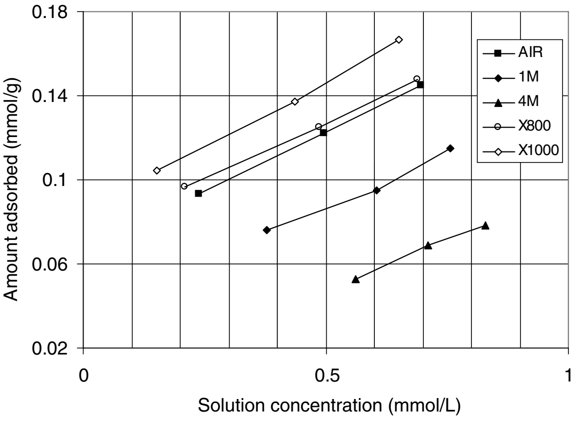

Figure 3. Adsorption isotherms for xylene in cyclohexane on G-70R carbons.

Adsorption isotherms were also measured in cyclohexane for xylene, a highly hydrophobic ($K_{\mathrm{ow}} =$ 1,413), non H-bonding molecule. These isotherms are shown in Fig. 3. The trend for xylene is similar to that observed for benzene. Adsorption capacity is shown to be inversely related to the surface oxygen concentration, and, consequently, to surface polarity. When comparing the adsorption capacities for benzene and xylene (Figs. 1 and 3), it is noticed that all five carbons have a higher capacity for xylene than benzene. However, the difference in capacity is smaller for G-70R-1M, and much smaller for the G-70R-4M carbon. This behavior can also be explained on the basis of hydrophobicity. Since the major fraction of surface of the G-70R carbons is non-polar (Table 3), the capacity for the more hydrophobic xylene is higher than for benzene for all five carbons. The highly oxidized carbons, G-70R-1M and G-70R-4M, do, however, have a significant polar surface fraction, which leads to a reduced difference in capacity between benzene and xylene.

Adsorption isotherms for xylene were also measured in heptane, and are shown in Fig. 4. Four significant features are observed. First, the adsorption capacities for xylene decrease with surface oxygenation, consistent with expectations. Secondly, the adsorption capacities for xylene are lower in heptane (Fig. 4) than in cyclohexane (Fig. 3), with the difference being smallest for the highly oxygenated G-70R-4M. Heptane is very hydrophobic ($K_{\mathrm{ow}} = 31{,}623$) compared to cyclohexane

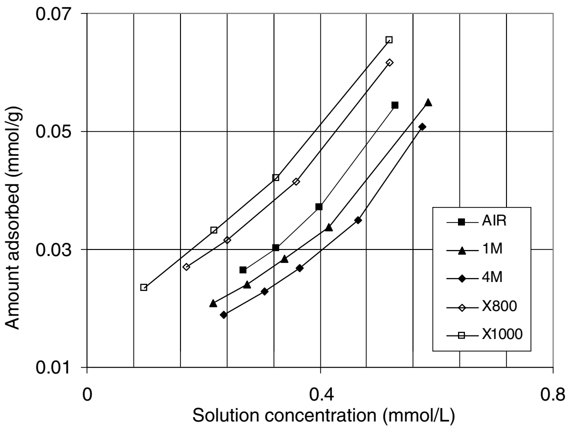

Figure 4. Adsorption isotherms for xylene in heptane on G-70R carbons.

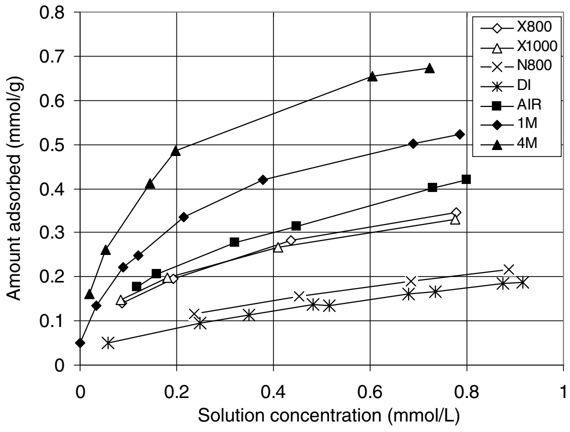

Figure 6. Adsorption isotherms for phenol in heptane on G-70R carbons.

($K_{ow} = 2{,}754$). Thus, heptane competes more effectively with xylene for the hydrophobic basal plane sites. For G-70R-4M, with its more polar surface, the influence of solvent hydrophobicity is reduced and capacities from cyclohexane and heptane are similar. In this case, the adsorption of the hydrophobic solvent becomes less favorable and the effect of the solvent is minimized. It is also worth noting that changes in capacity for xylene with surface oxygenation are smaller in the presence of heptane. This is also due to the higher affinity of heptane for the non-polar adsorption sites.

Adsorption isotherms were generated for phenol in cyclohexane and heptane. These are displayed in Figs. 5 and 6, respectively. In both cyclohexane and heptane, increasing surface oxygenation was found to increase the adsorption capacity, opposite to the trend observed for benzene and xylene. For a H-bonding molecule such as phenol, H-bonding with surface oxygen is a dominant mechanism of adsorption, in the absence of water. This is discussed in depth elsewhere (Arafat et al., 2003). Increasing the amount of surface oxygen groups will increase the number of sites available for H-bonding and, consequently, the adsorption capacity. This is further supported by adsorption isotherms for aniline, shown in Fig. 7 for cyclohexane medium, and in Fig. 8 for heptane medium, where adsorption capacity increases with surface oxygenation. Aniline has the functional group (—NH_2), which is capable of H-bonding with surface oxygen. Both aniline and phenol have a higher adsorption capacity when adsorption

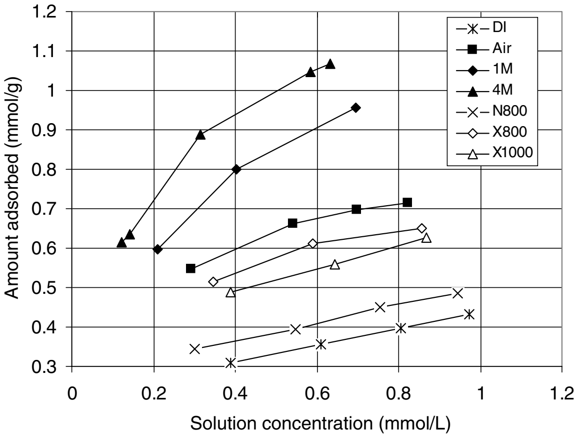

Figure 5. Adsorption isotherms for phenol in cyclohexane on G-70R carbons.

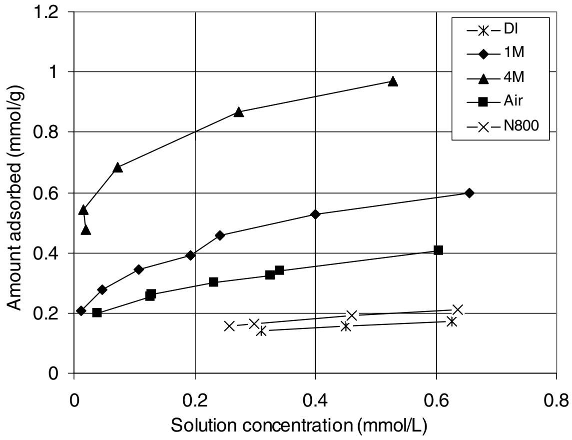

Figure 7. Adsorption isotherms for aniline in cyclohexane on G-70R carbons.

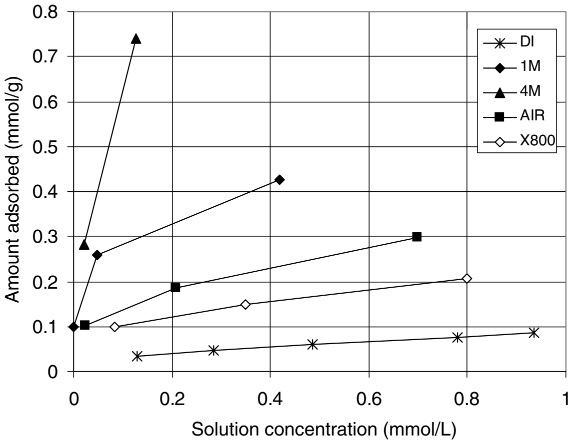

Figure 8. Adsorption isotherms for aniline in heptane on G-70R carbons.

takes place in cyclohexane, compared to heptane. The same interpretation for benzene and xylene data holds true for phenol and aniline. The higher hydrophobicity of heptane causes this solvent to strongly adsorb on the non-polar basal planes, reducing the availability of these adsorption sites.

Finally, by comparing adsorption capacities for phenol and aniline in cyclohexane and heptane media (Figs. 5–8), phenol is generally shown to have a higher adsorption capacity than aniline in both solvents. This is postulated to be due to the fact that phenol is more hydrophobic (Table 4) and has a stronger H-bonding functional group than aniline. This makes phenol a stronger adsorbent on both polar (oxygen) and non-polar (basal planes) sites. The stronger H-bonding property of the hydroxyl (—OH) group of phenol makes it capable of bonding with weaker polar sites, such as lactone groups. The difference in adsorption capacity between phenol and aniline is smallest for the highly oxygenated carbons G-70R-1M and G-70R-4M. It is suspected that the surplus of oxygen groups with strong polarity (such as carboxylic groups) that exist on the carbon surface result in similar capacities for aniline and phenol, because they minimize the influence of the difference in H-bonding strength of phenol and aniline.

Summary and Conclusions

The adsorption of phenol, aniline, benzene, and xylene on oxygenated and deoxygenated activated carbons was studied. The chemical heterogeneity of the carbons was characterized with Boehm titrations and flow microcalorimetry. Adsorption isotherms were measured from two solvents: cyclohexane and heptane. Based on these data, it was concluded that the adsorption capacity for the aromatics is strongly influenced by three factors: the surface acidity, hydrophobicity of the adsorbate, and hydrophobicity of the solvent. For aromatics that cannot hydrogen bond with surface oxygen, surface acidity influence the adsorption by changing the degree of polarity of the activated carbon. As surface acidity increases, surface polarity increases and adsorption capacity is lowered. For aromatics that can hydrogen bond with the surface, the effect is the opposite. In this case, increased oxygen leads to higher capacity because of additional hydrogen bonding sites. In general, for both H-bonding and non H-bonding aromatic adsorbates, the capacity is reduced in the presence of a more hydrophobic solvent, except for strongly oxygenated surfaces. In this case, the effect of the solvent on capacity is minimal.

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References

Arafat, H., M. Franz, and N. Pinto, "Effect of Salt on the Mechanism of Adsorption of Aromatics on Activated Carbon," *Langmuir*, **15**(18), 5997–6003 (1999).

Arafat, H., F. Ahnert, and G. Pinto, "Additional Evidence for Hydrogen Bonding of Aromatics on Oxygenated Activated Carbon," *Sep. Sci. & Tech.*, in press (2003).

Boehm, H., "Chemical Identification of Surface Groups," *Adv. Catal.*, **16**, 179 (1966).

Boehm, H., "Some Aspects of the Surface-Chemistry of Carbon-Blacks and Other Carbons," *Carbon*, **32**(5), 759–769 (1994).

Coughlin, R. and F. Ezra, "Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon," *Environ. Sci. Technol.*, **2**(4), 292–297 (1968).

CRC, *Handbook of Chemistry and Physics*, 71st ed., pp. 16–25, CRC Press, 1991.

Franz, M., H. Arafat, and N. Pinto, "Effect of Chemical Surface Heterogeneity on the Adsorption Mechanism of Dissolved Aromatics on Activated Carbon," *Carbon*, **38**(13), 1807–1819 (2000).

Groszek, A. and S. Partyka, "Measurements of Hydrophobic and Hydrophilic Surface Sites by Flow Microcalorimetry," *Langmuir*, **9**, 2721 (1993).

Groszek, A., "Irreversible and Reversible Adsorption of Some Heavy Transition Metals on Graphitic Carbons from Dilute Aqueous Solutions," *Carbon*, **35**, 1329–1405 (1997).

Leng, C.C., "Mechanisms of Adsorption and Desorption of Oxygen and Nitrogen Containing Aromatics on Activated Carbon," Ph.D. Dissertation, University of Cincinnati, Cincinnati, OH, 1996.

Leon y Leon, C. and L. Radovic, in *Chemistry and Physics of Carbon*, P. Thrower (Ed.), vol. 24, Mercel Dekker, New York, 1994.

Leon y Leon, C., J. Solar, V. Calemma, and L. Radovic, "Evidence for the Protonation of Basal-Plane Sites on Carbon," *Carbon*, **30**(5), 797–811 (1992).

Mattson, J., H. Mark, M. Malbin, W. Weber, and J. Critten, "Surface Chemistry of Active Carbon: Specific Adsorption of Phenol," *J. Col. Interface Sci.*, **3**(1), 116–130 (1969).

Menendez, J., D. Suarez, E. Fuente, and M. Montes-Maron, "Contribution of Pyrone-Type Structures to Carbon Basicity: Theoretical Evaluation pf the pKa of Model Compounds," *Carbon*, **37**(6), 1002–1006 (1999).

Nevskaia, D., A. Santianes, V. Munoz, and A. Guerrero-Ruiz, "Interaction of Aqueous Solutions of Phenol with Commercial Activated Carbons: An Adsorption and Kinetic Study," *Carbon*, **37**(7), 1065–1074 (1999).

Puri, B., in *Chemistry and Physics of Carbon*, P. Walker (Ed.), vol. 6, Mercel Dekker, New York, 1970.

Radovic, L., C. Moreno-Castilla, and J. Rivera-Utrilla, "Carbon Materials as Adsorbents in Aqueous Solutions," in *Chemistry and Physics of Carbon*, L. Radovic (Ed.), vol. 27, Mercel Dekker, New York, 2001.

Xie, F., J. Phillips, I. Silva, M. Palma, and A. Menendez, "Microcalorimetric Study of Acid Sites on Ammonia- and Acid-Pretreated Activated Carbon," *Carbon*, **38**(5), 691–700 (2000).