

Comparison of Activated Carbons for Removal of Perfluorinated Compounds From Drinking Water

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This article describes the challenge of treating drinking waters contaminated by perfluorinated compounds, especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). A goal of the study was to establish the relative effectiveness for perfluorinated compound removal by the two primary types of granular activated carbons (GACs) commonly used in the treatment of municipal drinking water: bituminous coal-based re-agglomerated GAC and coconut-based direct activated GAC. The effectiveness of GACs in removing PFOA and

PFOS to nondetectable levels is demonstrated through the use of rapid small-scale column testing. Results demonstrate that bituminous coal-based re-agglomerated carbons provide considerably greater removal capacity of the targeted compounds compared with the coconut-based direct activated carbon. In support of these findings, summaries of additional third-party test work and field installations are cited. In addition, the authors provide an overview of reactivation of activated carbon to improve the economics of the technology.

Keywords: *granular activated carbon, perfluorinated compounds, perfluorooctanoic acid, perfluorooctane sulfonate*

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), among other perfluorinated compounds (PFCs), have been used in the production of various fluoropolymers. These compounds, as well as the fluoropolymers made from them, have been used in stain-resistant fabrics, nonstick cookware, firefighting foams, and other applications. Although dozens of PFCs of varying chain lengths and compositions have been detected in water, the US Environmental Protection Agency (USEPA) has shown particular concern regarding the longer-chained PFCs with eight or more carbons, such as PFOA and PFOS (USEPA 2016). Because of their ubiquitous use in the past, PFOA and PFOS usually are detected more frequently than other PFCs and at higher concentrations. They are also more toxic and more bioaccumulative than shorter-chain PFCs, such as the hexyl and butyl analogues of PFOA and PFOS.

Given their stability and solubility in water, PFCs have now become widely distributed throughout the environment, particularly in water systems. Although PFOA is not reported as an analyte in the US Geological Survey National Water Quality Assessment Program and is not monitored by USEPA's National Aquatic Resource Surveys, it has been detected in many studies of US source waters including the Tennessee River, Mississippi River, Ohio River, Lake Erie, Lake Ontario, and many others (USEPA 2016).

BACKGROUND

PFOA and PFOS health concerns and occurrence. The International Agency for Research on Cancer (IARC 2016) has classified PFOA as possibly carcinogenic to humans (group 2B) on the basis of limited evidence of testicular and kidney cancers in humans and limited evidence in laboratory animals. Although no similar cancer classifications have been developed for PFOS, there is still evidence of developmental effects attributed to toxicity (suspected particularly in the developing fetus and newborns).

Exposure data collected by the National Health and Nutrition Examination Survey 2003–2004 found PFOA in human serum in 99.7% of the population (CDC 2005). Since then, levels in human serum have declined because of the phaseout of PFOA and PFOS. All manufacture and import of PFOS in the United States was voluntarily ceased by 2002. Similarly, all manufacture and import of PFOA in the United States was voluntarily halted by 2015. The USEPA (2017) included PFOA and PFOS as candidates for possible regulation under the Safe Drinking Water Act (SDWA). In accordance with the requirements of the SDWA to determine whether to regulate a new contaminant, PFOA was added to the third Contaminant Candidate List (USEPA 2009a) and was included as one of the 30 contaminants to be studied as part of the third

Unregulated Contaminant Monitoring Rule (USEPA 2012). Under the rule, large (and some smaller) water suppliers are required to monitor PFOA in their waters for a one-year period. This monitoring was conducted between 2013 and 2015. Results showed that PFOA was reported at or above the minimum reporting level of 20 ng/L by about 2% of the public water utilities. Approximately 0.3% of those surveyed reported levels at or above the USEPA's recently issued health advisory level of 70 ng/L, and approximately 1% reported results of combined levels of PFOA and PFOS above the health advisory level (USEPA 2016). This means that the drinking water supplies of more than six million people in the United States have concentrations of these compounds at levels exceeding the health advisory limit (Hu et al. 2016).

PFOA and PFOS have been found worldwide in soil, groundwater, surface water, and wastewater. Reported concentrations in water are typically in the nanograms-per-liter range, but much higher concentrations in micrograms per liter or even milligrams per liter are found in waters adjacent to industries where PFCs are in use (Ahrens 2011) and sites where aqueous film-forming foams have been used for firefighting and crash training (Anderson et al. 2016, Rumsby et al. 2009). For example, in communities downstream of a fluoropolymer manufacturing facility in West Virginia, PFOA was detected at concentrations ranging from 30 to 3,550 ng/L in public drinking water, and as high as 22,100 ng/L in private wells (Emmett et al. 2006). PFCs are mobile and leach into groundwater, whereas surface water sources are affected by PFCs present in treated wastewater that feeds into surface water sources, such as rivers. Most conventional wastewater processes are not effective in removing PFCs,

thereby leading to the presence of these compounds in treated wastewater effluent (ASTSWMO 2015).

To date there is no established primary drinking water regulation for PFCs—only the lifetime drinking water health advisory levels set by USEPA and several individual states. These levels are summarized in Table 1 (AWWA 2016).

PFOA and PFOS properties. PFOA and PFOS are synthetic fully fluorinated organic acids. PFOA ($C_8HF_{15}O_2$) and PFOS ($C_8HF_{17}O_3S$) are strong acids generally present in their ionic forms, perfluorooctanate ($pK_a = 2.8$) and perfluorooctane sulfonate ($pK_a = 3.27$ calculated), and both exhibit significant solubility in water (PFOA: 9,500 mg/L, PFOS: 570 mg/L). These compounds are highly stable because of their saturation of fluorine-carbon bonds. Their vapor pressures are very low, and the boiling points of PFOA and PFOS are 372 and 271°F, respectively.

Because of this combination of properties, these compounds are highly mobile in surface water and groundwater and resistant to most types of degradation. Their properties also make these compounds resistant to removal by most standard treatment technologies.

APPLICATION OF GRANULAR ACTIVATED CARBON FOR PFC TREATMENT

Currently the most researched and installed technology for PFC removal is granular activated carbon (GAC). GAC has been shown to be effective at removing compounds such as PFOA and PFOS and at favorable loading capacities.

Reported lab studies. Appleman and colleagues (2013) tested several activated carbons with and without the

TABLE 1 PFC concentration guidelines

Agency	Matrix	Contaminant µg/L
USEPA	Drinking water	Lifetime health advisory: PFOA and PFOS (combined or individually)—0.070
State	Matrix	Contaminant µg/L
Illinois	Groundwater	PFOA—0.400, PFOS—0.200
Maine	Groundwater	PFOA—0.060, PFOS—0.100
Michigan	Surface water	PFOA—0.420, PFOS—0.012
Minnesota	Drinking water and fish consumption	PFOA—0.610 (lake), PFOS—0.012 (lake) PFOA—0.720 (river), PFOS—0.006 (river)
New Jersey	Drinking water	PFOA—0.040
North Carolina	Groundwater	PFOA—2
Vermont	Drinking water	PFOA—0.020

Source: AWWA 2016

PFC—perfluorinated compound, PFOA—perfluorooctanoic acid, PFOS—perfluorooctane sulfonate, USEPA—US Environmental Protection Agency

presence of dissolved organic carbon (DOC) for perfluoroalkyl acid (PFAA) removal at levels of 1 µg/L. A coal-based GAC¹ was shown to have the highest adsorptive capacity, exhibiting less than 20% breakthrough of all PFCs at 125,000 bed volumes (BVs) treated. All carbons experienced a 20% breakthrough at 10,000 BVs when DOC was added.

Qiu et al. (2007) conducted isotherms using a coal-based GAC,² a coconut-based GAC,³ a peat-based GAC,⁴ and a wood-based GAC.⁵ The coal-based GAC was found to have the best overall performance for the PFCs tested. In general, all products performed better for the longer-chain PFCs, which include PFOA and PFOS. The presence of natural organic matter (NOM) was shown to adversely affect the adsorption capacity of these products.

Rahman (2014) conducted isotherm tests for the adsorption of three PFCs with the coal-based GAC,² a coconut-based GAC,⁶ and two wood-based GACs,^{7,8} along with a biochar⁹ and a bone char.¹⁰ The coal-based GAC was the superior product for the three targeted compounds, and even rivaled two different ion exchange resins in similar tests conducted by Rahman et al. Treatment of surface waters containing NOM negatively influenced the adsorptive capacities of all media but not to such an extent as to make the technologies infeasible.

Field experience. In full-scale field operation, activated carbon has proved to be a cost-effective means for meeting PFC effluent targets.

Little Hocking, Ohio. The public water supply was contaminated with concentrations of PFOA as high as 8.5 µg/L by discharges from a nearby manufacturing plant. A GAC plant began operation in 2007 to treat incoming groundwater with an average of 3.3 µg/L of PFOA. Carbon is exchanged at approximately three-month intervals. No detectable PFOA has been found entering the water supply for the town (Cummings et al. 2015).

Oakdale, Minn. Groundwater contamination with several PFCs from a manufacturing site led to the installation of ten 10,000 lb-capacity carbon vessels with a flow capacity of 2,000 gpm. The lead vessels of two vessel trains are changed when concentrations in the outlet reach 50% of the inlet level. By replacing carbon on the basis of PFOA breakthrough, the plant was able to treat 1.9 bil gal over 23 months, which amounted to a cost of \$0.12/1,000 gal treated (Bachmeier 2015).

New Jersey American Water: Logan System Birch Creek. GAC absorbers were designed to provide an empty bed contact time (EBCT) of 15 min using coal-based re-agglomerated GAC to remove PFOA and perfluorononanoic acid from groundwater at influent concentrations of 18–72 ng/L. The contaminants are removed to below reporting levels of 5 ng/L (Engineering Performance Solutions 2010).

Hoosick Falls, N.Y. Two 20,000 lb vessels in lead-lag configuration were in temporary use to treat drinking water contaminated from an industrial site. Sampling of

the public water supply before the installation detected PFOA at concentrations between 400 and 1,000 ng/L (Hoosick Falls 2016). The temporary system treated nearly 210 mil gal of groundwater in 290 days with no breakthrough in system effluent. A permanent system consisting of two 40,000 lb vessels filled with coal-based GAC has been effectively reducing PFOA levels from over 400 ng/L to below 2 ng/L since December 2016.

Anglian Water, United Kingdom. Five GAC filters with coal-based GAC producing an EBCT of 65–110 min are used to treat groundwater with 3.7 µg/L PFOS and other PFCs emanating from a nearby airbase. The carbon is reactivated annually after treating about 5,500 BVs of water. The breakthrough of PFOS and PFOA would occur at 8,000–9,000 BVs (Rumsby et al. 2009).

Reactivation of GAC. A key feature in GAC use is the thermal reactivation of the spent product by which it is essentially remanufactured for reuse in the application. Not only does the use of reactivation greatly improve the economics of applying GAC, but it also eliminates the need to dispose of spent carbon and its contaminant loadings, removing any future liabilities associated with those wastes. This process has been widely used at several municipal treatment plants and commercial facilities across the United States. In the reactivation process, the activated carbon is heated to temperatures of at least 800°C using steam as a selective oxidant. It should be noted that in testing of activated carbons containing PFCs, Watanabe et al. (2016) found no residual perfluoroalkyl substances on activated carbon when heated to 700°C in nitrogen. During reactivation, the adsorbed organic material either boils off the activated carbon or is broken down to a char in the carbon pores. The selective oxidation process restores the pore structure of the product and makes it suitable for reuse. All organic emissions are subsequently burned in the system's afterburner, and acid gases (including hydrogen fluoride) are neutralized in alkaline scrubbers.

CHARACTERIZATION OF GAC PORE STRUCTURES

As in all activated carbon adsorption applications, the carbon's performance in adsorbing PFCs from groundwaters should be influenced by the quality and characteristics of the GAC used. An extensive range of GACs are available for water treatment, and these differ by the source of carbonaceous starting material, the method of manufacture, and level of activation. There are no "bad" activated carbons, only "poorly applied" activated carbons; therefore, the challenge is to match the qualities and characteristics of the various activated carbons available to the specific water treatment task at hand. In the current study, performance testing was conducted to compare the PFC removal performance of two types of GACs, both of which are often used in the treatment of groundwater contamination. For inclusion in this study, the authors selected two bituminous, coal-based

re-agglomerated, steam-activated carbon products^{11,12} and two direct steam-activated coconut-shell-based carbons^{13,14} (Table 2).

The coal-based re-agglomeration process involves the following five steps: pulverization of the coal, addition of a carbonaceous binder, reforming of a briquette in the press room, sizing based on final product dimensions, and baking and steam activation. The direct activation process requires three steps: low-temperature charring of raw coconut shells, sizing of char on the basis of final product dimensions, and steam activation.

Re-agglomeration during coal-based carbon manufacture is a technique that has been used for many years to improve certain characteristics of GAC. In short, re-agglomeration provides “man-made” cracks and crevices that resemble the transport pore structure in the granulated carbon. The transport pore structure can be defined as those pores that are greater than 100 angstroms (Å) in diameter and have very limited adsorption energy but provide the important pathways by which contaminants travel to the adsorption pores located throughout the granule. Not only does the re-agglomeration process increase the number and volume of transport pores in the final product, but it also provides pathways that allow a more homogenous activation during the manufacturing process. This results in a more consistent adsorption pore size distribution ranging from the very outer surface of the granule to the innermost points of the particle. One of the re-agglomerated coal-based carbons was tested in its virgin state. The second coal-based carbon was a custom municipal reactivated (CMR) GAC that before use

TABLE 2 Activated carbon types used in RSSCT study

GAC Type	Description
Virgin bituminous coal, 12 × 40	Moderate-density bituminous re-agglomerated coal-based GAC, 12 × 40 mesh
Coconut, 8 × 30	Direct activated coconut-based GAC, 8 × 30 mesh
Coconut, 12 × 40	Direct activated coconut-based GAC, 12 × 40 mesh
Reactivated bituminous coal, 12 × 40	CMR re-agglomerated GAC, 12 × 40 mesh

CMR—custom municipal reactivated, GAC—granular activated carbon, RSSCT—rapid small-scale column testing

The four GACs tested in the RSSCT study were manufactured and supplied by Calgon Carbon Corporation, Moon Township, Pa.

was the same product as the virgin carbon tested. The CMR carbon was in service for 12 to 18 months at an unnamed drinking water treatment facility, removing surface water NOM and total organic carbon (TOC) for the prevention–reduction of disinfection byproducts post-chlorination. On the basis of the age of the custom reactivation pool, it was estimated that the CMR carbon used in this study had undergone three reactivation cycles. Custom reactivation is conducted with steam at approximately 800°C, well above the 700°C threshold reported by Watanabe et al. (2016). The direct activated coconut

TABLE 3 Activated carbon characterization data

Parameter	Virgin Bituminous Coal 12 × 40	Coconut 8 × 30	Coconut 12 × 40	Reactivated Bituminous Coal 12 × 40
Apparent density—g/cc	0.532	0.533	0.539	0.527
Ash—%	8	2.3	2.1	9.9
Iodine number—mg/g	948	1,039	1,149	932
TCN—g/cc	11.1	15.1	17.7	10.4
Molasses number	173	144	138	178
Screen mesh size—weight % on pan				
8	0	0.5	0	0
10	0	15.8	0	0
12	4.1	32.4	0.3	0.3
16	50.3	30.1	34.4	29.9
20	30.6	14.5	38.6	43.9
30	12.2	6.6	18.9	20
–30	0	0.1	0	0
40	2.4	0	7.4	5.3
–40	0.4	0	0.4	0.6

TCN—trace capacity number

carbons selected for inclusion in the comparison study described here were an 8 × 30 mesh product¹³ and a 12 × 40 mesh product.¹⁴

The following common standard carbon tests were conducted on each of the test carbons, including apparent density (ASTM International 2014a), iodine number (ASTM International 2014b), ash (ASTM International 2011), trace capacity number (TCN) test method (Nowicki 2014), and molasses number. Results are shown in Table 3.

Total adsorbent characterization via temperature influence correction (TACTIC) analyses (Greenbank et al. 1991) were performed to generate “fingerprint” pore size distribution comparisons for the GACs used in the testing. TACTIC analyses have been used by Calgon Carbon Corporation to characterize adsorption pore-size distributions for 35 years. During the test, the adsorbent is exposed to a pure gas adsorbate over a large range of temperatures. The adsorption of the gas requires more pore energy as the temperature increases. The energy of the pore is directly related to its size or average diameter. The weight of the carbon and adsorbed gas is precisely measured as the temperature is slowly increased and decreased, logging approximately 1,000 adsorption data points covering seven orders of magnitude in relative pressure and three orders of magnitude in carbon loading. The data are fit to a sixth-order polynomial equation, which can be used to directly compare adsorbents for a common application. Figure 1, parts A and B, shows the differential pore volume measured versus the adsorption potential energy (x-axis), which is directly related to pore size (secondary x-axis).

Although all four carbons exhibited very similar total cumulative adsorption pore volumes (approximately 40 cc/100 g), the distribution of the adsorption pores as shown in the graph (Figure 1, part A) of the differential pore volumes (pores of up to 100 Å in diameter) is much different for the re-agglomerated coal-based GACs versus the direct activated coconut GACs. The coconut-based GACs exhibited higher pore volumes for pores with diameters ≤10 Å, while the re-agglomerated coal-based carbons showed higher pore volumes in the larger pores (10–100 Å in diameter). Although TACTIC analysis does not measure the transport pore structure discussed previously, the slopes of the differential curves between 10 and 30 Å provide an estimation of the pore volumes of transport pores ranging from 100 to 1,300 Å in diameter. Therefore, the TACTIC curves suggest the coconut-based GACs have significantly less transport pore structure than the re-agglomerated coal-based GACs. This was also confirmed by the molasses number values for each of the GACs presented in Table 3, showing the coconut GACs between 138 and 144, while the coal-based GACs exhibited molasses numbers of 173 and 178. The molasses number test method has long been used

in the activated carbon industry to measure a carbon’s relative performance in color removal applications. The molasses test is a relatively good measure of adsorption kinetics, which is directly related to the amount of transport structure in an activated carbon.

Part B of Figure 1 is an expanded view of part A and shows the differences in pore volumes in the higher-energy pore structure range. The curves clearly indicate that the coconut-based GACs showed higher volume in the high-energy adsorption pores than the coal-based GACs. The TCN test method, developed by Calgon Carbon to measure the performance of activated carbons for the removal of very soluble, low-molecular-weight contaminants present at low concentrations (Nowicki 2014), also confirmed the coconut-based GACs’ superior pore volume in the higher-energy pore region, exhibiting high TCN values of 15.1 and 17.7 g/cc versus values of 11.1 and 10.4 g/cc for the coal-based GACs.

In terms of GAC treatment, typical PFC removal applications would be considered to be trace removal type applications, i.e., the adsorption of very soluble organic compounds at very low contaminant concentrations. This would suggest that GACs exhibiting higher volumes of higher-energy pore structure would outperform GACs having larger adsorption pores and lower overall adsorptive energy.

EXPERIMENTAL STUDY

In this research, a laboratory study was conducted to determine the relative efficacy of four different GAC products for the removal of PFOA and PFOS. The study detailed here used rapid small-scale column testing (RSSCT) to determine the relative adsorbability of PFOA and PFOS in the presence of typical TOC concentrations in groundwater, demonstrate the effectiveness of GAC for the control of these compounds, and compare the performance of re-agglomerated coal-based GACs with that of coconut-based GACs.

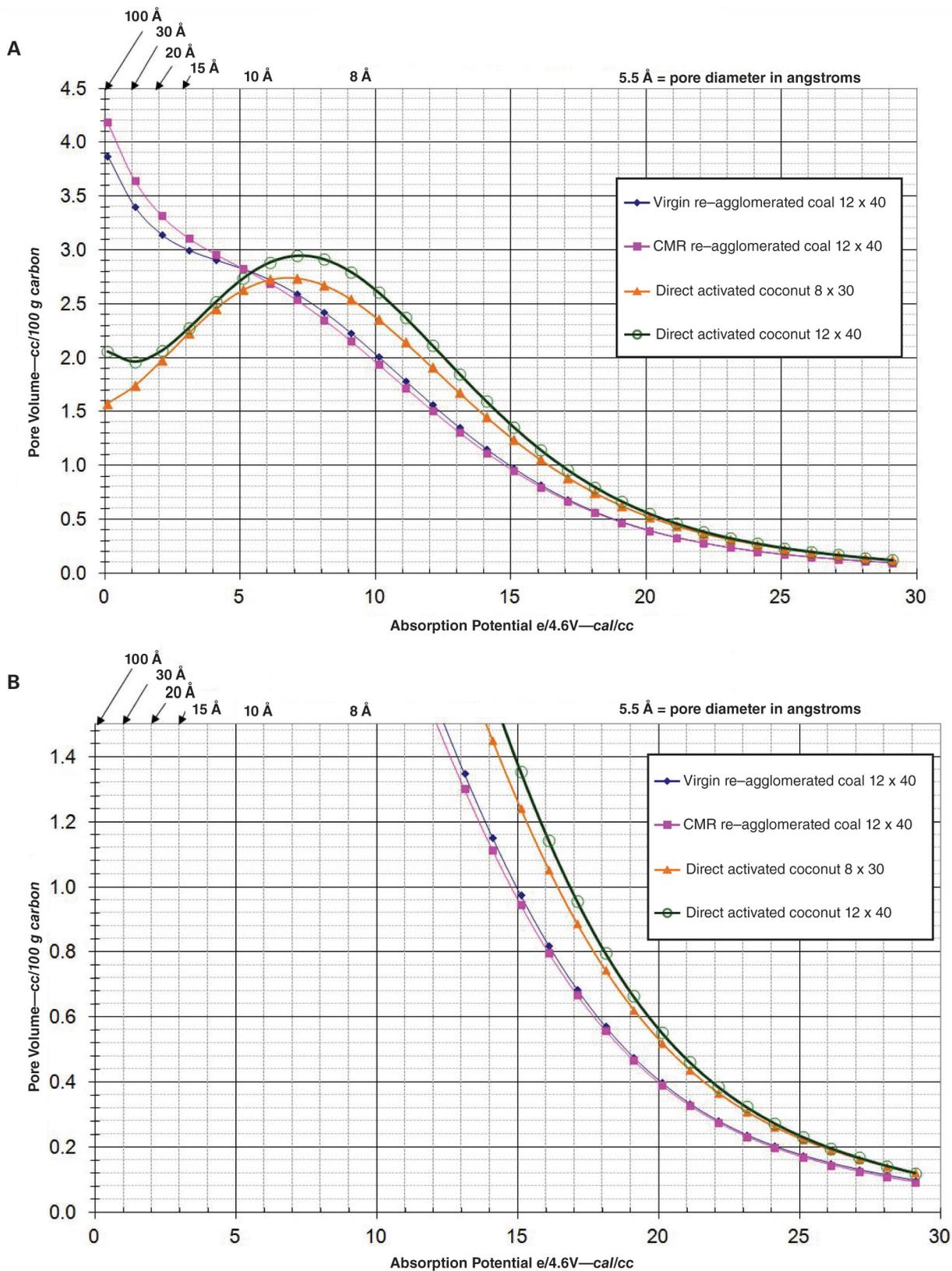
EXPERIMENTAL METHODS

RSSCT design. The RSSCT design simulated a fixed GAC bed providing a 10-min EBCT; RSSCT design parameters are listed in Table 4.

The RSSCT procedure uses a miniature carbon-filled column to rapidly simulate the adsorption breakthrough curve that would be obtained by treating an aqueous stream in a large adsorption system. This technique has been shown (Crittenden et al. 1986) to accurately simulate the carbon treatment of a wide range of waters and wastewaters under various conditions.

The principle advantage of the RSSCT procedure compared with the 1 in.-diameter column adsorption test is its increased speed. Typically, an RSSCT can be completed in less than 1–15% of the time required for a 1 in.-diameter study.

FIGURE 1 TACTIC differential adsorption pore size/pore energy distribution curves (A) and close-up view (B)



CMR—custom municipal reactivated, TACTIC—total adsorbent characterization via temperature influence correction

Part B of the figure is an expanded view of part A showing the differences in pore volumes in the higher-energy pore structure range.

TABLE 4 RSSCT design parameters

Parameter	Virgin Bituminous Coal 12 × 40	Coconut 8 × 30	Coconut 12 × 40	Reactivated Bituminous Coal 12 × 40
Particle diameter ($d_{p,LC}$)—mm	1.11	1.52	1.09	1.06
Particle diameter ($d_{p,SC}$)—mm	0.1229	0.119	0.1193	0.1209
AD—g/mL	0.532	0.533	0.539	0.527
Small column diameter—m	0.622	0.622	0.622	0.622
Scaling factor ($d_{p,LC}/d_{p,SC}$)	81.3	162.5	82.9	76.8
EBCT _{SC} —min	0.123	0.062	0.121	0.130
Reynolds _{LC}	12.70	17.38	12.45	12.14
Velocity _{SC} —m/h	16.5	16.5	16.5	16.5
Length _{SC} —m	0.0338	0.0169	0.0332	0.0358
Q—mL/min	8.36	8.36	8.36	8.36
Weight carbon _{SC} —g	0.5466	0.2741	0.5433	0.5736
Volume of carbon _{SC} —mL	1.027	0.514	1.008	1.088

AD—apparent density, EBCT—empty bed contact time, RSSCT—rapid small-scale column testing

Q is the flow rate, and $d_{p,SC}$ and $d_{p,LC}$ are the particle sizes for the small- and large-scale GACs, respectively.

The differing scale factors and operating conditions for the coconut 8 × 30 calculated using the RSSCT procedures are attributable to its larger mesh size compared with the 12 × 40 carbons.

To predict the volume breakthrough curve for the full-scale adsorber, the RSSCT results must be multiplied by the volume scale factor determined for each carbon type. The time breakthrough curve for the full-scale adsorber can be calculated by either of two methods. In the first method, the predicted volumes calculated by multiplying the RSSCT results by the volume scale factor are divided by the flow rate of the full-scale system. In the second method, the run time is multiplied by the scale factor determined for each carbon type.

Comparisons between small and full scale can be made using the following equations:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}} \right]^{2-x} = \frac{t_{SC}}{t_{LC}} \quad (1)$$

$$\frac{V_{SC}}{V_{LC}} = \frac{d_{p,LC}}{d_{p,SC}} \quad (2)$$

$$M_{SC} = EBCT_{LC} \left[\frac{d_{p,SC}}{d_{p,LC}} \right]^{2-x} Q_{SC} \times \rho_{LC} \quad (3)$$

where $d_{p,SC}$ and $d_{p,LC}$ are the particle sizes for the small and large GACs, respectively, and x is the diffusivity constant, which can be used (0 for constant or 1 for proportional diffusivity). In the current study, it was assumed that the intraparticle diffusivities do not change with particle size; therefore a constant diffusivity factor ($x = 0$) was used. In addition, t_{SC} and t_{LC} are the corresponding elapsed times in the small- and large-scale column tests, respectively; V_{SC} and V_{LC} are the velocities in the RSSCT and large-scale columns, respectively; M_{SC}

and Q_{SC} are the mass of carbon and flow rate, respectively, in the small-scale column; and ρ_{LC} is the apparent density of the full-scale carbon.

RSSCT carbon preparation. The RSSCTs were conducted using four different GACs—two re-agglomerated bituminous coal-based GACs and two direct activated coconut-based GACs (Table 2).

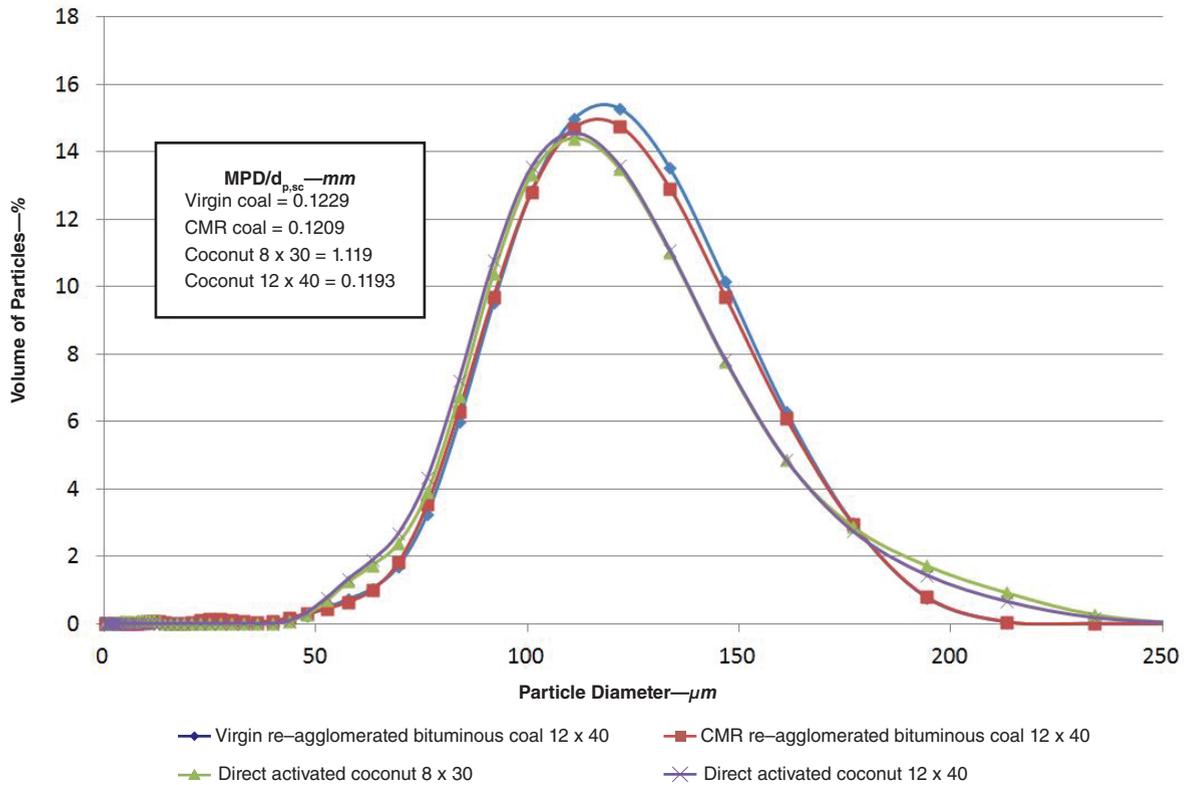
Current production samples of the two re-agglomerated bituminous coal-based GACs (virgin and CMR) and the 8 × 30 and 12 × 40 standard coconut-based GACs were obtained for this study. In preparation for the RSSCT, each GAC was systematically resized to approximately 100 × 200 mesh using a ball mill.¹⁵ The sized GACs were dry-screened to 100 × 200 mesh before particle size analysis.

The mean particle diameters of the sized carbons were determined using a particle size analyzer¹⁶ that records the particle size spectra by laser diffraction between 0.375 and 2,000 μm. The particle size distribution as well as the mean particle diameter of the sized carbons (the $d_{p,SC}$ value used in the RSSCT calculations) are presented in Figure 2.

The dry, sized carbons were installed in the test columns. Before the introduction of the feedwater, each carbon column was pre-wetted with purified water¹⁷ for approximately 16 h in an upflow direction, at a flow rate comparable to that used in the test runs. This procedure has proved very effective at degassing the small-scale column carbon bed over many years of practicing the method.

RSSCT feedwater preparation. Municipal tap water (which does not contain PFCs at any detectable

FIGURE 2 RSSCT carbon size distribution curves for test carbons



CMR—custom municipal reactivated, $d_{p,BC}$ —small-scale particle size, MPD—mean particle diameter, RSSCT—rapid small-scale column test

concentrations) was received in eight 55 gal drums from Center Township, Pa. This water was from the municipality’s groundwater sources (after chlorination) and was not treated with GAC at the time of the sampling. The chlorine level in the municipality distribution system averages <1 mg/L as reported in the township’s 2015 consumer confidence report. A standard water quality analysis was performed before addition/spiking of PFCs (Table 5).

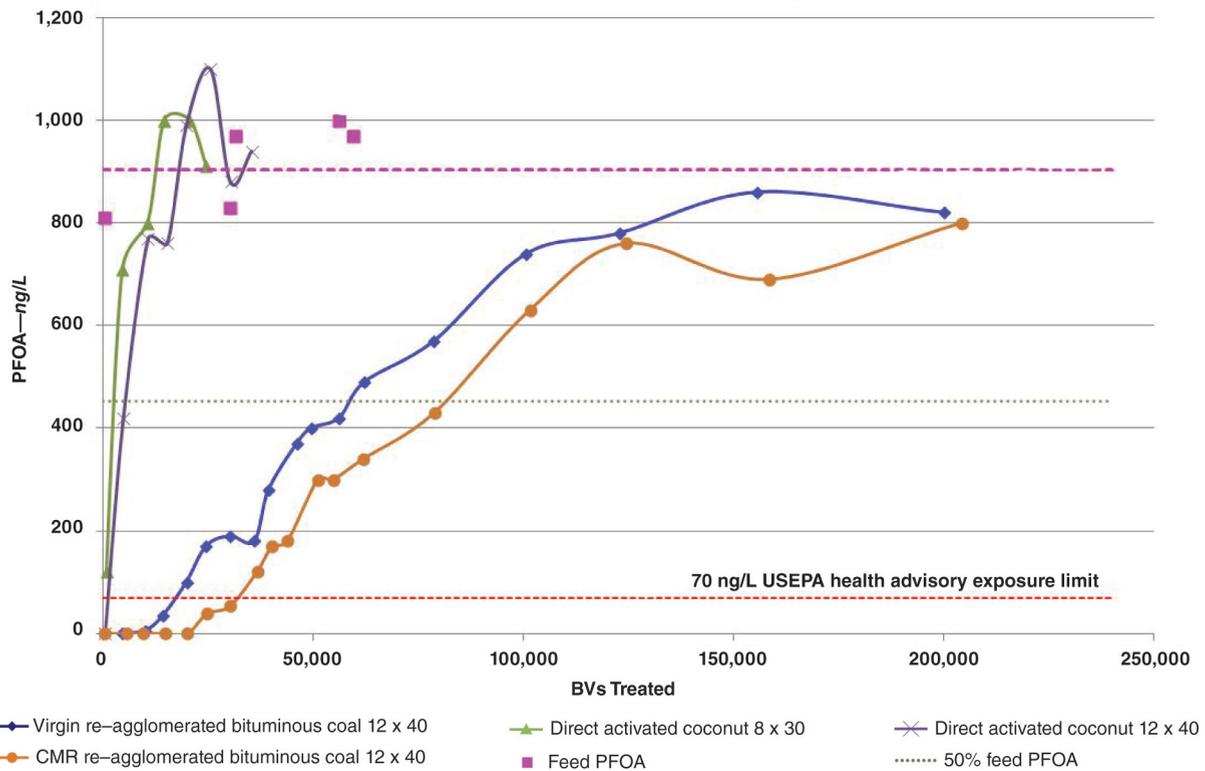
Stock solutions of 100 mg/L PFOA and PFOS were prepared using deionized water and potassium PFOS or PFOA, both purchased from a supplier¹⁸ and used as received. A calculated and precisely measured volume of the stock solutions was added to the feedwater containers to target 1 µg/L concentrations each of PFOA and PFOS. The feedwater averaged 0.8 µg/L PFOS and 0.92 µg/L PFOA after spiking. Although these concentrations are well above the USEPA health advisory level, and it is impossible to select a single concentration that is representative of all PFC removal scenarios, they are representative of concentrations that have been reported in both drinking water and remediation applications. Furthermore, these levels ensured a good analytical comparison among the

TABLE 5 Water quality data

Test	Result
TSS—mg/L	<1
TDS—mg/L	470
TOC—mg/L	1.42
Conductivity—µS/cm	815
pH	7.86
Total Fe—mg/L	<0.03
Total hardness—mg/L as CaCO ₃	300
Alkalinity (methyl orange)—mg/L as CaCO ₃	145
Common Anions (IC)	Result
Fluoride (F ⁻)—mg/L	0.17
Chloride (Cl ⁻)—mg/L	105.7
Bromide (Br ⁻)—mg/L	<0.2
Nitrate (as NO ₃ ⁻)—mg/L	4.37
Phosphate (PO ₄ ⁻)—mg/L	<0.5
Sulfate (SO ₄ ⁻)—mg/L	114.9

CaCO₃—calcium carbonate, Fe—iron, IC—ion chromatography, TDS—total dissolved solids, TOC—total organic carbon, TSS—total suspended solids

FIGURE 3 RSSCT breakthrough curves of PFOA



BV—bed volume, CMR—custom municipal reactivated, PFOA—perfluorooctanoic acid, RSSCT—rapid small-scale column test, USEPA—US Environmental Protection Agency

GACs as well as a reasonable testing time frame that would not require months to reach breakthrough.

RSSCT sampling and analyses. Effluent samples were collected eight times daily for five days and three times daily thereafter at regular intervals via automated sample collectors. Column effluent samples designated for PFC analyses were placed in high-density polyethylene bottles with preservative¹⁹ and shipped overnight on ice to a commercial laboratory²⁰ for analysis according to method 537 (USEPA 2009b).

The flow rates of the RSSCTs were closely monitored throughout the study. In addition to periodic flow rate checks, the RSSCT effluent water not placed in individual sample bottles was collected in a larger composite container and was gravimetrically measured to establish an accurate average flow rate over the course of the study.

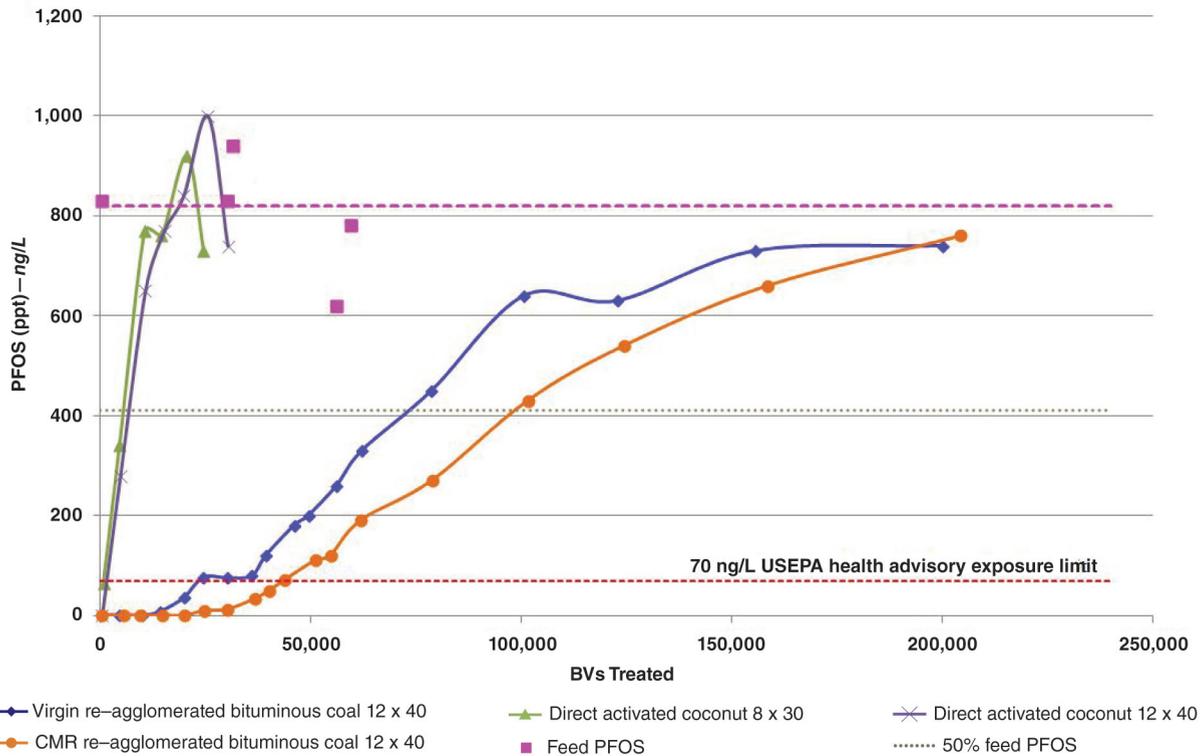
RESULTS AND DISCUSSION

The RSSCT simulated a GAC treatment system that provided an EBCT of 10 min. The weight of the carbon in the simulated system was approximately 23,500 lb. It was assumed that the full-scale system consisted of a

10 ft.-diameter adsorber operating at 530 gpm. Each RSSCT was run until the column effluent contained a minimum of 50% of the feed PFC concentrations. The longest of these ran for ~200,000 BVs, which simulated ~1,400 days of operation and the treatment of ~1 bil gal of water. The resulting breakthrough curves are shown in Figures 3 and 4 for PFOA and PFOS, respectively.

All four GACs tested performed better at removing PFOS than PFOA. Comparatively, the re-agglomerated bituminous coal-based carbons greatly outperformed the coconut-based carbons for removal of both PFOA and PFOS. The differences and similarities of the GACs used in this study were discussed previously in the section on application of GAC for PFC treatment. On the basis of the characteristics of the two coconut-based GACs used in this study, it would be reasonable to expect coconut-based GACs to perform well for the removal of PFC contaminants from water. However, the coconut-based GACs could not effectively remove PFCs for any reasonable treatment period. These GACs experienced rapid initial breakthrough and

FIGURE 4 RSSCT breakthrough curves of PFOS



BV—bed volume, CMR—custom municipal reactivated, PFOS—perfluorooctane sulfonate, RSSCT—rapid small-scale column test, USEPA—US Environmental Protection Agency

reached loading saturation much more quickly than the coal-based GACs. The reason for the poor performance of the coconut-based GACs in this application did not appear to be attributable to inadequate adsorption pore structure but rather to an inadequate transport pore structure. Although they possessed fewer high-energy adsorption pores and approximately the equivalent overall adsorption pore volume of the coconut-based GACs, the re-agglomerated coal-based GACs (both virgin and reactivated) were able to better use the adsorption pores available because they had a much larger and well-developed transport pore structure, attributable at least in part to the re-agglomeration manufacturing process.

The reactivated coal-based GAC was observed to outperform even the virgin coal-based GAC. In theory, repeated reactivation reduces adsorption pore volume, decreases carbon structure, and increases transport pore volume. It would appear that through at least three reactivation cycles, the increase in transport pore volume of the reactivated coal-based GAC resulted in even better PFC removal performance than that of its virgin counterpart, despite the loss of some adsorption pore volume.

Comparisons of the four carbons' performance in terms of service life are shown in Tables 6 and 7 for a single-vessel design and a lead-lag dual-vessel design, respectively. The single-vessel design change-out criterion was assumed at the 70 ng/L breakthrough of PFOA, the USEPA health advisory exposure limit for PFCs. For a lead-lag design, the change-out criterion was set at 50% breakthrough in the lead bed. During the period when the first bed would be achieving high loadings and eluting up to 50% of the PFC present in the influent water, the lag bed would consistently produce an effluent water below 70 ng/L PFOA.

It should be noted that the presence of other adsorbing organic compounds present in groundwaters from different sources/regions could compete with the adsorption of PFCs, changing the maximum loadings and subsequent service lives of full-scale treatment systems. For that reason, the carbon use rates and predicted service lives presented in this study may not match those in other source waters, even when PFC concentrations are similar. Therefore, performance testing is recommended when accurate carbon use rates and system size information are required.

TABLE 6 Carbon service life estimates for PFOA in single-vessel design

Activated Carbon	BVs Treated <i>n</i>	Simulated Days <i>n</i>	Water Treated <i>gal</i>	Carbon Use Rate <i>lb/1,000 gal</i>	Total PFC Loading at Initial PFOA Breakthrough <i>μg/g</i>
Coconut, 8 × 30	300	2	1,590,000	14.84	1.3
Coconut, 12 × 40	500	3	2,650,000	9.01	1.5
Virgin bituminous coal, 12 × 40	17,200	119	91,160,000	0.26	50
CMR bituminous coal, 12 × 40	31,000	215	164,300,000	0.14	100

BV—bed volume, CMR—custom municipal reactivated, *n*—number, PFC—perfluorinated compound, PFOA—perfluorooctanoic acid

TABLE 7 Carbon service life estimates for PFOA in lead-lag, dual-vessel design

Activated Carbon	BVs Treated <i>n</i>	Simulated Days <i>n</i>	Water Treated <i>gal</i>	Carbon Use Rate <i>lb/1,000 gal</i>	Total PFC Loading at 50% PFOA Breakthrough <i>μg/g</i>
Coconut, 8 × 30	3,000	21	15,900,000	1.48	7
Coconut, 12 × 40	5,400	38	28,620,000	0.83	12
Virgin bituminous coal, 12 × 40	59,200	411	313,800,000	0.075	157
CMR bituminous coal, 12 × 40	82,000	592	434,650,000	0.054	220

BV—bed volume, CMR—custom municipal reactivated, *n*—number, PFC—perfluorinated compound, PFOA—perfluorooctanoic acid

CONCLUSION

The study described here yielded the following findings.

- The re-agglomerated bituminous coal-based GACs (both virgin and reactivated versions) outperformed the coconut-shell-based GACs in the column studies reported here. The performance ranking of the carbons tested were in agreement with other published isotherm results (Rahman 2014, Qiu et al. 2007), although in the current case, using this particular groundwater, coconut carbons demonstrated near non-effective PFOA and PFOS removal performance. It is likely that the abundant adsorption pore structure of the coconut-based GACs was not accessible because of the relatively narrow transport pore structure of direct activated coconut-based GACs, relative to re-agglomerated coal-based GACs. Although the re-agglomerated bituminous coal-based GACs contained fewer high-energy pores relative to the coconut-based carbons, the larger transport pore structure allowed access to the adsorption pores that were effective at adsorbing the PFC contaminants.
- The CMR bituminous coal-based re-agglomerated GAC used in many municipal water treatment applications proved to be very effective at removing PFOA and PFOS after repeated cycles of high temperature reactivation and even outperformed its virgin counterpart. At this time, it remains unknown if there is a greater number of reactivation cycles beyond which

PFC removal performance might begin to decline, but reactivation would clearly provide an economic benefit for the effective control of PFC contaminants in groundwater.

- The carbon use rates exhibited by the coal-based re-agglomerated GAC products indicated that cost-effective systems and operating costs can be achieved for the treatment of PFC-contaminated waters. In this case, the 411-day service life of the virgin bituminous coal-based re-agglomerated GAC translated into an operational cost of \$0.12/1,000 gal treated and capital costs of approximately \$275,000/mgd treated (excluding auxiliary systems). If custom reactivation is included, operating costs drop to \$0.08/1,000 gal treated (again, based on the data set described here). Total actual capital and operating costs will depend on source water quality, contaminant concentrations, and other requirements that can influence the facility design and site preparation.

SUMMARY

Adsorption via bituminous coal-based re-agglomerated GAC appears to be the most widely used and cost-effective technology to remove PFCs from water. To date, it is the only technology applied specifically for the treatment of PFC-laden drinking water at full scale (Dickenson & Higgins 2016). Furthermore, with the ability to minimize

treatment residuals and recycle the spent media, additional cost benefits can be realized.

Differing performance results have been found at various application sites because of different combinations of the PFCs and background NOM. Testing can be used to determine the expected use rates for activated carbon at specific locations.

ENDNOTES

- ¹FILTRASORB® 300, Calgon Carbon Corporation, Moon Township, Pa.
- ²FILTRASORB® 400, Calgon Carbon Corporation, Moon Township, Pa.
- ³Diasorb W10-30, Calgon Carbon Japan, Tokyo
- ⁴PK1-3, Cabot Norit Activated Carbon, Marshall, Tex.
- ⁵Wako GAC, Wako Pure Chemical Industries, Osaka, Japan
- ⁶AquaCarb CX 1230®, Evoqua Water Technologies, Warrendale, Pa.
- ⁷C-Gran®, Cabot Norit Activated Carbon, Marshall, Tex.
- ⁸WV B30®, Mead Westvaco, North Charleston, S.C.
- ⁹Dairy manure-based biochar, Char Technologies, Toronto, Ont., Canada
- ¹⁰Fija Fluor, Apelsa Carbon, Jalisco, Mexico
- ¹¹FILTRASORB®, Calgon Carbon Corporation, Pittsburgh, Pa.
- ¹²Custom Reactivated FILTRASORB®, Calgon Carbon Corporation, Pittsburgh, Pa.
- ¹³TN5, Calgon Carbon Corporation, Pittsburgh, Pa.
- ¹⁴OLC 12 × 40, Calgon Carbon Corporation, Pittsburgh, Pa.
- ¹⁵Red Devil ball mill, RADIA, Plymouth, Minn.
- ¹⁶LS13320, Beckman Coulter, Brea, Calif.
- ¹⁷Milli-Q®, MilliporeSigma, Burlington, Mass.
- ¹⁸Sigma-Aldrich, St. Louis, Mo.
- ¹⁹Trizma®, Sigma-Aldrich, St. Louis, Mo.
- ²⁰Eurofins Eaton Analytical, Monrovia, Calif.

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