



Changes in GAC pore structure during full-scale water treatment at Cincinnati: a comparison between virgin and thermally reactivated GAC

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Abstract

During full-scale water treatment operation at the Richard Miller water treatment plant (Cincinnati, Ohio) we frequently evaluated the changes in pore volume distributions of a reactivated (F-400) granular activated carbon (GAC), as compared with that of its virgin counterpart. The reactivated GAC had experienced six cycles of water treatment and thermal reactivation. The reactivated GAC was slightly more effective at removing TOC (total organic carbon) than was the virgin GAC during the first half-year of service. Yet, the pore size distributions of the two GACs were very different. The virgin GAC was mostly microporous, with less mesopores. Conversely, the reactivated GAC was mostly mesoporous, with less micropores. For the virgin GAC, adsorption changed the volume of pores below 50 Å in width most significantly, and there was minor change in pores larger than 50 Å. In contrast, the reactivated GAC showed the greatest volumetric change in pores that were 100 to 500 Å in width. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

1.1. Richard Miller water treatment plant

Since 1992, the City of Cincinnati Water Works (CWW) has operated granular activated carbon (GAC) contactors at the Richard Miller water treatment plant (Miller plant), which has a design capacity of 220 MGD and on-site reactivation facilities. The average daily flow during our study was 112 MGD. This treatment plant has been recognized as the world's largest municipal GAC potable water treatment system [1].

At this plant, water is simultaneously processed in parallel through as many as 11 of its 12 GAC beds on-site. Each of these beds contains roughly 21,000 ft³ of GAC.

During our 1-year study, the empty bed contact time for the GAC contactors ranged from 16.6 to 21.2 min, and averaged 18.1 min. In addition, TOC (total organic carbon) entering the GAC beds ranged from 1.0 to 2.0 mg/l, with an average of 1.5 mg/l. (TOC is a measure of the total amount of organic carbon present in water.)

At the Miller plant, spent GAC is reactivated on-site by multihearth furnaces, which are dedicated solely to reactivation of Cincinnati GAC. These furnaces can reactivate 40,000 pounds of GAC per day. Once the GAC in a contactor has become spent, the GAC bed is fluidized into a slurry and pumped to a holding tank, where it remains until being reactivated. At Cincinnati, GAC is generally considered 'spent' once it can no longer produce an effluent with less than 1.0 mg/l of TOC. After reactivation, the GAC is returned to the holding tank or an empty contactor, and make-up GAC is added as necessary in the contactor before being put into service. With regard to the reactivated GAC that was evaluated in this study, virgin

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make-up GAC was added after the first and second reactivation cycles. However, following subsequent reactivation cycles, reactivated GAC of similar vintage was used as make-up GAC.

1.2. GAC feasibility study

The decision to use GAC at the Miller plant was based upon the results of a GAC feasibility study performed between August 1977 and May 1982 [2]. The study was unique because it employed full-scale GAC contactors and reactivation furnaces, rather than a pilot-scale system. The study showed that thermal reactivation restored the TOC adsorption capacity of the GAC to that of the virgin, through one reactivation cycle.

1.3. Reactivation

Reactivation of spent GAC offers the possibility of reusing a valuable resource in the water purification process, while simultaneously eliminating a waste load to landfills [3,4]. Furthermore, reactivation of GAC is typically cheaper than replacement with new GAC. Costs reported in the 1989 literature were \$0.22–0.70/lb for reactivation, as compared with \$0.80–1.00/lb for replacement [5]. Specific to this study, Cincinnati records have shown that GAC reactivation at the Miller plant represents roughly one-third the cost of replacement, and the CWW staff favor reactivation over replacement.

However, it has been recognized that GAC pores have often been shown to widen during thermal reactivation, ultimately altering the GAC pore structure [6]. With this in mind, GAC conceptually could only endure a finite number of reactivation cycles before it could no longer be effectively renewed. At such a conceivable point, thermal reactivation of the GAC would produce an unsatisfactory GAC, characterized by a diminished adsorption capacity or high friability. In short, optimization of the reactivation process offers the possibility to (a) increase the GAC bed life, (b) help minimize reactivation and operation costs, and (c) maximize the useful life of the GAC.

1.4. Objectives of the study

The objectives of this research were to (i) relate the removal of TOC by the virgin and reactivated GAC with the pore structure characteristics of these GAC samples, and (ii) determine the manner in which adsorption was linked to pore structure. It had been predicted that pore volume distributions would provide important information regarding how the integrity of the GAC has progressed after six cycles of thermal reactivation.

2. Literature review

2.1. Adsorption in GAC

The importance of recognizing pore sizes (for IUPAC classification, see Ref. [7]) stems from the fact that each wall in a GAC pore exerts an attractive force on nearby adsorbate molecules [8,9]. Because of this, molecules entering the smallest pores could experience attractive potentials from both walls in an overlapping manner, and one might traditionally consider that these pores would become filled with adsorbate molecules more readily than larger pores. With this in mind, it makes sense that a large volume of micropores has been related to a high surface area and proficient removal of small molecules [10]. However, for water treatment applications, where larger molecules can likewise be present, mesopores can also be important [1].

Aqueous phase adsorption onto GAC is known to be influenced by several variables, including (a) the GAC's pore size distribution and internal surface area [1,10,11], (b) the chemical properties of the GAC surface (such as functional groups [12–16], electrostatic interactions [17–19], acidic/basic characteristics [13,20,21], hydrophobicity [22,23], ash content [1]), (c) the sizes, shapes and chemical properties of the dissolved organic matter (DOM) and other molecules being adsorbed [24–29], and (d) characteristics of the water (such as pH [10,30], molecular oxygen concentration [31–35], ions in solution [36–38]). In addition, during full-scale water treatment processes, microbes can play an important role in the removal of DOM [10].

Indeed, molecules of varying sizes, shapes, functionality and polarity characterize DOM found in source waters. Moreover, one could anticipate that the most important GAC pore size distribution for a particular water purification process will depend largely upon the size of the organic compounds in that water source. A breakdown of the approximate sizes of compounds of varying molecular weights (Table 1) helps to explain the fact that the mesopores may be as important as the micropores when high-molecular-weight compounds are also present [1,26].

In a pilot study, Owen et al. found that roughly 33% of the dissolved organic matter (DOM) in Ohio River raw water had $M_{ws} < 500$ Daltons (Da), 45% had $M_{ws} < 1000$ Da, 74% had $M_{ws} < 3000$ Da, and 90% had $M_{ws} < 10,000$ Da [30]. After pilot ozonation and GAC treatment, Owen found that nearly all (70–90%) of the DOM had M_{ws} below 3000 Da [30]. Based on the information in Table 1, this upper limit of 3000 Da would loosely correspond to a 20 Å diameter molecule.

2.2. DOM adsorption studies

When studying adsorption of DOM onto a bituminous

Table 1
Molecular weights and respective diameters for organic molecules

Compound	Molecular weight (Da)	Approximate diameter (Å)	Reference
Generic globular protein	100	6	[39]
2-Methylisoborneol (MIB)	168	5.5–6	[22]
NOM ^d fraction	650 ^a	7.5 ^a	[26]
FA ^d -tap water Arvada, CO	500–1000	13.6 ^b	[40]
FA-Colarado River, Yuma, AZ	500–1000	12.2 ^b	[40]
FA-St. Peter Aquifer, MN	500–1000	9.6 ^b	[40]
Polyglycol	800	10 ^b	[40]
FA-Biscayne aquifer, Miami, FL	800–1000	10.6 ^b	[40]
Generic globular protein	1000	13	[39]
Polyglycol	1200	13.6 ^b	[40]
NOM fraction	1370 ^a	11.1 ^a	[26]
FA-Suwanee River, Fargo, GA	1000–1500	16.4 ^b	[40]
FA-Yampa River, Yampa, CO	1000–1500	15.8 ^b	[40]
Suwannee FA	1000–1500 ^c	16.4 ^c	[41]
HA ^d -Biscayne aquifer, FL	1500–2000	17.6 ^b	[40]
North Carolina FA	1500 ^c	17.2 ^c	[41]
Polyglycol	2000	14.2 ^b	[40]
Polyacrylic acid	2000	19.2 ^b	[40]
NOM fraction	2440 ^a	15.1 ^a	[26]
FA-Yampa River, Yampa, CO	2000–3000	21.0 ^b	[40]
NOM fraction	3200 ^a	17.5 ^a	[26]
Polyglycol	4000	18.4 ^b	[40]
Polyacrylic acid	5000	23.4 ^b	[40]
FA-Hawaii wetland, Hawaii	5000	23.0 ^b	[40]
HA-Trona water, WY	5000–10,000	24 ^b	[40]
FA-Laramie-Fox Hills Aquif., SD	5000–10,000	28 ^b	[40]
Generic globular protein	10,000	29	[39]
Generic globular protein	100,000	63	[39]

^a Peak molecular weight and hydrodynamic diameters measured via FIFFF.

^b Diameters are representative of 2×radius of gyration values.

^c Molecular weights and respective diameters determined via small-angle X-ray scattering. (Note: diameters representative of 2×radius of gyration values.)

^d FA, fulvic acid; HA, humic acid; NOM, natural organic matter.

based carbon (under batch conditions) at pH 3, Newcombe et al. [17,26] proposed that DOM with nominal molecular weights below 3000 loaded largely into the micropores, with somewhat less adsorption occurring in the mesopores. In contrast, when comparing GAC that had been in service for 2 years at a full-scale water treatment facility with its virgin counterpart, Newcombe et al. [42] concluded that pore volume was lost roughly equally through the micropores and mesopores. In other work done by the same research group, the adsorption of microcystin-LR onto numerous powdered activated carbons was related to mesopore volume [43] and small mesopore (20–80 Å) volume [17].

Adsorption of gallic acid onto numerous activated carbons that were produced from several different starting materials was evaluated by Utrera-Hidalgo et al. [44]. The authors concluded that high mesoporosity and macroporosity were necessary to increase the removal of gallic acid

under dynamic conditions. In addition, they concluded that the activated carbons' capacities for gallic acid were related to the volume of the activated carbon pores that were accessible to water.

In a bench-scale study performed by Ogino et al. [45], a commercial humic acid was fractionated into a <1000 Da fraction and a 1000–5000 Da fraction. The two humic fractions were subsequently adsorbed onto an activated carbon fiber, an activated carbon, and a carbon black. The authors concluded that most of the <1000 Da fraction adsorbed into the micropores, while adsorption of the 1000–5000 Da fraction was related to the volume of pores less than 60 Å in width.

During a bench-scale BAC (biological activated carbon) adsorption study performed by Kameya et al., the DOM that followed coagulation and filtration of river water was adsorbed onto two (unused) commercially available bituminous based GACs that were largely microporous

[46]. Based on cumulative pore volume data, the authors showed that adsorption occurred almost exclusively in pores with widths less than 20 Å for both GACs studied. (The authors presented total cumulative pore volume at 20 Å, but did not monitor the differential pore volume distribution within the range below 20 Å.)

Ebie et al. [47] concluded that pores in the 30 to 100 Å range showed a good correlation with (batch test) adsorption capacity for humic compounds present in raw water and coagulated water, with molecular weight ranges of 500–50,000 Da and 500–18,000 Da, respectively. In addition, they concluded that pores smaller than 15 Å correlated well with adsorption of small halogenated organic substances having molecular weights of a few hundred.

Similarly, others have shown a relation whereby the adsorption of *p*-nitrophenol by activated carbons increased with increasing volume of micropores [48,49]. It has also been observed that the adsorption of certain organic dyes, with molecular weights of several hundred, increased with increasing volume of small mesopores [48].

2.3. Pore characterization by density functional theory (DFT)

In this study, GAC pore structures were determined using the density functional theory (DFT) via an ASAP 2000m (accelerated surface area and porosimetry system) unit, manufactured by Micromeritics (Norcross, GA). The ASAP 2000m generated an experimental adsorption isotherm of argon adsorbing into the pores of GAC. The isotherms were then used to calculate pore size distributions, via the DFT software package provided with the ASAP 2000m.

In the DFT software package the pore wall has been modeled as a semi-infinite graphite-like solid with a topologically and energetically smooth, rigid surface of infinite lateral extent [50,51]. Although the surface of GAC is not perfectly energetically smooth, a typical GAC has somewhere in the range of 10^{21} micropores per gram [3], which allows for a great deal of statistical power and permits this assumption to be appropriate. It is also obvious that GAC is not composed of graphite layers of infinite extent (as rigorously modeled by DFT), but on a molecular level, this approximation is considered to be appropriate.

To further define the porosity of the adsorbent, the DFT software models the slit-shaped pore as two parallel surfaces, with each wall exerting an attractive potential. Hence, a smaller pore will have more overlapping of potentials and will attract argon more than a larger pore. In addition to adsorbate–adsorbent interactions, the DFT also accounts for the interactions of the argon atoms with each other, namely short-range repulsive forces and long-range attractive forces.

For a more thorough explanation of this technique, see Refs. [50–56] and references therein. The DFT method has been used to characterize the pore structure of GACs that are used for air and water phase adsorption [57,58], and to suggest a relationship between the DFT pore structure and dye adsorption [48].

3. Materials and methods

3.1. Full-scale operations

As a project design, the performance and pore structure of activated carbons from two contactors have been monitored and analyzed. To ensure that the comparison was fair and unbiased, the two contactors were run in parallel during full-scale operations under equivalent conditions (i.e. temperature, flow, influent concentration, similar backwashing at start-up, empty bed contact time, etc.) for 1 year. The important difference between these two contactors was that one contained virgin F-400 GAC (Calgon Carbon Co.) and the other contained F-400 GAC that had been through six cycles of water treatment and thermal reactivation. The two GAC beds contained equal volumes of activated carbon. Full-scale performance of Cincinnati reactivated GAC during earlier water treatment/ reactivation cycles is discussed elsewhere [59].

Following the initial fluidization of the two newly filled contactors, samples were taken, commencing in November 1995. Both contactors were then brought on-line at the same time, and samples were taken simultaneously from the two contactors at 4- to 6-week intervals for the duration of this study. Parenthetically, the GAC contactors were briefly ‘fluffed’ (lightly backwashed) after each sampling event, in order to eliminate the coring hole that could have otherwise allowed short-circuiting of water.

3.2. GAC sampling

For each sampling event, three GAC cores were drawn from each contactor. These cores were drawn from the center, width-wise; and at 16 ft, 32 ft, and 48 ft from the inlet edge, lengthwise. Each GAC core was divided into seven samples: six 18-inch sections plus a bottom 12-inch section. Next, the sample sections from equal depths of the three cores were combined and completely mixed to produce a composite sample. Descriptions of each composite sample (discussed in this paper) are shown in Table 2.

After the first core samples were taken, both contactors were brought on-line together in late November 1995; subsequent samples were taken simultaneously from the two contactors at 4- to 6-week intervals. These GAC samples were then evaluated for their pore structures and apparent densities. In addition, TOC influent and effluent concentrations were measured for each GAC contactor frequently throughout the study.

Table 2

GAC samples and the respective locations they were sampled from (for both the virgin and reactivated GAC contactors)

Sample	Sampling location (distance from top of contactor)
Top depth	0–18"
Depth 2	18–36"
Depth 4	54–72"
Bottom depth	108–120"

3.3. Apparent density

For apparent density measurement, about 20 g of each sample were dried in an oven for 24 h. Then, each GAC sample was placed in a desiccator and cooled to room temperature. Once cooled, each sample was weighed and the volume was measured in accordance with ASTM method D2854-83 (1988), with exceptions being that a 50-ml graduated cylinder was used rather than a 100-ml cylinder, the GAC sample size was roughly 50 ml, and the drying temperature was 110°C.

3.4. Pore structure and surface area determinations

Prior to conducting pore structure analyses, GAC samples were dried in an oven (110°C, 24 h), then put into a sample tube and degassed (110°C, 5×10^{-3} Torr, or 7×10^{-4} kPa, for 24 h) to remove any moisture and weakly bound volatiles that could interfere with the analysis process. Next, the analysis process was started, whereby the sample tube was evacuated (1×10^{-5} Torr or 1.3×10^{-6} kPa) for 1 to 3 h, then submerged into a liquid argon bath. Subsequently, the sample was dosed with a known incremental amount of gaseous argon that was 99.999% pure (supplied by MG Industries). Once pseudo-equilibrium conditions had been reached, the instrument repeated this process until an adsorption isotherm covering the relative pressure range of 10^{-6} to 0.99 was produced. (The instrument includes a saturation pressure tube that is also submerged in liquid argon, which adjusts equilibrium measurements to account for thermal transpiration effects [60].) Isotherms measured for each sample were then analyzed via the DFT software, and the pore volume distributions were computed for 77 pore sizes, over the range of 4 to 1300 Å.

It should be noted that for any gas adsorption analysis technique, the theoretical accuracy of pore volume data for pores wider than 500 Å diminishes with increasing width as the relative pressure approaches the saturation pressure [61]. In fact, the 500 Å boundary between mesopores and macropores is set by practical problems associated with quantifying pore volume via capillary condensation theories [61]. With this in mind, our attention has been focused on the pores with diameters <500 Å. Hence, the

term ‘total pore volume’ is used for describing the cumulative pore volume up to this 500 Å threshold.

Duplicate pore size distribution analyses were performed for each GAC sample. Total pore volumes of the duplicate samples were typically within 4% of each other. Whenever pore size distributions did not show a 4% agreement, an additional pore size distribution analysis was performed; in these instances all pore size distributions were retained and considered equally valid when analyzing the results.

In addition to DFT pore volume data, BET surface area values [62] were measured. Of course, the concept of BET surface area should be used with care when studying activated carbons, since this value relates not only to the pore walls, but also to the volume of liquid contained within the micropores [1]. Hence, the term apparent surface area may be more appropriate when considering microporous adsorbents [63].

The relatively high vacuum associated with the pore structure analysis process may remove waters of hydration that may have been associated with the adsorbed organic matter inside the GAC pores. This degassing step was mandatory: if omitted, water would have volatilized during the pore volume analysis, and detrimentally altered the adsorption data. While the GAC was used in water treatment service, these waters of hydration may have rendered the effective pore volumes and widths smaller than those determined via argon adsorption tests for the loaded GACs. In addition, although it might be insignificant in comparison with the GAC, the adsorbed organic matter would probably have a surface area and pore size distribution of its own. This represents an inherent limitation of this or other known methodologies for characterizing the micropores and mesopores of GAC.

3.5. Total organic carbon (TOC) analysis

TOC analyses were conducted with a Dohrman DC 180 TOC analyzer with a Dohrman model 182 autosampler. These analyses were performed in accordance with the manufacturer’s recommendations and Standard Methods (APAA, AWWA, and WPCF 1989) Method 5310C [64].

4. Results and discussion

4.1. Pore size distributions of virgin versus reactivated GACs

We have shown the pore size distributions of GAC samples (Fig. 1) that were taken from the top 18 inches of the virgin and reactivated beds at the start of the experiment. For each sample, cumulative pore volume as normalized on a volumetric basis (ml pores/ml bed) has been calculated via the multiplication of pore volume (ml pores/g GAC) and apparent density (g GAC/ml bed). We chose to express the data in these units (ml/ml) for purposes of

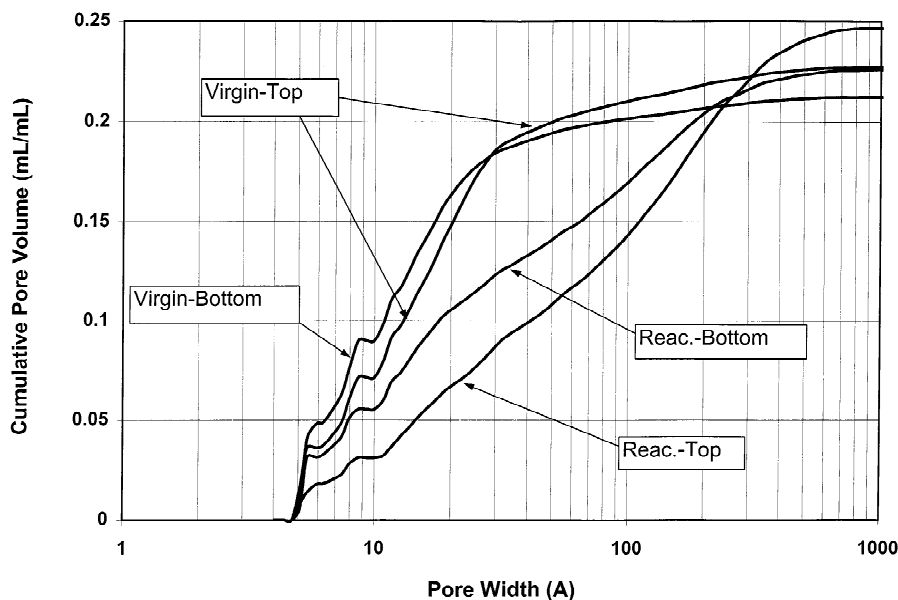


Fig. 1. Pore size distributions of virgin and reactivated GAC taken from the top depth and bottom depth of each contactor at the commencement of the full-scale comparison study.

normalizing the pore volumes to a unit bed volume basis [48,65–67].

After experiencing six reactivation cycles, the reactivated GAC contained a pore size distribution differing considerably from that of the virgin GAC. This distinction is shown in Fig. 1, which shows pore size distributions of GAC sampled immediately following the first backwash when the study commenced. The reactivated GAC pores had been widened through the multiple reactivation cycles, resulting in a decreased micropore volume and increased mesopore volume. This type of behavior has been observed by others as well [6]. Specifically, Fig. 1 shows that the virgin GAC contained a volume of micropores that was roughly twice the amount present in the reactivated GAC. Conversely, the volume of mesopores present in the reactivated GAC was more than two times greater than the volume of mesopores in the virgin GAC. In addition, the reactivated GAC had more total pore volume than the virgin GAC.

Other research has shown similar trends when reactivating GAC that had been loaded with organic matter and calcium [66,68]. Calcium has been shown to act as a catalyst, promoting the undesirable widening of pores [4,7,66,68]. The notable differences we observed in pore size distributions between the virgin and reactivated GAC might have been partly attributable to calcium catalysis, since calcium is ubiquitously present in spent carbon.

The virgin and reactivated GACs from the bottom of the beds are also shown in Fig. 1. The GACs from the top of the GAC beds contained less micropore volume and more

mesopore volume than their counterparts at the bottom of the beds.

For both GAC contactors, the GAC from the top depth had a pore structure somewhat different from the bottom depth GAC. During the activation/reactivation process, each grain experiences somewhat different levels of activation/reactivation, resulting in slight variations in pore structure. Further, one could anticipate that the particle density would decrease with increasing total pore volume. After each contactor was filled with GAC, they were backwashed, resulting in stratification of the GACs with more dense and less activated grains at the bottom; and less dense, more activated grains at the top.

The pore volume distributions shown in Fig. 1 depict rather low populations of pores that are 5.5 to 6 Å in width, and almost an absence of pores in the 9 to 10 Å range. The dominant feature responsible for these minima are believed to be related to the modeling of argon adsorption, namely the strong packing effects that are exhibited by the rigid parallel pore wall model, as discussed in detail elsewhere [69].

4.2. TOC influent and effluent data

The TOC influent and effluent curves for the virgin and reactivated contactors are shown in Fig. 2 for the entire period of the study [64]. During the first 168 days of water treatment service, the reactivated GAC removed TOC more effectively than the virgin did. Specifically, after 168

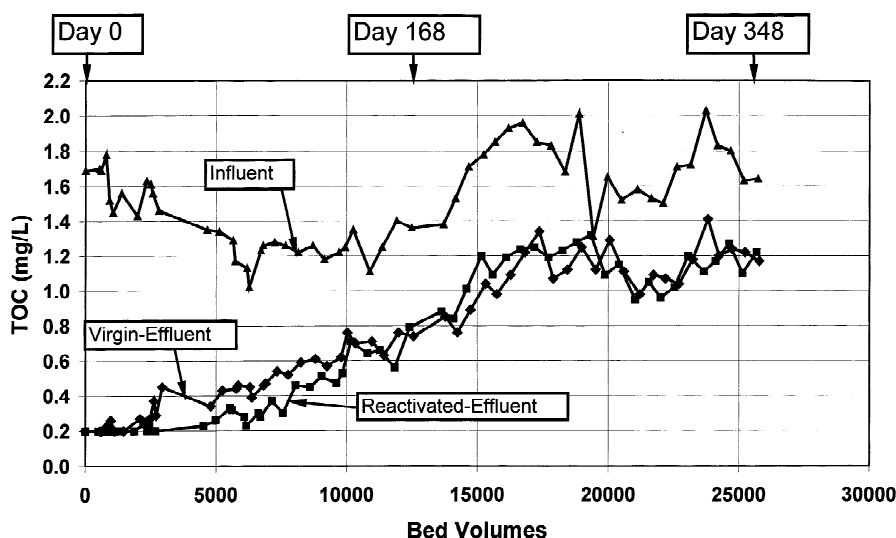


Fig. 2. Influent and effluent TOC for the virgin and reactivated GAC contactors.

days of service, the reactivated GAC had removed 73% of the influent TOC, whereas the virgin GAC had removed 65%.

For the remaining time of the study, the virgin GAC was marginally more effective at TOC removal than the reactivated GAC (Fig. 2). However, this marginal difference may not have been statistically significant. During the latter portion of GAC operation, other factors besides internal porosity may have influenced TOC removal. One such factor could have been biological growth. By the end of the 1-year study, the virgin GAC had removed 48% of the influent TOC, while the reactivated GAC had removed 51% of the influent TOC. (This topic is evaluated more extensively in a companion paper [64].)

Others have found that GACs that had been reactivated one, two and three times were able to perform comparably to their virgin counterpart with regard to TOC removal [70]. In addition, other researchers have observed near-equivalent TOC removal by virgin GAC and GAC that had been thermally reactivated once [71–73].

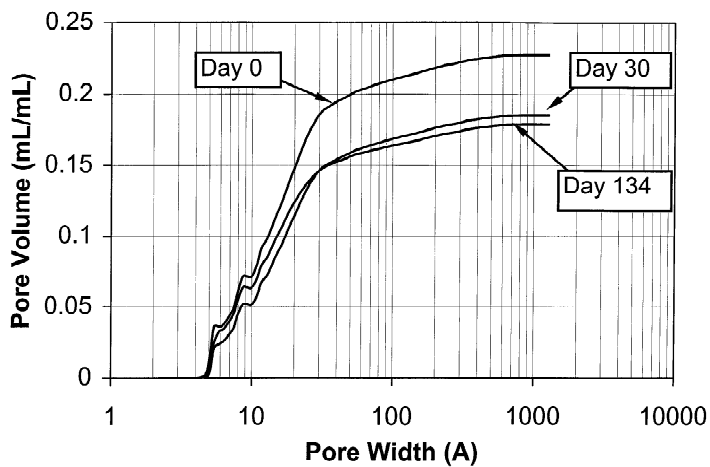
Dussert and Tramposch [74] proposed that adsorption of ozonated DOM onto GAC theoretically takes place in three phases: (i) initial removal occurring largely via physical adsorption (during the first 3 months), (ii) removal via adsorption and biological oxidation (during the next 3 to 4 months), (iii) steady state removal mostly via biological oxidation after the first 6 to 7 months. When applying such phases to other GAC beds, one notes that the duration of each of these stages would be influenced by numerous factors [75,76]. In particular, temperature can greatly influence microbial activity, with activity typically being less when temperature is decreased [75–77]. For instance, Glaze et al. [75] found the impact of biological activity

upon DOM removal to be relatively insignificant during winter months when temperatures dropped to 8 to 12°C.

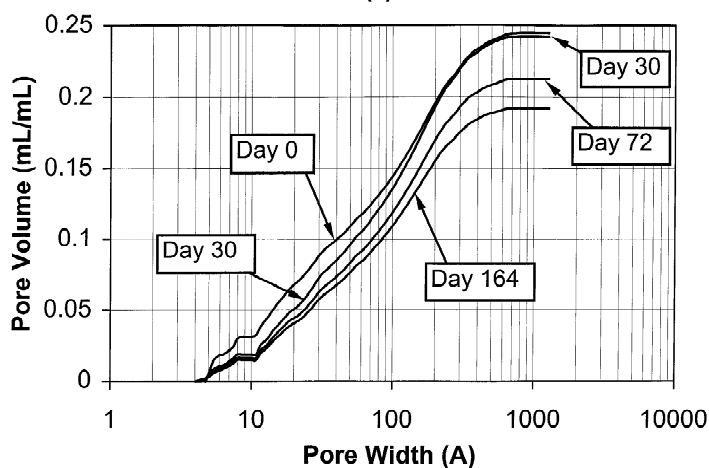
At Cincinnati, water temperatures were within the 8 to 12°C range during most of the winter and early spring months of this study (i.e. for the first 5 to 6 months). In addition, because the DOM was not ozonated in this study, one might expect the DOM at the Miller plant to be less biodegradable. Although bacterial activity was not evaluated in this study, one could hypothesize that adsorption occurred largely via physical adsorption during these colder months; perhaps during the first 7000–10,000 bed volumes (i.e. 95–135 days) of this study. By the time that roughly 15,000–20,000 bed volumes had been processed (i.e. 200–265 days), steady state removal conditions were reached, indicating that DOM removal was occurring largely via microbial oxidation. Thus, when the reactivated GAC bed was removing more TOC than was the virgin GAC, the temperatures were low, and physical adsorption would have predominated over biological activity. When the adsorption capacity of both beds had become mostly exhausted, and the initial adsorptive nature of the GAC no longer mattered, then the two beds behaved roughly the same, and the TOC removal would have occurred mostly via biological activity.

4.3. Pore size distribution data

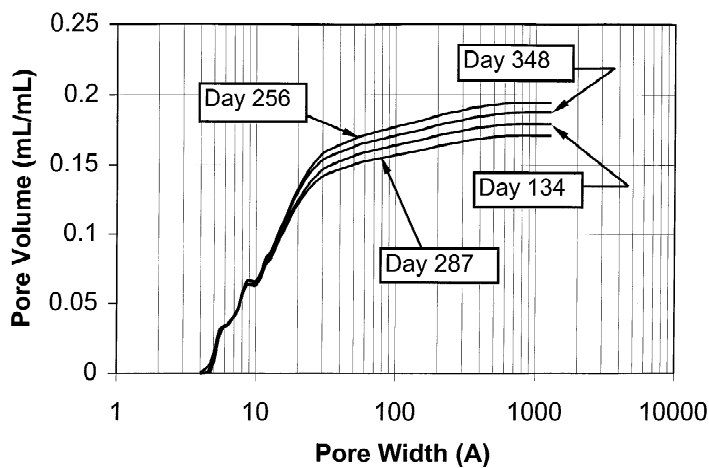
Cumulative pore volume data for the top depth of the virgin and reactivated contactors are presented in Fig. 3. Each distribution shown in Fig. 3 represents the averaging of all pore volume data measured for that sample. Strictly for the purpose of clarity, pore volume data for roughly half of the sampling dates are shown in Fig. 3 (rather than



(a)



(b)



(c)

Fig. 3. (a) DFT cumulative pore volumes of virgin GAC (top depth) for the time period of day 0 to day 134; (b) DFT cumulative pore volumes of reactivated GAC (top depth) for the time period of day 0 to day 164; (c) DFT cumulative pore volumes of virgin GAC (top depth) for the time period of day 134 to day 348.

all sampling dates). The complete set of pore volume data, representing every sample taken at each sampling date (i.e. no averaging), is presented in another format later in this paper.

Pore volume distributions for virgin GAC samples from the top depth of the contactor during the first 134 days of operation are shown in Fig. 3a. As shown, the GAC sample from day 0 (Nov. 28, 1995) had 0.23 ml/ml of total pore volume. This was indeed more than the loaded GAC sample from day 134, which had 0.18 ml/ml of total pore volume. After a rapid decrease in total pore volume during the first 30 days, subsequent changes in total pore volume were less pronounced. (However, there were important differences in the incremental of pore volumes, as discussed later in the paper.)

Pore size distributions for depth 2 of the virgin bed (not shown) displayed qualitatively similar trends to those of the top depth. Specifically, there was a large decrease in total pore volume during the first 30 days of operation, followed by a less pronounced reduction in total pore volume that had ended by day 164. Indeed, the pore size distributions for the two top depths of the virgin contactor indicated that the greatest reduction in pore volume occurred in the 5 to 30 Å range; a reduced slope in the 5 to 30 Å region highlighted this trend. The reader could observe how these results compare to those of Kameya et al. [46], as discussed above.

Regarding the top depth of the reactivated bed, pore size distributions of GAC sampled during the first 164 days of treatment are shown in Fig. 3b. Between day 0 and day 30, there was a small decrease in total pore volume. GAC samples taken on day 72 contained a total pore volume that was considerably reduced as compared to the GAC from day 30, and those from day 164 were yet further reduced.

GAC samples from depth 2 of the reactivated GAC bed (not shown) were characterized by a substantial reduction in total pore volume by day 30, followed by a less substantial decrease in total pore volume up to day 134.

Consistently at the two uppermost depths of each bed, total pore volume decreased during the first 134 to 164 days, as supported by Fig. 3a and b. Yet, pore size distributions of GAC samples taken after day 134 or day 164 showed no clear trend with respect to total pore volume, as depicted for the virgin GAC in Fig. 3c. Although pore size distributions between days 134 and day 348 are shown strictly for the top depth of the virgin bed, this scattering of total pore volume was typical for the other samples we studied beyond day 134 or 164.

As a point of reference, for GAC used and reactivated at the Miller plant, we found similarities between the Dubinin–Radushkevich (DR) micropore volume [78,79] and the results of the DFT (as shown elsewhere [59]). Specifically, a fairly good match was found between DR micropore volumes and DFT cumulative pore volumes in the range of 28 to 32 Å. (Recall that Dubinin classified micropores as pores having widths less than 28–32 Å [78,79].)

4.4. Apparent density data

Apparent density (bulk density) values represent the packed density of a bed of GAC (i.e. mass of GAC/unit bed volume) [65]. Both particle density and the particle alignment (i.e. number of grains per unit volume) of a GAC sample could conceptually influence changes in apparent density. The particle alignment and bed volume would not be expected to change significantly during water treatment. In contrast, adsorption of TOC would occur within the interior of the particle, and should therefore only alter the particle density.

Apparent densities (g/ml) for the virgin GAC samples (as measured at The Pennsylvania State University) have been plotted with respect to time in Fig. 4a. GAC samples from the two top-most depths demonstrated the greatest overall increases in apparent density. In addition, samples taken from the two top-most depths showed significant increases in apparent density for the first 225 days.

The apparent densities of the reactivated GAC samples demonstrated trends that were qualitatively similar to those shown for the virgin contactor. As shown by Fig. 4b, the samples taken from the topmost depths of the contactor experienced the greatest increase in apparent densities. Moreover, samples taken from the two topmost depths experienced substantial increase in apparent density during the first 200 days of operation.

We hypothesize that the increases in apparent densities with respect to time reflect loading of TOC and inorganics, and that the upper layers of GAC experienced more TOC and inorganics loading than did the lower layers. The bed sampling could also have been influenced slightly by a brief bed ‘fluffing’ step that followed each sampling event, which may have re-stratified the beds slightly.

4.5. Incremental pore volume distribution data

The DFT software package provided us with detailed pore size distribution data: specifically, pore volume data was calculated for 64 pore sizes below 500 Å in width. Because of this level of detail, we were able to investigate how pore volume changed over time for various incremental pore size ranges. As shown in Fig. 5a–d, we have evaluated five incremental pore size ranges: two in the micropore region (<10 Å and 10–20 Å) and three in the mesopore region (20–50 Å, 50–100 Å, and 100–500 Å).

The significance of distinctions amongst these results, which are discussed below, was placed in perspective by conducting triplicate analysis at each depth. Specifically, during the August 10, 1996 (day 256) sampling event, core samples were collected from three locations (16 ft, 32 ft, and 48 ft from the inlet, lengthwise), as usual. However, for this event, GAC samples from equal depths, but separate coring locations, were not combined into a single composite sample. Rather, they were analyzed for pore structure separately, to allow a statistical analysis of sampling sensitivity. This was conducted to ensure that the

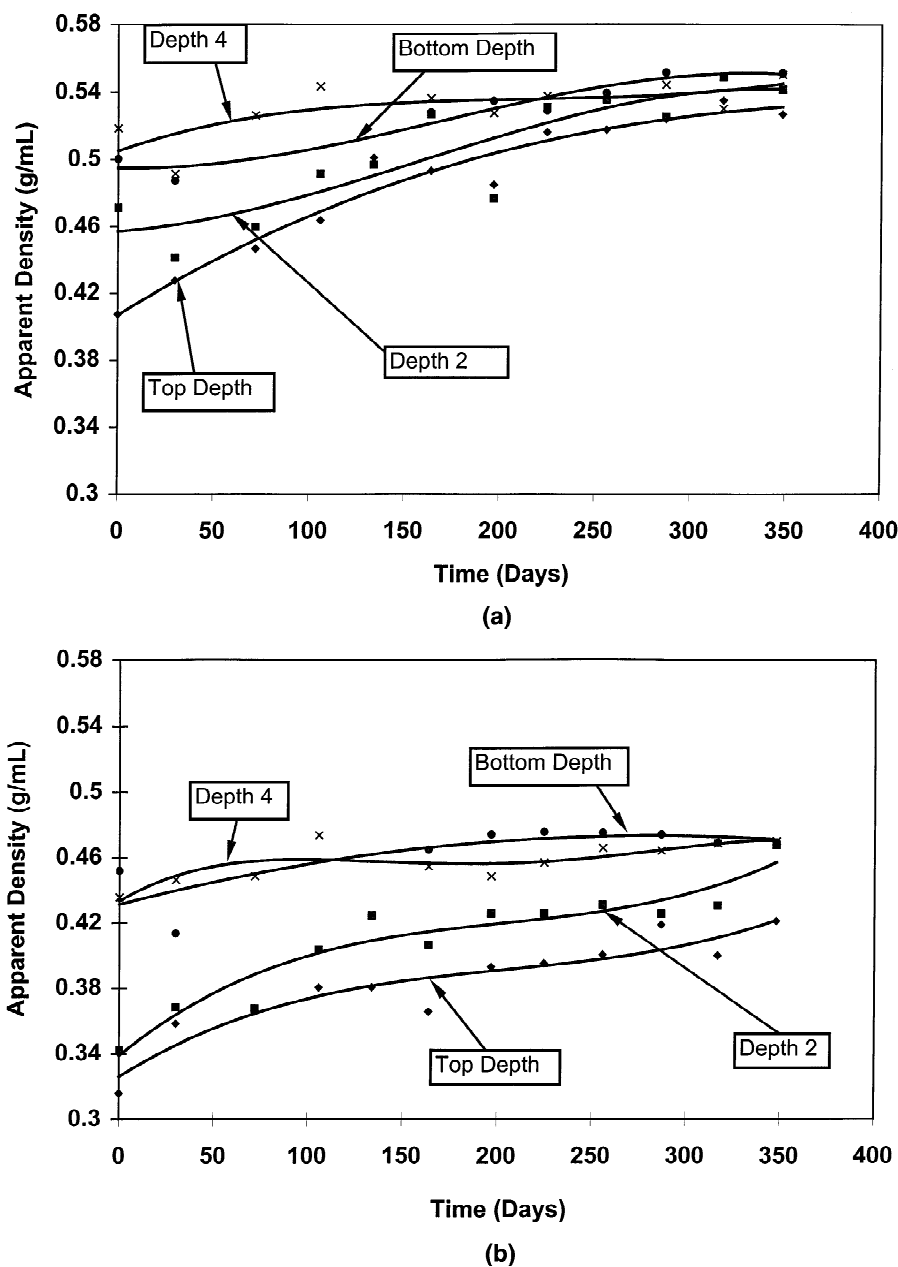


Fig. 4. (a) Time-wise variations in apparent densities of virgin GAC sampled from the top depth, depth 2, depth 4, and bottom depth of the contactor. (b) Time-wise variations in apparent densities of reactivated GAC sampled from the top depth, depth 2, depth 4, and bottom depth of the contactor.

pore size distribution trends that occurred during the other sampling events did not merely reflect artifacts of variations in sampling location. Specifically, separate pore structure analyses were performed on duplicate samples from the three sampling locations.

We have determined standard deviation values for the three locations that are representative of the two uppermost depths of each bed (Table 3). The standard deviations for

each triplicate-location GAC sample are quite small. We propose that the trends highlighted in the balance of the text are statistically significant because they differ by more than two standard deviations above the level of these triplicates (Fig. 5). In addition, all of our experimental data have been shown in these incremental pore volume figures, without any averaging of data points. Based on these confidence intervals, we submit that the trends that we

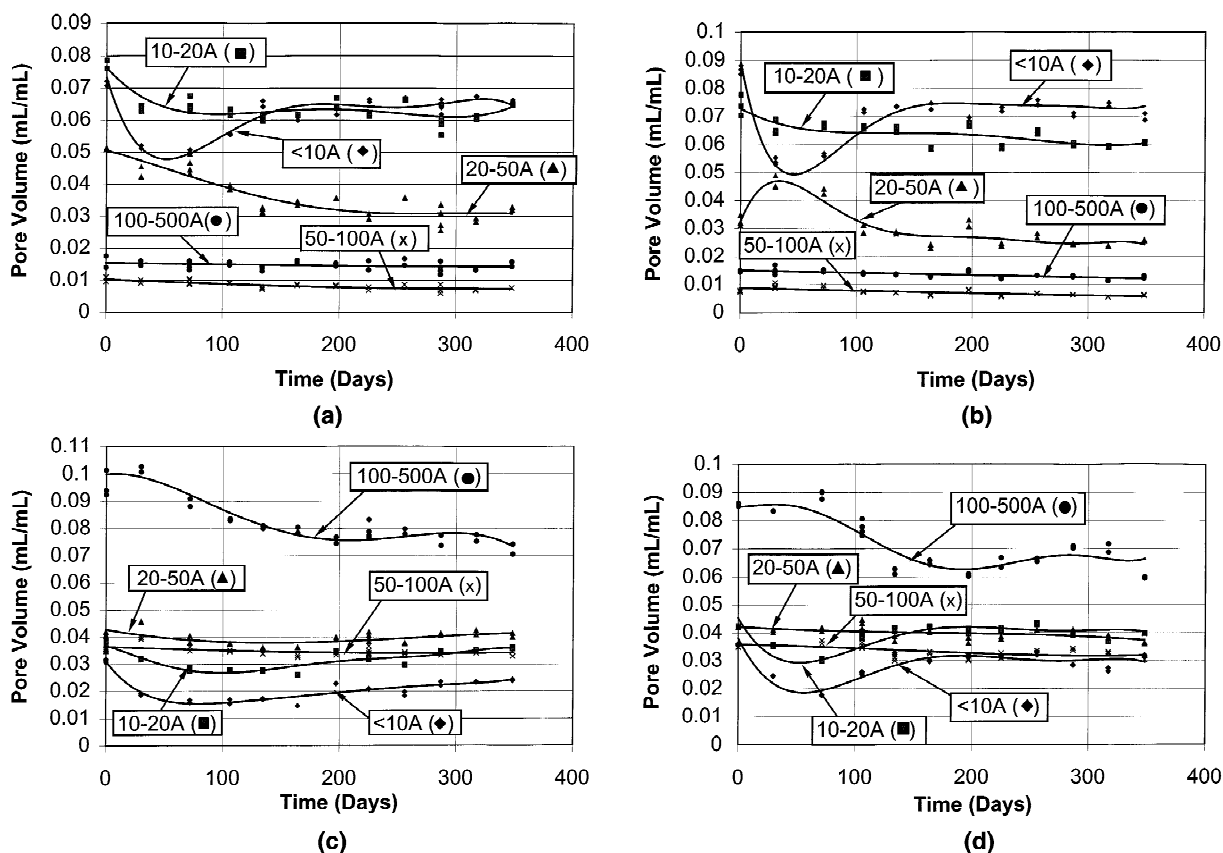


Fig. 5. (a) Incremental pore volume data for virgin GAC at the top depth (with respect to time); (b) incremental pore volume data for virgin GAC at depth 2 (with respect to time); (c) incremental pore volume data for reactivated GAC at the top depth (with respect to time); (d) incremental pore volume data for reactivated GAC at depth 2 (with respect to time).

have specifically highlighted below are statistically significant.

Time-wise changes in pore volume increments of the GAC from the top depth of the virgin contactor are shown in Fig. 5a. As shown, all three ranges of pores <50 Å experienced large volumetric decreases during the first 70 days of operation. In particular, the <10 Å pores experienced a dramatic reduction in pore volume, within even the first 30 days, down to 65–70% of their initial value. Interestingly, samples taken after the 70th day of operation showed a substantial increase in pore volume in

the <10 Å range. In fact, samples taken after the 130th day of operation showed more pore volume (in this range) than on the 30th or 70th day. We will return to discuss this at length below. In comparison, the pores in the 10–20 Å range continued to decrease in volume well beyond day 30–70, leveling off after roughly 130 days of treatment, to 80–85% of their initial value. In the 20–50 Å range, considerable reduction in pore volume occurred, down to 55–60% of the original value following about 225 days of service. In contrast, the mid-sized and larger mesopores (50–100 Å and 100–500 Å) seemed to have experienced

Table 3

Standard deviations for virgin GAC samples from the top depth and depth 2, and for reactivated GAC samples from the top depth and depth 2

	Total pore volume	Volume <10 Å	Volume 10–20 Å	Volume 20–50 Å	Volume 50–100 Å	Volume 100–500 Å
Virgin: depth 1	0.00453	0.00085	0.00153	0.00163	0.00043	0.00093
Virgin: depth 2	0.00410	0.00080	0.00075	0.00136	0.00065	0.00185
React: depth 1	0.01117	0.00128	0.00156	0.00303	0.00189	0.00396
React: depth 2	0.00482	0.00165	0.00199	0.00108	0.00078	0.00087

only slight change in pore volume throughout the 1-year duration; although there was not much pore volume to start with in these sizes. The changes that we have identified for the <10 Å, 10–20 Å, and 20–50 Å ranges are all statistically significant. These trends indicate that for the virgin GAC, considerable loading of DOM and inorganics occurred in the <50 Å pores. Cross-comparing this with subsequent ongoing M_w characterization research in our laboratory and the data in Table 1 would suggest that these pores were roughly one to eight times wider than the majority of organic molecules that were adsorbed. This range was determined from considering that the smallest molecule in Table 1 (6 Å) is eight times smaller than a 50 Å pore. The effects on pore volume are further discussed below.

Incremental pore structure results for the second depth of the virgin contactor (Fig. 5b) were remarkably similar to those of the first depth (Fig. 5a). Indeed, the parallelism between the top two depths coupled with the relatively small confidence intervals further validated the trends presented in Fig. 5a. Regarding the <10 Å pores, the same valley during days 30–70 was observed, as discussed at length below. Again, we observed that most pore volume changes in the virgin GAC seemed to have taken place in the pores less than 50 Å.

Similarly, others have also found mesopores (as well as micropores) to be important when adsorbing lower molecular weight DOM (<5000 Da) [26,45,47]. In comparison, some researchers have suggested that the adsorption of small organic acids [80] is correlated to the volume of micropores. Other researchers have proposed that the adsorption of small synthetic organics and selected organic dyes (with molecular weights of a few hundred) is correlated to the volume of micropores and/or smaller mesopores [48,49].

For the reactivated GAC, changes in pore volume fractions for the top depth are shown in Fig. 5c. For the first 70–100 days, pore volume diminished in all pore size ranges, although changes in pores 20–50 Å and 50–100 Å might not be statistically significant to the 95% confidence interval. After 1 year of water treatment, the greatest pore volume decrease occurred in the 100–500 Å pores, declining from an initial 0.10 ml/ml, down to a final 0.072 ml/ml, which represented a drop to 70–75% of the initial value.

This implies that the reactivated GAC adsorbed a substantial amount of DOM (and perhaps inorganics) within the 100–500 Å pore size. In light of Table 1 data, these pores were 4 to 80 times wider than the majority of organic molecules that they were adsorbing. It is unlikely, under these circumstances, that both pore walls could exert an adsorption attractive energy on the same molecule at the same time. Thus, this loading represents a single-wall adsorption phenomenon that exhibits more prominence than some researchers might previously have anticipated.

Further investigation of this (seemingly) preferential single-wall adsorption phenomenon is needed, and will be the focus of our further research.

Also significant, the volume of pores <10 Å decreased to 50% of their initial value after 30–70 days of service, and then rose up to 70–75% of their initial value by the end of the study. This behavior was reminiscent of the behavior for the virgin GAC, except there was an important distinction: the initial <10 Å pore volume for the reactivated GAC was only 40–45% as much as for the virgin GAC. Thus, neglecting any disconcerting effects attributable to differences in surface chemistry [16,81], the absolute magnitude of adsorption that the <10 Å pores offered was considerably less for the reactivated GAC than for the virgin GAC. At the same time, volumetric changes occurred in the pores of 10–20 Å diameters in GAC from the top depth of the reactivated contactor. These changes were very similar to those that occurred in the <10 Å pores. In particular, the volume of pores in the 10–20 Å range decreased to 70–75% of their initial value after 30–70 days; followed by a subsequent rise to 95–100% of their initial value.

One could also observe how the volume of pores in the 100–500 Å range did not change substantially during the first 30 days of treatment (Fig. 5c). Instead, our results show that during the first 30 days of treatment the greatest volumetric decrease occurred in the micropores. These results strongly suggest that adsorption initially took place in the most high-energy pores, which would have predominantly been in the micropores. After the most high-energy pores had become loaded (i.e. after day 30), it is clear that adsorption occurred preferentially in the 100–500 Å pores. Preferential adsorption in the 100–500 Å pores may have occurred for various reasons, including: (i) these pores may have been the next highest in attractive potential, (ii) the larger width of these pores would allow DOM to adsorb in the most favorable orientation, (iii) these pores would have likely been more accessible than other smaller pores.

The second depth of reactivated GAC (Fig. 5d) was remarkably similar to the first depth (Fig. 5c). Once again, the greatest quantitative pore volume change occurred in the 100–500 Å range, with an ultimate pore volume equal to 70–75% of its initial value. Additionally, the pores <10 Å and those 10–20 Å were characterized by initial drops in pore volume, followed by increases. Specifically, after 30–70 days, the <10 Å pore volume dropped to 50% of its initial value, followed by an increase to 85–90% of its initial value; while the 10–20 Å pores decreased to 70–75% of their initial value after 30–70 days, followed by an increase to 95–100% of the initial value. Also important, during (roughly) the first 70 days of treatment the volume of 100–500 Å pores did not change significantly. Instead, during the first 70 days of service the greatest change occurred in the micropores. Beyond day 70, adsorption

occurred extensively in the 100–500 Å pores. Indeed, this is quite similar to the trend that was discussed above for the top depth of the reactivated contactor (Fig. 5c).

Regarding the virgin and reactivated GACs (Fig. 5), most changes in pore volume occurred during the first 100–150 days of service, which is somewhat similar to the period in which we believe DOM removal had occurred largely via physical adsorption. After the GAC had been in service for around 200 days, pre volume changes were minimal, yet DOM was still being removed. Consequently, one might speculate that after 200 days of service DOM removal had occurred largely via biological oxidation (hence the small changes in pore structure). This speculation is consistent with observed TOC removal trends (Fig. 2). Further, since microorganisms would have been brought into both GAC contactors at the same rate, it makes sense that both contactors would reach steady state concurrently.

One could speculate that the effect of microbial activity might be a reduction in the molecular weight of incoming DOM. When considering the large size of microorganisms (of the order of 0.5–5 µm, or 5000 to 50,000 Å) relative to the size of adsorption pores (5–500 Å), one discerns that the microbes could achieve only limited decomposition of previously adsorbed high or medium molecular weight DOM that would be relatively non-adsorbable.

4.6. Discussion of pore volumes <10 Å and 10–20 Å: DOM loading mechanisms

As discussed above for both the virgin and reactivated GACs the <10 Å pores experienced an initial decrease in pore volume, followed by an increase. For the reactivated GAC, this trend was also observed for the 10–20 Å pores.

We offer the following explanation for why this occurred. During the first 30–70 days, the <10 Å pores experienced substantial loading at the most energetically attractive sites. This loading caused the initial volumetric decrease in the <10 Å range for both the virgin and reactivated GAC. Also, during this time and thereafter, adsorption caused a layering or colloidal accumulation within pores that were initially larger than 10 Å such that these larger pores shrank down to the <10 Å range. By this process, the volume of pores <10 Å experienced a net increase. This same rationale would hold for the 10–20 Å pores of the reactivated GAC.

Furthermore, this DOM accumulation (and perhaps the waters of hydration) could have isolated narrow adsorption sites (<10 Å) from subsequently adsorbing DOM. Therefore, the subsequently adsorbing DOM ended up loading in the slightly larger pores, even though the attractive potentials of these pores (on average) would have been lower than for the smallest pores that were inaccessible.

Parenthetically, even though some DOM molecules

could have been precluded from these <10 Å pores during water treatment service, the smaller argon molecule (3.6 Å diameter) was not precluded during pore volume characterization tests.

In light of this rationale, we conclude the following.

1. If within a certain range of pore widths the pore volume distribution manifests no change, it can either mean that (i) no measurable adsorption occurred within this width range or (ii) the loading-incurred shrinkage of pores to widths smaller than this increment equaled the shrinkage of wider pores into this incremental range.
2. If within a certain width range the pore volume distribution decreased, then the adsorption loading that caused a decrease in pore volume in the region occurred in excess of those that produced an increase of pores in this region.
3. If within a certain width range the pore volume increased, then adsorption mechanisms produced an increase in pore volume in this region that was greater than the loss of pore volume in this region.
4. Concerning the <10 Å range, these pores as a combined whole cannot constrict to a yet smaller size. Thus, if the <10 Å pore volume decreased, the pores in this range became filled or blocked in a manner that rendered them inaccessible to argon. If the <10 Å pore volume increased, the pores of larger width (perhaps 10–20 Å or 20–50 Å) became coated in such a manner as to form pores with effective widths <10 Å.

These changes in pore volumes are depicted in Fig. 6, which conceptually illustrates the probable adsorption behavior of organic matter in GAC pores over time. Fig. 6 has been loosely modeled after Stoeckli's schematic representation of the structure of activated carbon [82] in addition to the high resolution electron microscopy findings of Marsh et al. [83] and Fryer [84]. For clarity, changes in pore volume during the course of this study are shown in a 2-dimensional rendition of the structure of activated carbon (Fig. 6a–c), whereby each line represents a basal plane (i.e. graphene layer). Fig. 6a portrays time=0 (i.e. prior to water treatment), when the pores would ideally be free from adsorbed organic matter. Fig. 6b shows the same GAC pores at some time, 't', soon after water treatment has started; when adsorption has occurred most substantially at the high-energy sites, which includes micropores, with somewhat less adsorption occurring in the mesopores [3]. At this point, the micropores have experienced a loss of pore volume (and pore area), largely due to pore filling/blockage; while the mesopore volume has also decreased somewhat. Fig. 6c shows how several mechanisms of physical adsorption may have altered GAC pore structure at some time later than 't' (say after 100–150 days). Specifically, the various adsorption regions of Fig. 6c, labeled A through F, are described in Table 4.

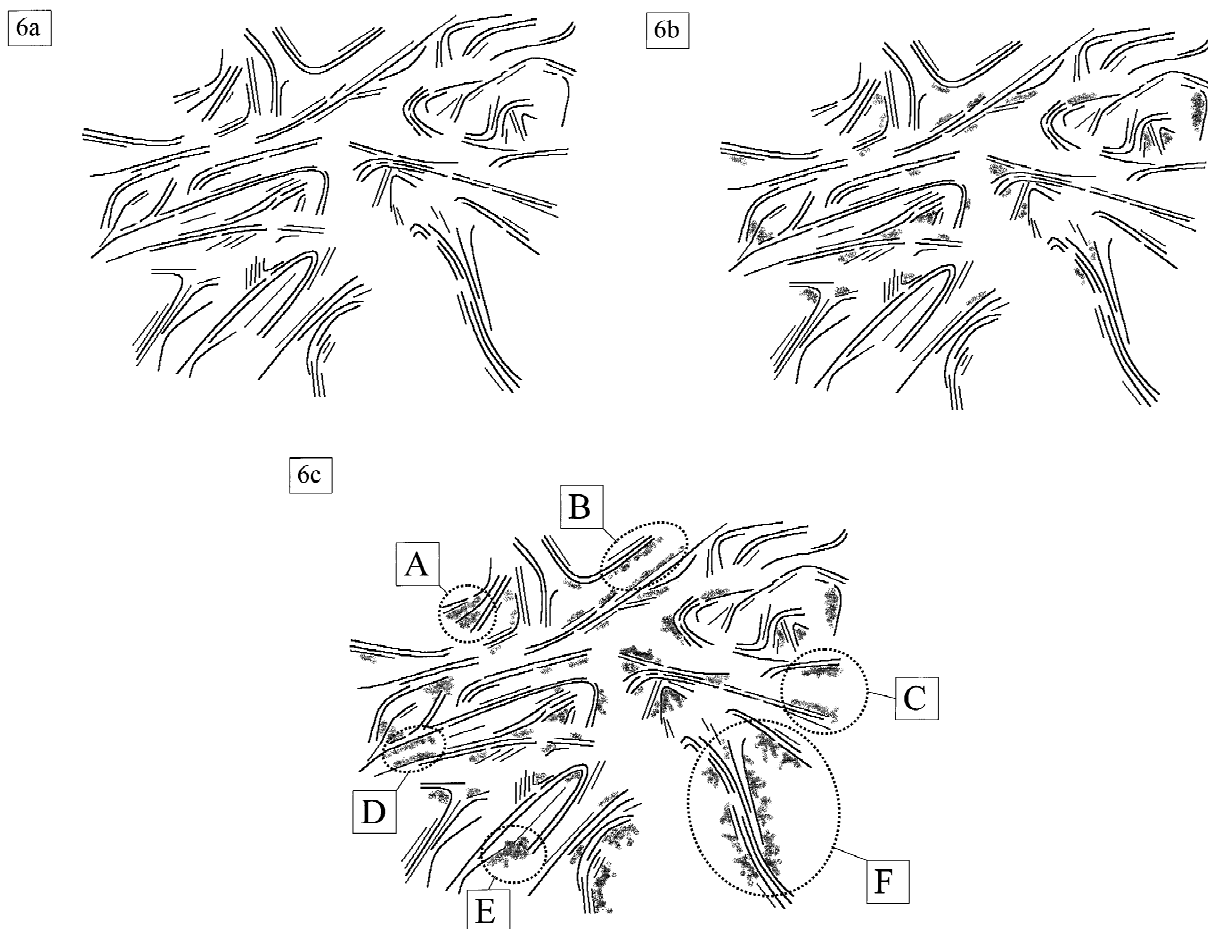


Fig. 6. Conceptual representation of pore structure changes in GAC due to adsorption: (a) pore structure at time=0; (b) pore structure at time='t' (shortly after water treatment has started); (c) pore structure at some time beyond time='t', depicting mechanisms by which pore structure may have been altered.

Several of these phenomena in combination with one another could account for the initial drop in <10 Å (or 10–20 Å) pore volumes, followed by a subsequent increase in these pore volumes.

To further highlight the trend in the fine-pore range, incremental pore volumes were evaluated for several alternative micropore divisions of the virgin contactor (Fig. 7). Specifically, four alternative fine-pore spans were evaluated: (i) <8 Å, (ii) <12 Å, (iii) <6 Å, and (iv) 6–10 Å. In the first two cases, the lower pore size ranges (i.e. <8 Å and <12 Å) exhibited an initial decrease in pore volume followed by an increase. Furthermore, when we evaluated the third and fourth alternative micropore divisions, the two lowermost size ranges (<6 Å and 6–10 Å) both demonstrated a drop in pore volume followed by an increase. Indeed, this confirmed that the trend was not occurring exclusively in the smallest pores (<6 Å); rather,

it was occurring throughout the entire range of pores <10 Å in width.

4.7. BET surface areas

BET surface area values are shown for the two uppermost depths of each contactor in Fig. 8, for the 1-year span of the study. Similar to the pore size distribution data, BET values have been normalized to a unit bed volume basis (i.e. m^2/ml). As shown, the virgin GACs had higher BET surface areas than the reactivated GACs. Although the GACs from the two contactors were dissimilar with regard to their BET values, they shared a general commonality in the shape of their respective curves. In particular, all GACs experienced an initial decrease in their BET values, which was followed by a more subtle increase

Table 4

Descriptions of the adsorption phenomena and the respective impacts (on pore structure) of the areas highlighted in Fig. 6c

Label	Phenomenon	Impact
A	Pore filling of micropores	Micropore volume (and surface area) decreases
B	Wall-coating type adsorption narrowing effective width of pore; consequently, this pore is categorized into a smaller size range	Volume of pores in this size region decreases, while volume of pores in smaller size region increases
C	Wall coating adsorption narrows pore width, without shifting pore into a smaller size range	Pore volume decreases in this size range, while surface area may not change substantially
D	Constriction of pore opening	Argon can fit through constriction to measure pore volume behind constriction during analysis, but organic matter cannot pass through constriction during water service
E	Pore blockage	Pore volume is lost to both argon adsorption and organic adsorption
F	Small, high surface area–low volume micropores formed within and between adsorbed organic matter (perhaps adsorbed with tails or loops present) on mesopore walls	Micropore volume (and surface area) increases. Volume of pores in this mesopore range decreases, while area of pores may not decrease substantially. This phenomenon could occur in the mesopores or micropores

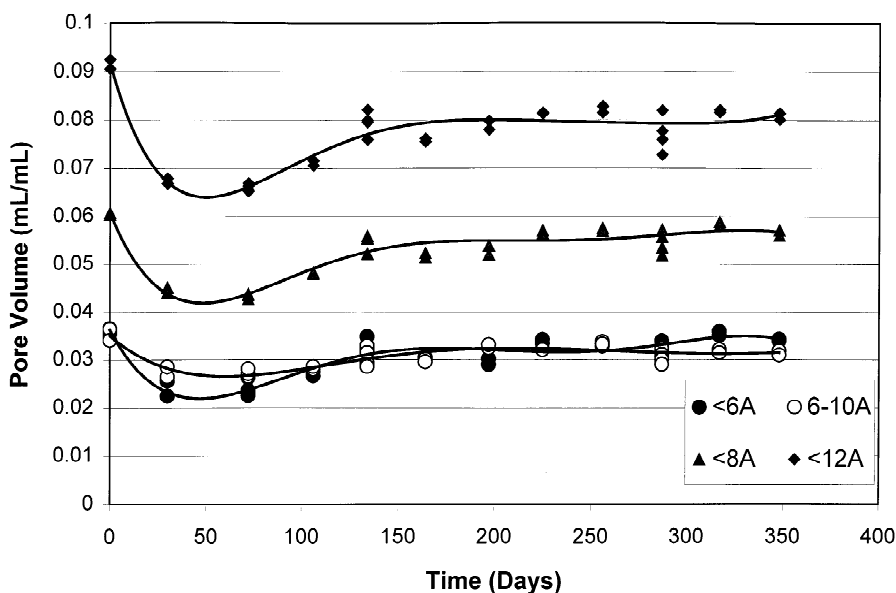


Fig. 7. Comparison of incremental pore volumes for alternative micropore divisions (virgin GAC from the top depth).

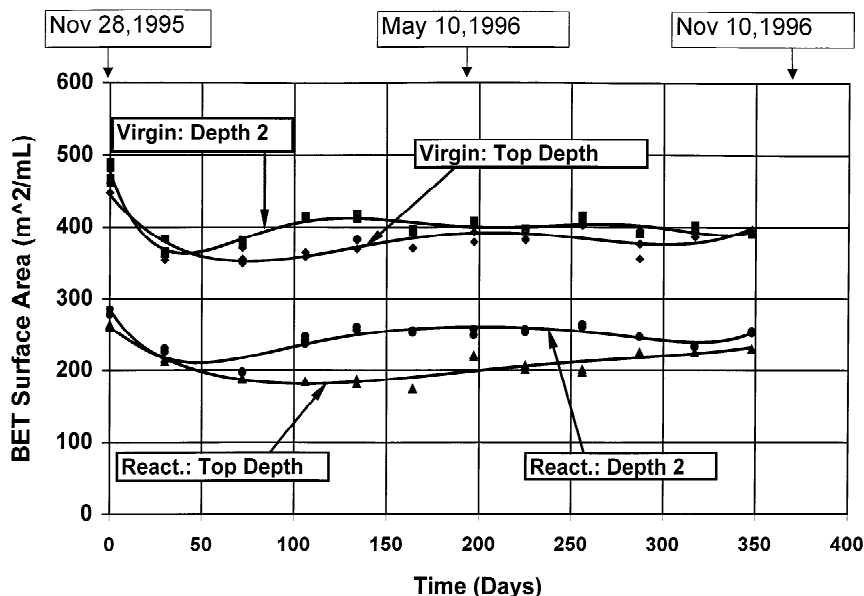


Fig. 8. Time-wise changes in BET surface areas for the virgin GAC (top depth and depth 2) and the reactivated GAC (top depth and depth 2).

in BET values. This trend was somewhat reminiscent of those we observed for micropore volume in Fig. 5.

5. Summary and conclusions

Several important conclusions can be made from the full-scale comparison between virgin and reactivated GAC at Cincinnati, Ohio. Firstly, GAC that had been through six cycles of water treatment and reactivation was effective at removing TOC; see also Ref. [64]. In particular, during the first 168 days of treatment, the reactivated GAC removed TOC more effectively than the virgin GAC. This is an important finding because during operation at the Miller plant, GAC contactors are typically only kept in service for 6 months; for the present study, they were kept in service for a year in order to facilitate prolonged testing. These findings are also important because upcoming regulations [85] are recommending reactivation of GAC following 6 months of operation.

Secondly, the trends that we observed concerning pore volume revealed a commonality between depths one and two within each contactor. Yet, pore size distributions (Fig. 3) and pore volume fractions (Fig. 5) revealed that the virgin and reactivated GACs did not predominantly adsorb TOC in similarly sized pores. Fig. 5a and b illustrated the importance of pores smaller than 50 Å in the virgin GAC. Conversely, our results show that the 100–500 Å pores were most important in the reactivated GAC. Furthermore, for both the virgin and reactivated GAC, the volume of

pores <10 Å experienced an initial decrease, followed by an increase. This was also observed for the 10–20 Å pores in the reactivated GAC. We have offered a conceptual diagram (Fig. 6) highlighting the physical adsorption processes that may have been responsible for this behavior in the micropore region.

In addition, we have proposed that one can discern a link between pore volume changes and the dominant adsorption behaviors responsible for these changes (Table 4). For instance, when pore volume <10 Å decreased, it meant that the dominant adsorption factor was the filling or blocking of these pores (i.e. more pore volume was lost than gained). In contrast, when pore volume <10 Å increased during subsequent days, it meant that pores wider than 10 Å were becoming coated or partially filled with adsorbate in a manner that resulted in a net volumetric increase in pores <10 Å, which exceeded the rate at which pores <10 Å were lost.

Finally, when the 100–500 Å pores in the reactivated GAC exhibited a dramatic volumetric reduction, this indicated that far more pores within this width range were diminishing in width to smaller pores than there were pores larger than this that were diminishing into the 100–500 Å range. This highlighted the importance of the 100–500 Å pores in the reactivated GAC. When comparing this 100–500 Å width to the approximated 6–20 Å dimensions (Table 1) of the majority of organic molecules entering the contactors, one discerns that either coating of a single wall, organic molecule-to-molecule interactions, or colloid-forming mechanisms caused this pore width range to play such an important role for the reactivated GAC.

The surface chemistry of these mesopores may have also played an important role, but this aspect has not been studied here.

Above all, these findings offer an opportunity to water utilities who seek to comply with anticipated disinfection by-product (DBP) regulations by employing GAC. If GAC can be successfully reactivated and reused through six cycles, this represents considerable potential cost savings, when compared to discarding the spent GAC after each water treatment cycle, and replacing it with virgin GAC.

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