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Effect of Surface Oxygen Complexes of Activated Carbon on Phenol Adsorption from Single and Mixed Non-Aqueous Solvents

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ABSTRACT

The effects of heterogeneous oxygen groups of activated carbon on the adsorption of dissolved phenol in single and mixed solvents have been studied. Cyclohexane, heptane, and mixtures of cyclohexane and heptane with different volumetric ratios have been used as solvents. Solvent hydrophobicity, the capability of the molecules to H-bond, and dispersive/repulsive interactions were found to be the main factors that affect the adsorption capacity. In a homogeneous mixed solvent, all phenol isotherms were very close to the pure heptane rather than pure cyclohexane isotherm for the untreated carbon, which has the lowest surface oxygen concentration. However, as the concentration of surface

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oxygen increases, phenol isotherms from the mixed solvents are more evenly distributed. It is suggested that selective segregation of the different solvents molecules (cyclohexane and heptane) can occur in the adsorbed phase based on differences in hydrophobicity between solvent molecules.

Key Words: Adsorption; Activated carbon; Multicomponent; Phenol; Hydrophobic mixed solvents.

INTRODUCTION

Activated carbon (AC) has been used widely in decontamination processes and hazardous waste treatment because of its unique adsorption characteristics, which originate from its porous structure, surface area, and surface chemical properties. The adsorption capacity of a given AC depends on the complicated interactions between the adsorbent, the adsorbate, and the solvent. Normally the affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption. However, the affinity between the adsorbate and the solvent can also play a major role in adsorption.[1]

Effect of Carbon Surface Oxides

Heterogeneous oxygen groups bonded to the edges of the graphitic basal plane[2,3] have been reported in the literature to have a significant effect on the adsorption capacity of aromatic compounds on activated carbon. Many mechanisms have been suggested to explain this effect. Water clusters, which mainly form on carboxylic groups by H-bonding, can hinder the penetration of aromatic molecules into the micropores.[4–7] On the other hand, oxygen groups can enhance the adsorption capacity in the absence of water by forming H-bonds with the aromatics.[8] Franz et al.[9] contend that oxygen groups influence dispersive/repulsive interactions between the basal planes and the adsorbed molecules by attracting and localizing electrons. If the functional group attached to the aromatic adsorbate is an activating group, such as $-OH$ and $-NH_2$, this interaction enhances the dispersive forces with the basal planes and hence, increases the adsorption capacity. However, if the functional group is deactivating, such as $-NO_2$, this will result in weakened interactions and, thus, reduced adsorption capacity.

Effect of Solvent Hydrophobicity

To study the effect of solvent hydrophobicity on the adsorption of aromatic compounds, Arafat et al.[10] used cyclohexane and heptane as solvents with a number of aromatic adsorbates. They found that adsorption capacities for hydrophobic aromatic compounds (i.e., benzene and xylene) are lower in heptane than in cyclohexane. This is due to the competition between the hydrophobic solute and solvent molecules for the non polar sites. Since heptane ($K_{ow} = 31{,}623$) is far more hydrophobic than cyclohexane ($K_{ow} = 2754$) or any of the solutes used, heptane molecules are expected to occupy a significant portion of the hydrophobic basal plane site. The difference in capacity between cyclohexane and heptane media was found to be minimal for the highly oxygenated carbon, indicating a very minimal effect of the solvent hydrophobicity at high surface oxygen concentration.

Mixed Solvents Effect

Understanding the behavior of organic chemicals in complex solvent mixtures is essential in the treatment of mixed contaminant plumes originating from different sources since co-disposal of such contaminants can result in environmental problems at waste disposal sites.[11] Seippel et al.[12] studied the adsorption of binary liquid mixtures containing *n*-alkanes, cycloalkanes, and 1-alkanols on activated carbon. Extensive studies have been reported on the effect of mixed solvents on the sorption of organics by soil. Lee et al.[13] measured sorption of a few substituted phenols and several substituted carboxylic acids from methanol/water solutions; they studied the impact of several binary mixtures of water and various organic co-solvents including (actone, acetonitrile, methanol, and 1,4-dioxane) on the sorption of benzoic acid by a surface soil. Khodadoust et al.[14] investigated the desorption of pentachlorophenol from contaminated soils in mixed solvents of water and ethanol. The effect of methanol as a co-solvent with water on the sorption of naphthalene and diuron by organoclays was studied by Nzengung et al.[15]

A theoretical study of the adsorption behavior of gaseous water-methanol mixtures in slit activated carbon micropores was reported by Shevade et al.[16] They observed that water in the mixtures is preferentially adsorbed in activated carbon pores over a wide range of pressures, due to the stronger hydrogen bonding interactions, and except at lower pressures where methanol is the major component in the pore due to stronger dispersion interactions. The effect of hydrophobic mixed solvents on aromatic adsorption capacity of activated carbon has not been studied to our knowledge. The purpose of this work is to further the understanding of aromatic adsorption on activated carbon from single and mixed hydrophobic solvents.

EXPERIMENTAL

Materials

Kureha G-70R Spherical Bead Activated Carbon (0.7 mm diameter) purchased from Kureha Chemical Industry Company (New York, NY, USA) was used in all experiments. The G-70R carbon is made from petroleum pitch and is metal free. The carbon was boiled in de-ionized water for 1 hr and dried in an oven at 110 ± 5°C for 24 hr. This carbon is referred to as G-70R-DI. Part of this G-70R-DI carbon was oxygenated with 1 M or 4 M HNO_3 and is referred to as G-70R-1 M and G-70R-4M, respectively. 10 g of G-70R-DI were boiled in 100 ml of 1 M or 4 M HNO_3 solution for 1 hr with total condensation. After cooling, the solution was decanted and washed with DI water several times until a neutral, constant pH was achieved. The carbon was dried in a vacuum oven at 115°C for 24 hr. All the organic compounds used in this study were purchased from Fisher Scientific (Pittsburg, PA, USA) in the highest purity available; no further purification was performed.

Surface Area and Pore Size Distribution

The surface area of the carbons was measured using a Micromeritics Gemini 2360 (Norcross, GA, USA) BET apparatus after degassing the samples with helium. The pore-size distribution was measured using a Micromeritics ASAP 2010 BET machine with nitrogen, utilizing the Barrett, Joyner, and Halenda (BJH) method (ASTM D4641-94). Pore-size distribution calculations were performed automatically by the BET machine using the built-in BJH method. Table 1 shows the results of the BET test.

Table 1. Surface characterization of G-70R carbons.

Carbon	Surface area (m^2/g)	Micropore area (m^2/g)	Microporosity (%)	Total acidic groups (mmol/g)
G-70R-DI	1158	922	79.6	0.05
G-70R-1M	1010	808	80	1.35
G-70R-4M	1008	721	71.5	2.50

Adsorption Isotherms Measurements

Equilibrium adsorption isotherms were determined using the bottle point method, following ASTM standard procedure (ASTM D3860-89a). Adsorption isotherms were generated at 23 ± 1°C, using phenol as the adsorbate and either cyclohexane or heptane, or mixtures of cyclohexane and heptane as the adsorption solution medium. The initial phenol concentration was in the range 115 to 125 mg/L. 50 ml of the adsorbate solution was added to 50-ml bottles that contained preweighed amounts (0.01 to 0.12 g) of carbon. All samples were agitated for 7 days on G24 Environmental Incubator shaker (New Brunswick Scientific, Edison, NJ, USA) at 280 rpm to ensure that equilibrium was achieved. A UV-spectrophotometer (Milton Roy Company, Spectronic 1001) was used at 270 nm wavelength to measure the adsorbate concentration in the solution. A blank sample solution was used with every isotherm in order to account for adsorbate volatilization and adsorption on the walls of the tube.

Measurements of Surface Oxygen Groups Concentration

The total concentration of oxygen groups on the activated carbon surface was determined using Boehm titration.[17] 25 ml of 0.1 mol/L NaOH solution was added to 0.25 g activated carbon and shaken for 24 hr at 23 ± 1°C. 20 ml of this solution was then back titrated with 0.05 mol/L HCl solution. The results are summarized in Table 1.

RESULTS AND DISCUSSION

Effects of Surface Oxygen

It has been reported previously that oxygenation of DI carbon with 1 M and 4 M HNO_3 will result in an increase in the total number of acidic oxygen groups and a reduction in the total number of basic groups on the surface.[10] Furthermore, acidic groups were reported to account for more than 90% of the total surface oxygen groups.[10] Adsorption isotherms were measured for phenol in cyclohexane and heptane to study the effects of heterogeneous surface oxygen groups on the adsorption capacity of G-70R carbons in the presence of hydrophobic solvents. The isotherms are shown in Figs. 1 and 2. The adsorption capacity increases with increasing carbon surface oxygenation. This observation can be explained based on the adsorption mechanisms postulated by Franz et al.[9] In the absence of

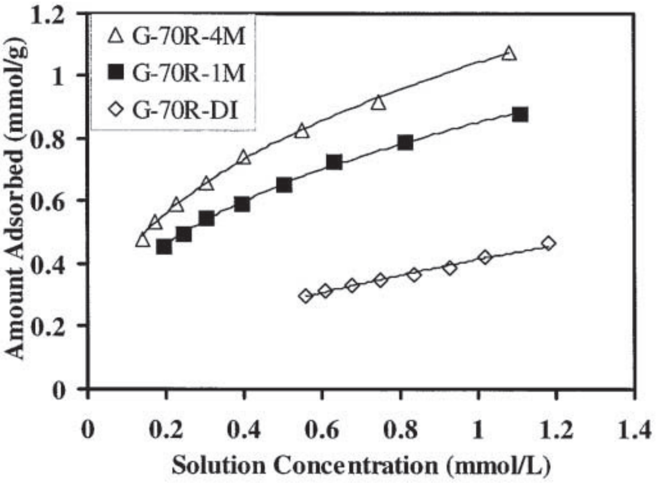

Figure 1. Adsorption of phenol on G-70R carbon in cyclohexane solution.

water, H-bonding with surface oxygen groups is a significant mechanism of adsorption for phenol molecules. The number of sites available for H-bonding increases with increasing surface oxygen groups concentration. Consequently, the adsorption capacity of activated carbon for phenol will increase. Also, the heterogeneous oxygen groups form partially positive

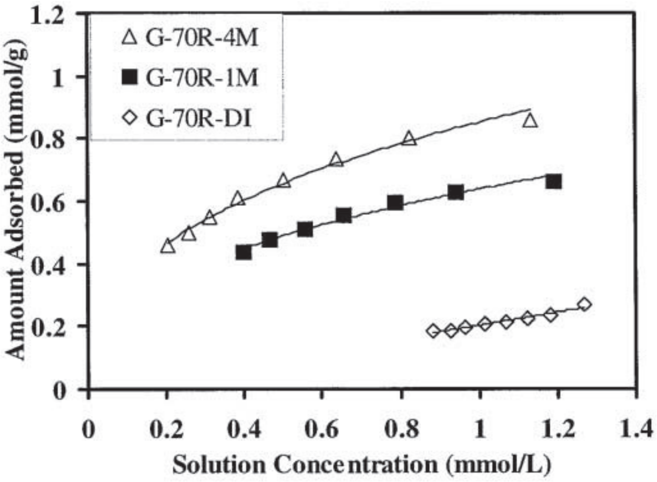

Figure 2. Adsorption of phenol on G-70R carbon in heptane solution.

islands in the basal planes by attracting and localizing the electrons around them.[18] The hydroxyl group (-OH) attached to the aromatic adsorbate is an activating group, which creates a partially negative benzene ring. The positive local islands created by the surface oxygen groups on the adsorbents will attract the partially negative benzene ring of the phenol molecules and, therefore, increase the adsorption capacity relative to G-70R-DI. It is noted that the increase in capacity observed in G-70R-1M and G-70R-4M relative to G-70R-DI cannot be explained by changes in surface area or pore size since both decrease with surface oxygenation, as shown in Table 1.

Effects of Solvent

To study the effects of solvent strength, adsorption isotherms for phenol were generated using mixtures of cyclohexane and heptane with different volumetric ratios. As for adsorption from a single hydrophobic solvent, the adsorption capacity of phenol increases as the amount of surface oxygen groups is increased for all solvent mixture ratios, as shown in Figs. 3–5. These results are consistent with H-bonding and/or the dispersive/repulsive interactions, as discussed earlier, significantly influencing the adsorption capacity. The effect of the solvent is more easily observed by comparing adsorption isotherms for each type of carbon at various solvent conditions, as in Figs. 6–8. It is seen

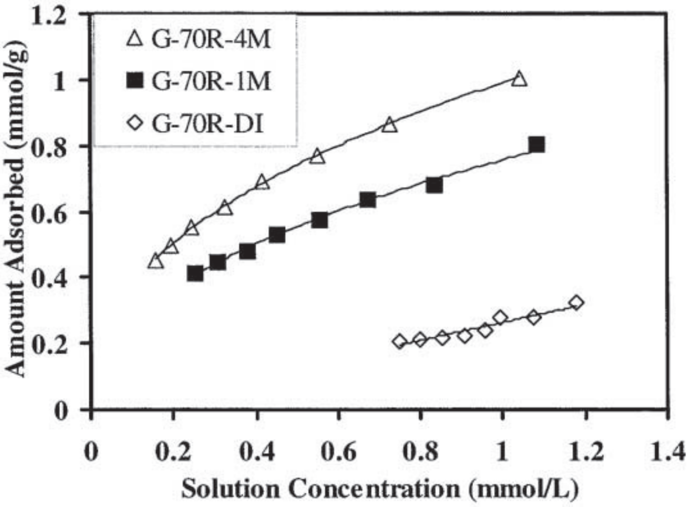

Figure 3. Adsorption of phenol on G-70R carbon in 75/25 (v/v) cyclohexane to heptane solution.

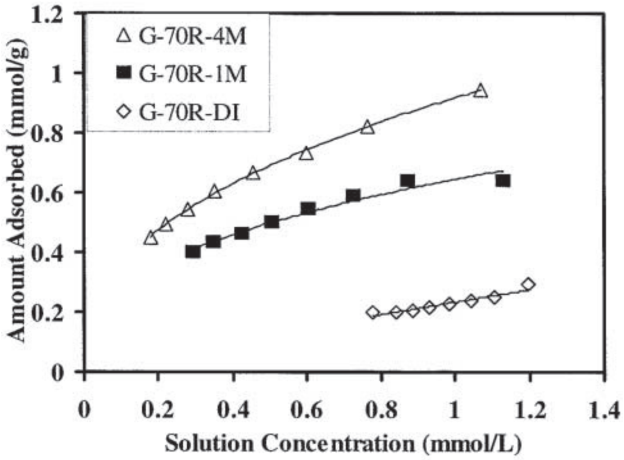

Figure 4. Adsorption of phenol on G-70R carbon in 50/50 (v/v) cyclohexane to heptane solution.

that the adsorption capacities on G-70R-DI carbon from all solvent mixtures are very close to the pure heptane isotherm. As the concentration of oxygen groups on the surface increases, the difference in capacity in pure cyclohexane and pure heptane is smaller. Also, the mixed solvents isotherms are more evenly distributed between the pure solvent limits for G-70R-1M and G-70R-4M.

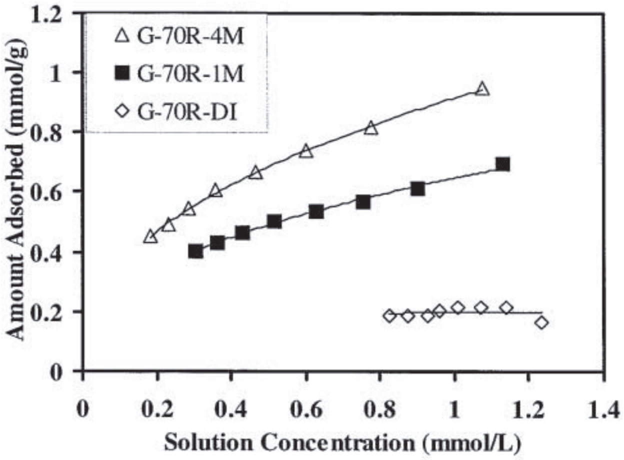

Figure 5. Adsorption of phenol on G-70R carbon in 25/75 (v/v) cyclohexane to heptane solution.

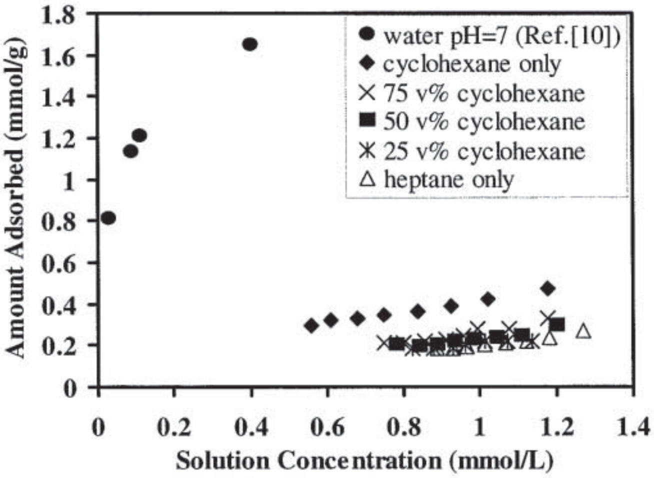

Figure 6. Effect of solution hydrophobicity on phenol adsorption (G-70R- DI carbon).

The observed trends with mixed solvents suggest that selective segregation of the solvent molecules occurs on the adsorbed phase. The more hydrophobic heptane is attracted more strongly than cyclohexane to the hydrophobic basal planes of activated carbon. Simultaneously, cyclohexane will be concentrated around the hydrophilic surface oxygen groups. At low surface

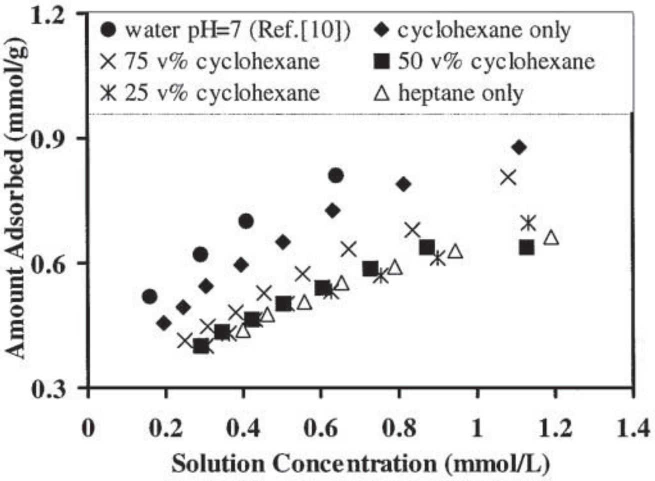

Figure 7. Effect of solution hydrophobicity on phenol adsorption (G-70R-1M carbon).

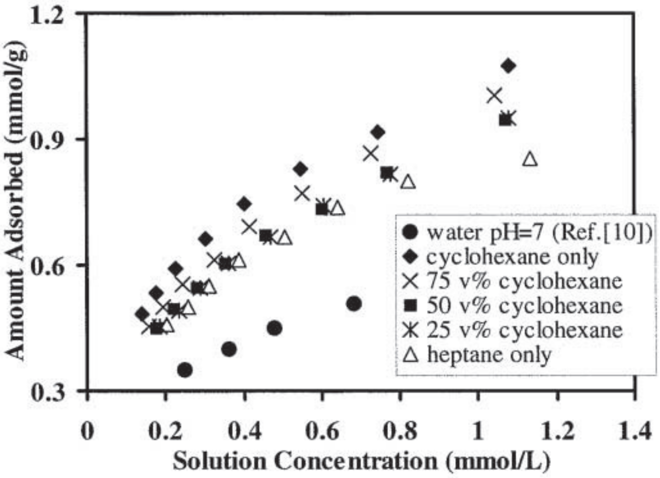

Figure 8. Effect of solution hydrophobicity on phenol adsorption (G-70R-4M carbon).

oxygen concentration (Fig. 6), the dominance of heptane in establishing capacity, even at high concentrations of cyclohexane (75 v%), indicates that basal plane sites are almost exclusively wetted by heptane. As the amount of oxygen increases (Figs. 7 and 8) the migration of the mixed solvent isotherms toward an even distribution between the pure component isotherms suggests that the oxygenated regions of the carbon surface are almost exclusively wetted by cyclohexane. These oxygenated sites are bonded to the edges of the graphitic basal plane.[2,3] Therefore, increasing the concentration of surface oxygen groups will significantly reduce the accessibility of heptane molecules to the basal plane. Also, as the concentration of cyclohexane in the mixed solvents increases, the size of cyclohexane clusters around the oxygen sites will increase, resulting in increased phenol adsorption. This segregation of solvents at the surface has a strong influence on the adsorption capacity.

Also, plotted on Figs. 6–8 are isotherms obtained in water; these are from Arafat et al.[10] It is interesting to note that the adsorption capacity in water for G-70R-DI is much higher than in cyclohexane and heptane. This is because the carbon basal planes form more than 90% of the carbon surface.[9] The phenol molecules ($K_{ow} = 32$) have a stronger affinity for the hydrophobic basal plane relative to water. On the other hand, at higher surface oxygen concentrations, the water cluster effect is stronger,[16] and a smaller fraction of the basal planes are accessible for phenol adsorption, leading to a lower adsorption capacity in water than in cyclohexane and heptane (Fig. 8). For all three types of carbon, the phenol adsorption capacity from cyclohexane is higher than from heptane. This is expected since heptane molecules are far more hydrophobic than either cyclohexane or phenol, and will compete more effectively for the non-polar sites of the basal planes.

Seippel et al.[12] reported surface excess isotherms of binary organic liquid solvents (no solute present) on activated carbons with different surface group concentrations at 25°C. The organic liquid mixtures used were classified into three groups: nonpolar–nonpolar, polar–nonpolar, and polar–polar. Their results showed that surface excess for nonpolar–nonpolar binary solvents decreased as the amount of polar surface groups increased. Also, the solvent with the smaller size and lower hydrophobicity was preferentially adsorbed. For polar–nonpolar solvents, higher overall adsorption capacity, as well as significantly higher affinity for the polar solvent was observed for activated carbon with high concentrations of oxygen. These results are consistent with observations in this study, and can be explained by the combined effects of basal plane adsorption and H-bonding, as was discussed earlier. However, for polar–polar solvent mixtures, Seippel et al.[12] reported that the surface excess for the highly polar solvent decreased as the acidic oxygen groups concentration increased. This behavior is not expected according to the postulated adsorption mechanisms and needs further investigation.

CONCLUSIONS

The adsorption capacity of phenol from single hydrophobic solvents, cyclohexane, and heptane, as well as from mixtures of cyclohexane and heptane on activated carbon was studied. It was observed that the phenol capacity increased with increasing the carbon surface oxygenation. Both dispersive/repulsive interactions and hydrogen-bonding are indicated as responsible mechanisms for this increase in carbon adsorption capacity. The experimental data suggest that for mixed hydrophobic solvents selective segregation of the solvent molecules can occur in the adsorbed phase, depending on difference in hydrophobicity between the solvent molecules and the carbon surface.

NOMENCLATURE

K_{ow}	Octanol-water distribution coefficient

REFERENCES

1. Furuya, E.; Chang, H.; Miura, Y.; Noll, K. A fundamental analysis of the isotherm for the adsorption of phenolic compounds on activated carbon. Sep. Purif. Technol. **1997**, *11*, 69.

2. Thomas, J. Microscopic studies of graphic oxidation. In *Chemistry and Physics of Carbon*; Walker, P., Ed.; Marcel Dekker: New York, 1965; Vol. 1.
3. Henning, G. Electron microscopy of reactivity changes near lattice defects in graphite. In *Chemistry and Physics of Carbon*; Walker, P., Ed.; Marcel Dekker: New York, 1966; Vol. 2.
4. Coughlin, R.; 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.
5. Mahajan, O.; Morena-Castilla, C.; Walker, P. Surface-treated activated carbon for removal of phenol from water. Sep. Sci. Technol. **1980**, *15*, 1733–1752.
6. Oda, H.; Kishida, M.; Yokokawa, C. Adsorption of benzoic acid and phenol from aqueous solution by activated carbons—effect of surface acidity. Carbon **1981**, *19*, 243–248.
7. Nevskaia, D.; 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.
8. Leng, C.C. Mechanisms of adsorption and desorption of oxygen and nitrogen containing aromatics on activated carbon. University of Cincinnati: Cincinnati, OH, 1996; Ph.D. Dissertation.
9. Franz, M.; Arafat, H.; Pinto, N.G. Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon. Carbon **2000**, *38* (13), 1807–1819.
10. Arafat, H.; Ahnert, F.; Pinto, N.G. On the adsorption of aromatics on oxygenated activated carbon in nonaqueous adsorption media. Sep. Sci. Technol. **2003**, *39* (1), 43–62.
11. Lee, L.; Rao, C. Impact of several water-miscible organic solvents on sorption of benzoic acid by soil. Environ. Sci. Technol. **1996**, *30*, 1533–1599.
12. Seippel, J.; Ulbig, P.; Siegfried, S. Adsorption equilibrium data of binary liquid mixtures containing *n*-alkanes, cycloalkanes, and 1-alkanols on activated carbons. J. Chem. Eng. Data **2000**, *45*, 780–783.
13. Lee, L.; Bellin, C.; Pinal, R.; Rao, P. Cosolvent effects on sorption of organic-acids by soil from mixed solvents. Environ. Sci. Technol. **1993**, *27*, 165.
14. Khodadoust, A.; Suidan, M.; Sorial, G.; Dionysiou, D. Desorption of pentachlorophenol from soils using mixed solvents. Environ. Sci. Technol. **1999**, *33*, 4483–4491.
15. Nzengung, V.; Voudrias, E.; Nkedi-Kizza, P.; Wampler, J.; Weaver, C. Organic cosolvent effects on sorption equilibrium of hydrophobic

organic chemicals by organoclays. Environ. Sci. Technol. **1996**, *30*, 89–96.

16. Shevade, A.; Jiang, S.; Gubbins, K. Molecular simulation study of water-methanol mixtures in activated carbon pores. J. Chem. Phys. **2000**, *113*, 6933–6942.
17. Boehm, H. Some aspects of the surface-chemistry of carbon-blacks and other carbons. Carbon **1994**, *32* (5), 759–769.
18. Leon y Leon, C.; Radovic, L. Interfacial chemistry and electrochemistry of carbon studies. In *Chemistry and Physics of Carbon*; Thrower, P., Ed.; Mercel Dekker: New York, 1994; Vol. 24.
19. Puri, B. Surface complexes on carbon. In *Chemistry and Physics of Carbon*; Walker, P., Ed.; Mercel Dekker: New York, 1970; Vol. 6.

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