# PORE SIZE DISTRIBUTION IS IMPORTANT: A MOLECULAR PROBE STUDY OF COMPETITIVE ADSORPTION

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## Introduction

Pelekani and Snoeyink [1] used microporous activated carbon fiber (ACF) adsorbents with homogeneous and heterogeneous micropore size distributions to assess the impact of pore size on the adsorption of the pesticide, atrazine, in the presence of natural organic matter (NOM). When NOM could not access pores, pore blockage was the dominant competition mechanism. When NOM could access pores, direct competition for adsorption sites dominated. However, the polydisperse nature of NOM complicates the assessment of the mechanism as a function of pore size. Kasaoka et al. [2] used a series of ACFs of increasing pore size heterogeneity in conjunction with compounds of known size, primarily dyes, to assess the impact of pore size on adsorption. It was concluded that adsorption did not occur until the pore size increased to 1.7 times the molecule's second widest dimension.

The objective of this research was to use ACFs with uniform pore size distributions to evaluate the competitive adsorption mechanism between atrazine and three dyes of increasing molecular size, thus eliminating the difficulties encountered with NOM.

## Experimental

Two Kynol™ phenolic resin-based ACFs were used as the adsorbents. These were designated ACF-10 and ACF-25. Surface area and pore volume data are shown in Table 1. $^{14}C$-labelled atrazine (Novartis, Greensboro, NC.) was used to facilitate rapid and accurate analysis of low µg/L concentrations. Methylene Blue (MB), Malachite Green (MG) and Congo Red (CR) dyes were selected as the competing adsorbates, with molecular weights of 289, 329 and 651 for the charged organic ions, respectively. Seven day adsorption tests consisted of single solute adsorption (in deionized-distilled water (DDW) at pH 7.0), simultaneous adsorption of atrazine and dye, pre-adsorption of dye followed by atrazine contact, and pre-adsorption of atrazine followed by dye contact. In the simultaneous adsorption tests, the initial atrazine concentration was 50 µg/L and 8 µM for the dyes. For the dye preloading tests, the adsorbents were saturated with dye prior to 50 µg/L atrazine exposure.

## Results and Discussion

Table 1 shows that ACF-10 mainly consists of small primary micropores. Single solute isotherm data revealed that MB had a similar saturation adsorption capacity to atrazine (40 µmol/g), consistent with the similar size of these molecules (7-8 Å). MG and CR had four-fold and twenty-fold lower saturation capacities, consistent with the increasing size of these adsorbates and the molecular sieve properties of ACF-10. Atrazine adsorption was greatly depressed by all three dyes under simultaneous adsorption conditions (Figure 1). MB and CR displayed the same level of competition, but CR was twenty times less adsorbable than MB. MB competes for sites in the primary micropores. The low capacity of CR is consistent with less than monolayer coverage of the external fiber surface, supporting selective adsorption at high energy sites at the pore mouth, and a pore blockage mechanism. MG, intermediate in size between MB and CR impacted atrazine adsorption to the greatest degree, consistent with surface pore blockage, as well as pore blockage via adsorption inside the surface micropores.

Preloading ACF-10 with MB (Figure 2) yielded an isotherm with a negative slope, supporting strong adsorption of MB in the primary micropore region, due to enhanced adsorption associated with overlapping pore wall potentials. Preloading with MG and CR gave similar results to simultaneous adsorption, supporting pore mouth blockage and surface pore blockage, respectively.

Table 1 shows that ACF-25 has a broader micropore volume distribution than ACF-10, with an appreciable volume of secondary micropores. The saturation adsorption capacities of MB, MG and CR increased to 2300, 300 and 200 µmol/g, respectively, consistent with the increased pore volume in the larger micropores. There is still an effect on atrazine capacity under simultaneous adsorption conditions (Figure 3) with MB and MG, but little impact from the largest dye, CR. The capacity reduction is less than with ACF-10, highlighting the importance of having a broad distribution of micropores, to minimize the impact of pore blockage on competitive adsorption. CR adsorbs only in the large micropores via a surface adsorption mechanism rather than pore filling, and does not block these pores. Both MB and MG reduced the adsorption rate of atrazine but CR did not, consistent with the smaller dyes competing with atrazine for adsorption sites in the smaller micropores.

Preloading ACF-25 with the dyes (Figure 4) showed a small effect with CR, but a significant impact from MB and MG. The flatter atrazine isotherms support micropore filling, leaving only the large secondary micropores available for atrazine adsorption. The loading of MG was eight times less than for MB but it yielded a similar competitive effect, supporting pore blockage of intermediate secondary micropores by MG, in addition to direct competition for adsorption sites.

## Conclusions

When only primary micropores are present, adsorbates of similar size compete directly for adsorption sites. Increasing the size of the competing adsorbate results in a shift to pore blockage. Broadening of the pore size distribution to include secondary micropores results in a shift to direct competition for sites for a larger range of molecular sizes, reducing the degree of competition by pore blockage.

## References


1. Pelekani C. and Snoeyink V.L. Competitive adsorption in natural water: Role of Activated Carbon Pore Size. Water Research 1999; 33(5):1209-1219.
2. Kasaoka S., Sakata Y., Tanaka E. and Naitoh R. Design of molecular sieve carbon. Studies on the adsorption of various dyes in the liquid phase. Int. Chem. Eng. 1989; 29(4):734-742.


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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-25 | 2312 | 0.550 | 0.215 | 0.038 |

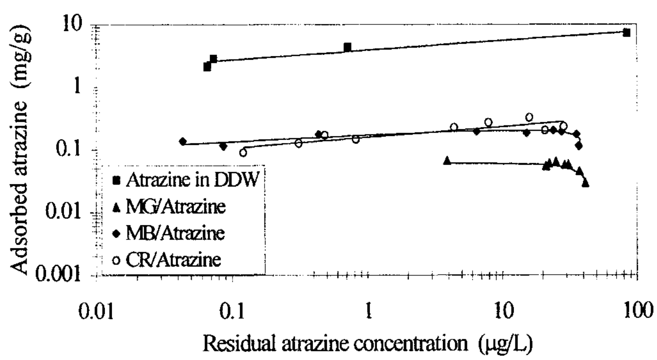


Figure 1. Simultaneous adsorption isotherms for atrazine in the presence of each dye (ACF-10).

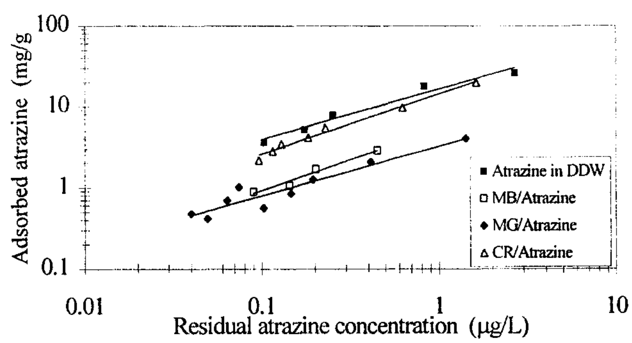


Figure 3. Simultaneous adsorption isotherms for atrazine in the presence of each dye (ACF-25).

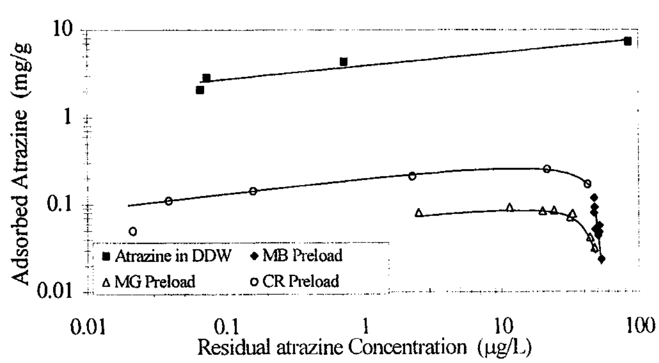


Figure 2. Dye preloaded adsorption isotherms for atrazine (ACF-10).

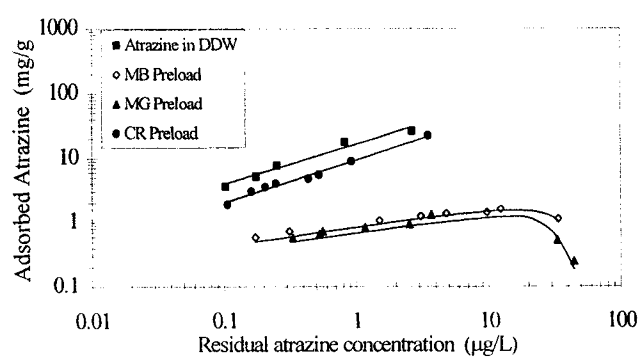


Figure 4. Dye preloaded adsorption isotherms for atrazine (ACF-25).