THE IMPORTANCE OF MICROPORE SIZE IN ELIMINATING COMPETITIVE ADSORPTION

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Introduction

The pore size distribution of an activated carbon can control the adsorption rate, and the degree and mechanism of competition between adsorbates of different size. Pelekani and Snoeyink [1] used an activated carbon fiber (ACF) adsorbent containing mostly primary micropores (pore width < 8Å), to assess the impact of dyes of increasing molecular size on the adsorption of atrazine. The dye similar in size to atrazine competed for the same adsorption sites. Increasing the dye size reduced adsorption by molecular sieving, but still impacted atrazine adsorption via a shift to pore mouth blockage and surface pore blockage. Pore blockage impacted the adsorption rate to a much higher degree than direct competition for sites.

Broadening of the pore size distribution to include a significant volume of secondary micropores (pore width 8-20Å) increased the adsorption rate, with direct competition for sites over a wider range of molecular sizes, reducing the degree of competition attributable to pore blockage [2].

This study assesses the role of the pore distribution in the secondary micropore region for competitive adsorption between atrazine and natural organic matter (NOM).

Experimental

Kynol^{TM} ACFs, designated ACF-15 and ACF-20 were used as the adsorbents. Surface area and pore volume data are compared with ACFs used in previous studies [1,2] in Table 1. ^{14}C-labelled atrazine was used to facilitate rapid and accurate analysis of low concentrations. Groundwater containing 2.5 mg/L of dissolved organic carbon was used as the NOM source. Seven day adsorption isotherm tests (pH 7.0) included single solute (deionized-distilled water (DDW)), simultaneous adsorption and NOM preloading. The initial atrazine concentration in competitive adsorption tests was 50 μg/L. Kinetic tests were also conducted.

Results and Discussion

Table 1 shows that ACFs-15/20 have micropore size distributions intermediate of ACFs-10/25. The volume of secondary micropores is more than 40 percent less than for ACF-25, indicating the presence of small and intermediate secondary micropores, in addition to primary micropores.

With broadening micropore size distribution, the adsorption capacity of NOM increases (Figure 1). ACF-10 showed poor NOM adsorption, consistent with its small pores and molecular sieve properties. ACF-25 displayed the highest NOM capacity due to its large volume of secondary micropores. ACFs-15/20 yielded intermediate NOM adsorption. Thus, NOM adsorption is related to the pore volume in the secondary micropore region.

The impact of NOM on atrazine adsorption capacity with ACF-15 and ACF-20 are shown in Figures 2 and 3, respectively. For ACF-15, the simultaneous adsorption and NOM preload isotherms lie on the single solute isotherm, providing evidence for no competitive effect. However, these data corresponded to carbon doses greater than 6 mg/L. When lower doses were used (1, 2 and 4 mg/L) for the NOM preload test, the isotherm showed deviation from the single solute. This sensitivity to carbon dose is attributable to the increase in adsorbed NOM loading. The absence of competition at higher carbon doses suggests NOM does not block these pores or compete for the same adsorption sites, likely as a result of molecular sieving in the small secondary micropores. At high NOM loadings, NOM constricts these pores to a large degree, resulting in a large reduction in atrazine diffusivity. Therefore, seven days is insufficient to attain equilibrium. No effect was observed with ACF-20, although very low carbon doses were not tested.

Figures 4 and 5 show the impact of NOM on atrazine adsorption rate under simultaneous adsorption, for ACF-15 and ACF-20, respectively. Compared to single solute adsorption there is significant retardation in the adsorption rate when NOM is present. For ACF-20, three days was required to attain the single solute capacity, consistent with the isotherm results. Using the pseudo homogeneous surface diffusion model the diffusion coefficient was reduced by a factor of 10^6 in the presence of NOM. This supports a pore constriction mechanism by NOM without pore blockage. For ACF-15, three days was no sufficient to attain the single solute capacity. The lower volume of secondary micropores shifted to smaller pore sizes results in intrinsically slower adsorption, with pore constriction by NOM yielding a larger effect than with ACF-20.

Conclusions

Controlling the size distribution of pores in the secondary micropore region can eliminate the competitive effect of NOM. However, hindered adsorption kinetics via pore constriction occurs, and is sensitive to NOM loading.

References

1. Pelekani C. and Snoeyink V.L. Competitive adsorption on activated carbon: I. The importance of primary micropores. Submitted to Carbon 1999.
2. Pelekani C. and Snoeyink V.L Competitive adsorption on activated carbon: II. The importance of secondary micropores. Submitted to Carbon 1999.

Acknowledgments

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Table 1. Pore volume distributions and surface areas of ACFs

Adsorbent	BET Surface Area (m^2/g)	Primary Micropore Volume ($d < 8$ Å) (cm^3/g)	Secondary Micropore Volume ($8 < d < 20$ Å) (cm^3/g)	Mesopore Volume ($d > 20$ Å) (cm^3/g)
ACF-10	885	0.298	0.027	0.014
ACF-15	**1536**	**0.483**	**0.096**	**0.020**
ACF-20	**1641**	**0.509**	**0.115**	**0.023**
ACF-25	2312	0.550	0.215	0.038

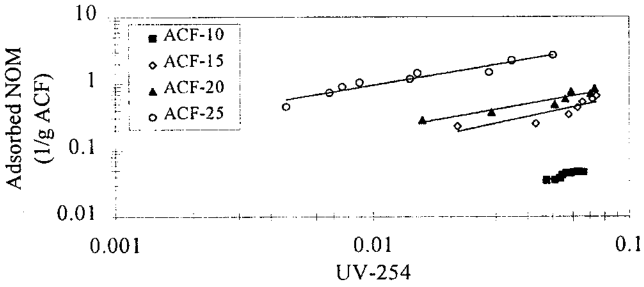

Figure 1. UV-254 NOM adsorption isotherms for ACFs.

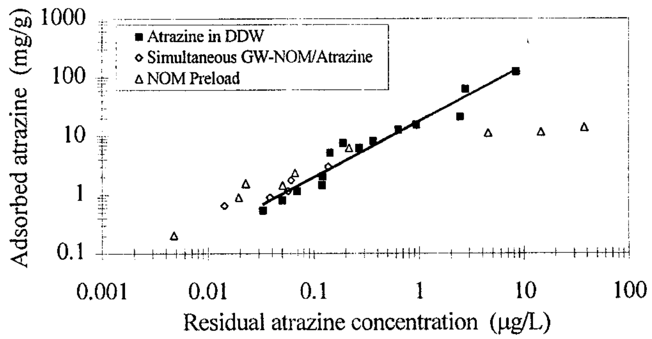

Figure 2. Atrazine isotherms with ACF-15.

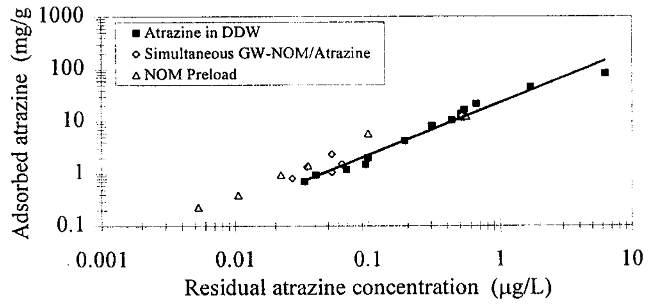

Figure 3. Atrazine isotherms with ACF-20.

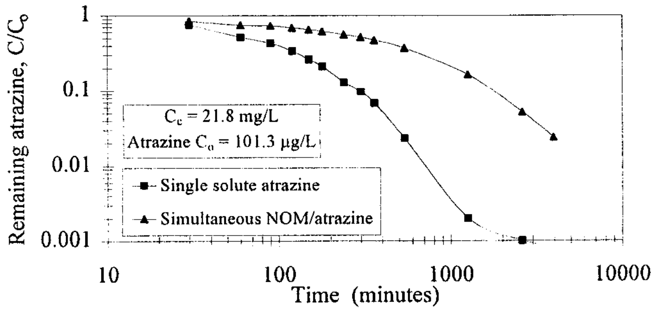

Figure 4. Effect of NOM on adsorption kinetics (ACF-15).

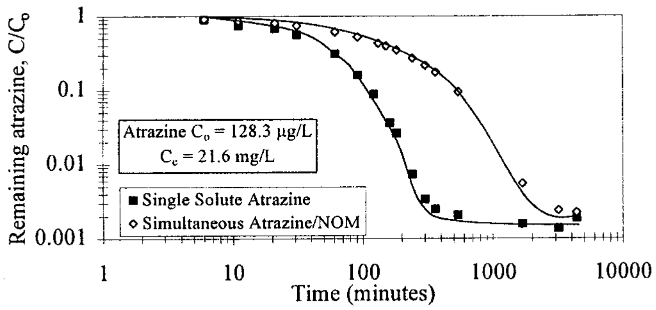

Figure 5. Effect of NOM on adsorption kinetics (ACF-20).