THE PROGRESSION OF GAC PORE STRUCTURE THROUGH SIX CYCLES OF WATER TREATMENT AND THERMAL REACTIVATION: A FULL-SCALE STUDY AT CINCINNATI, OHIO

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Introduction

We have evaluated GAC during full-scale water treatment operation at the Richard Miller water treatment plant in Cincinnati, Ohio. Starting with a contactor containing roughly 21,000 ft^3 of virgin F-400 GAC, we monitored the GAC as it progressed through six cycles of water treatment and subsequent on-site thermal reactivation. The GACs became more mesoporous with each cycle, as determined by density functional theory. In addition, total organic carbon concentrations in the influent and effluent of the contactor revealed that the reactivated GACs performed (qualitatively) as well as the virgin counterpart.

Experimental

Virgin GAC was sampled prior to water treatment. At the end of the first cycle of water treatment, the contents of the GAC contactor were sent to the multiple hearth furnaces for reactivation, whereby 100 mL samples were taken every two hours prior to entering the furnace. These samples were combined and represented GAC sample 'Spent 1' (cycle 1 spent), evaluated herein. Similarly, as the reactivated GAC exited the furnace, GAC samples were taken and combined. This composite sample represented GAC sample Reac 1 (cycle 1 reactivated). Subsequent samples were taken in the same manner as described above for Spent 1 and Reac 1.

Total organic carbon (TOC) was measured in the GAC influent and effluent during water treatment. Micromeritics ASAP 2000m units were used to assess pore structure via DFT pore size distributions, BET surface areas, and DR micropore volumes.

Results and Discussion

DFT pore size distribution (PSD) data for the Virgin, Spent 1, and Reac 1 GACs are shown in Figure 1, while those for the Reac 3, Spent 4, and Reac 4 are shown in Figure 2. During the first cycle of water treatment, pore volume loss occurred largely in the micropores. Subsequent reactivation caused an increase in pore volume in the 10-300Å range. Other cycles will be discussed at the conference. In contrast, during the fourth cycle of water treatment, the largest pore volume change occurred in the mesopores. Subsequent reactivation of the spent GAC resulted in increase in pore volume in the 100-500Å range, with no statistical change occurring in smaller pores.

DFT pore volume data, separated into pore size fractions is shown in Figure 3. The trends suggest that during the earlier cycles of water treatment, adsorption occurred largely in the micropores, which were the most abundant. As thermal reactivation caused an overall pore-widening effect, the zone of active adsorption began to shift in the larger pores. At the same time, the zone of active reactivation also was shifting to larger pore sizes. Despite these differences in pore structure, all GACs were (qualitatively) equally effective at removing TOC (as will be shown at the conference).

BET surface areas (Table 1) decreased during the first and second cycles of water treatment (i.e. Virgin to Spent 1 and Reac 1 to Spent 2). Because F-400 is largely microporous, and because the BET surface area is related to surface area and micropore filling, it is probable that adsorption in the micropores caused the decreases. Changes in BET surface areas were minimal during subsequent water treatment cycles, suggesting less loading in the micropores. The first thermal reactivation cycle caused an increase in BET surface areas, while subsequent reactivation cycles did not produce statistically significant changes in BET values.

DR micropore volumes decreased during each cycle of water treatment, with the greatest reductions occurring during the first and second water treatment cycles. Reactivation of each spent GAC restored only a portion of the DR micropore volume. DFT cumulative pore volume data at 31Å is also included, which shows very good correlation with the DR values. (Recall, that Dubinin defined micropores as pores having widths less than 28-32Å [1].) Apparent density data is also shown.

References

1. Dubinin MM. Generalization of the Theory of Volume Filling of Micropores to Nonhomogeneous Microporous Structures. Carbon 1985;23(4):373-380.

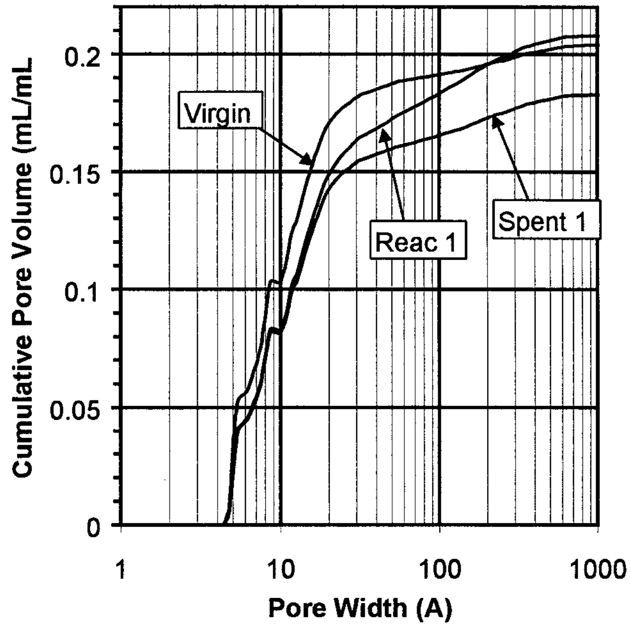

Figure 1. PSDs of Virgin, Spent 1, Reac 1.

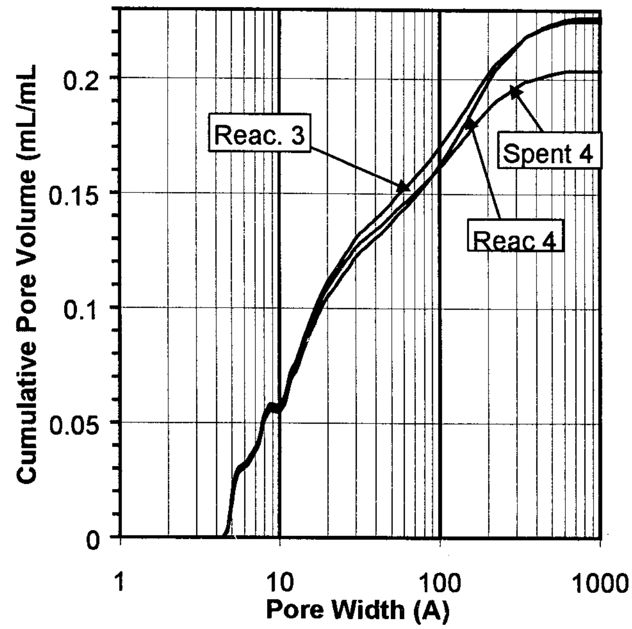

Figure 2. PSDs of Reac 3, Spent 4, Reac 4.

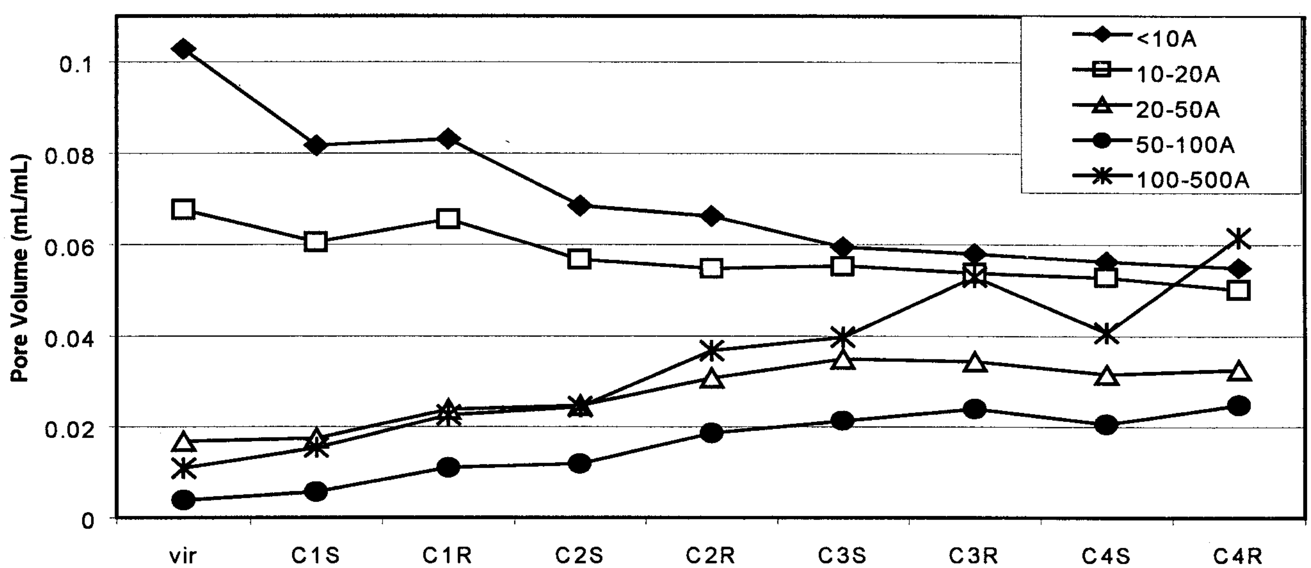

Figure 3. DFT Pore volume fractions for GAC from first 4 cycles of treatment and reactivation

Table 1. BET Surface area, DR micropore volume, DFT- 31Å pore volume, and Apparent Density.

	Virgin	1 Spent	1 Reac.	2 Spent	2 Reac.	3 Spent	3 Reac.	4 Spent	4 Reac.
BET (m^2/mL)	502	424	448	380	379	368	364	351	345
DR Micro. Vol. (mL/mL)	0.363	0.294	0.335	0.269	0.299	0.279	0.320	0.276	0.303
DFT-31Å (mL/mL)	0.363	0.294	0.336	0.278	0.300	0.283	0.315	0.277	0.294
AD (g/mL)	0.501	0.525	0.488	0.507	0.464	0.478	0.418	0.461	0.421