

HYDROGEN BONDING IN THE ADSORPTION OF LIQUID AROMATICS ON OXYGEN-CONTAINING ACTIVATED CARBON

H. A. Arafat and N. G. Pinto

*Chemical Engineering Department, University of Cincinnati
ML 0171, Cincinnati, OH 45220*

Introduction

Activated carbon has been used for a long time as an effective adsorbent for a wide variety of compounds. However, the specific mechanisms by which the adsorption of many compounds, especially liquid aromatics, takes place on this adsorbent are still ambiguous.

A few mechanisms have been proposed in the literature to describe the effect of oxygen groups on the adsorption process. These include: the donor-acceptor mechanism [1]; the water adsorption effect [2]; and the effect of oxygen groups on van der Waals interactions [3]. In this work, the significance of H-bonding between the surface oxygen and aromatic adsorbates has been reported.

Experimental

Synthetic, ash free, spherical activated carbon was used for this study. Three forms of this carbon, with different amounts of surface oxygen have been produced. Oxygenation and deoxygenation of the surface was achieved by heat treatment in air and nitrogen atmosphere, respectively. Adsorption isotherms for phenol, aniline, and nitrobenzene were generated in both aqueous solution, buffered at pH 7 and in cyclohexane medium, using the bottle point method. Flow microcalorimetry (FMC) was also used to study thermal effects during adsorption and desorption.

Results and Discussion

The influence of surface oxygen content on the adsorption of phenol from aqueous and cyclohexane solutions is shown in Figures 1 and 2, respectively. A comparison of the results in these figures shows opposite trends for adsorption from water and cyclohexane. For the former the capacity decreases with an increase in surface oxygen, while for the later it increases. This is postulated to occur because of the presence of at least two major effects: water adsorption and H-bonding. For adsorption of phenol from water, the former is dominant. In this case, water cluster formation on oxygen groups located at edge sites blocks access to part of the internal pore structure, and hence reduces capacity. In the absence of water adsorption, i.e., for adsorption from cyclohexane, the influence of H-bonding is dominant. This bonding can occur between the phenol's (-OH) group and the carboxylic and carbonyl

surface groups. Thus, an increase in surface oxygen leads to an increase in capacity, as is observed in Figure 2.

The presence of H-bonding is supported by the adsorption behavior of aniline and nitrobenzene. Since aniline can H-bond through the (-NH₂) group to surface oxygen, it is to be expected that its behavior will be similar to phenol. This is indeed what is observed. For example, Figure 3 shows an increase in adsorption capacity for aniline with an increase in surface oxygen. The behavior of nitrobenzene, a non H-bonding compound, is, in contrast, different. Adsorption isotherms for this compound in aqueous and cyclohexane solutions are shown in Figures 4 and 5, respectively. It is observed that while the adsorption capacity decreases with surface oxygenation in aqueous medium (Figure 4), due to water adsorption, surface oxygenation has little effect on capacity in cyclohexane solution (Figure 5). In the latter case, since both water adsorption and H-bonding are absent, the surface oxygen content has no significant influence.

The heats of adsorption of aniline and nitrobenzene, in cyclohexane, were also compared to detect a difference in adsorption mechanism. These were obtained by FMC and the data are shown in Table 1. There is clearly a large difference in the effect of surface oxygen on the heat of adsorption for aniline and nitrobenzene. Since H-bonding is present for aniline, the exothermic heat is much larger for the oxygenated surface as compared to the deoxygenated surface; this variation is much smaller for nitrobenzene. Additionally, if the heats of adsorption and desorption are compared, it is seen that while the nitrobenzene adsorption is essentially reversible in all cases, this is not so for aniline. For the latter, the stronger H-bonding mechanism reduces reversibility.

Conclusions

H-bonding has been proposed to be a significant mechanism of interaction between the surface oxygen groups and liquid organics capable of H-bonding. This mechanism can be observed in the absence of water adsorption.

References

1. Mattson J., Mark H., Jr., Malbin M., Weber W., Jr., and Critten J. Surface chemistry of active carbon:

Specific adsorption of phenols. *J. Col. Interface Sci.* 1969; 31(1):116.

- Muller E., and Gubbins K. Molecular simulation study of hydrophilic and hydrophobic behavior of activated carbon surface. *Carbon* 1998; 36(10):1433-1438.
- Coughlin R., and Ezra F. Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. *Environ. Sci. Technol.* 1968; 2(4): 291-297.

Acknowledgment

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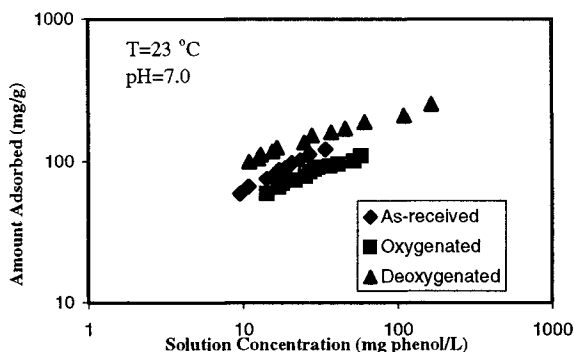


Figure 1. Adsorption of Phenol on Carbon in Aqueous Medium

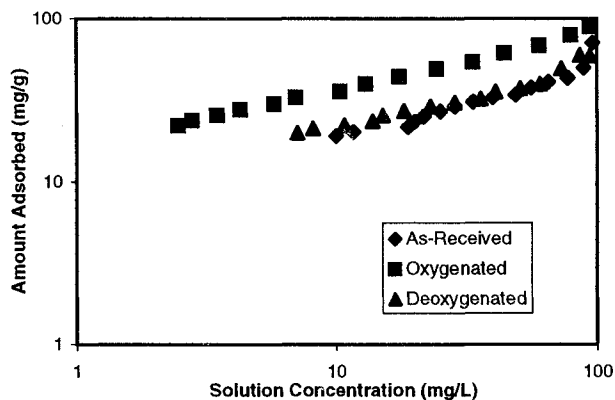


Figure 2. Adsorption of Phenol in Cyclohexane Medium

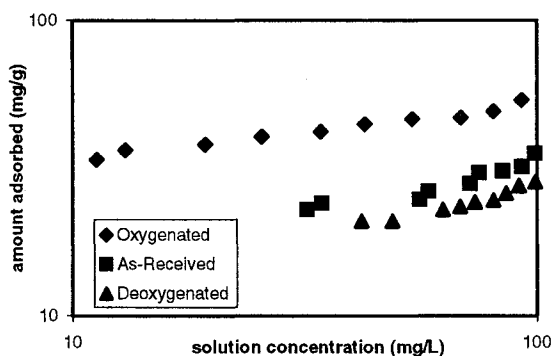


Figure 3. Adsorption of aniline from cyclohexane

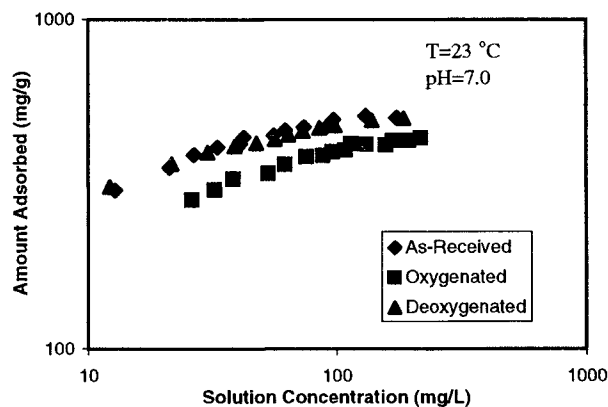


Figure 4. Adsorption of Nitrobenzene in Aqueous Medium

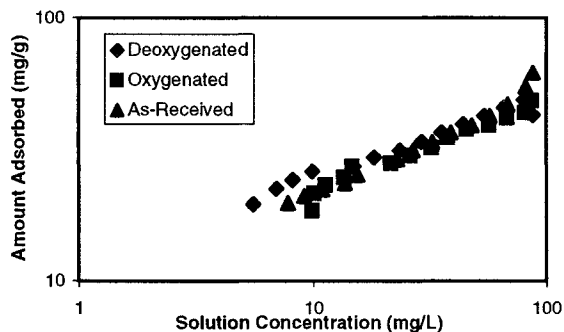


Figure 5. Adsorption of Nitrobenzene in Cyclohexane Solution

Table 1. Heat of adsorption/desorption for aniline and nitrobenzene from cyclohexane

Adsorbate	Heat of Adsorption (mJ/g)			Heat of Desorption (mJ/g)		
	Deoxygenated	As-Received	Oxygenated	Deoxygenated	As-Received	Oxygenated
Aniline	-1789	-6119	-20239	1397	5620	3672
Nitrobenzene	-3084	-3120	-6939	3312	3124	6830