

Effect of granular activated carbon type and age on quenching H₂O₂ residuals after UV/H₂O₂ drinking water treatment

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ABSTRACT

Granular activated carbon (GAC) can be used to quench residual hydrogen peroxide (H₂O₂) after ultraviolet (UV)-H₂O₂ advanced oxidation processes in drinking water treatment. Bench- and pilot-scale studies examined the possible loss of GAC reactivity due to continuous exposure to natural water from a water treatment plant in both the presence and absence of H₂O₂. Six common types of GAC were evaluated. The bench- and pilot-scale tests consistently showed that all GACs lost a significant degree of reactivity with H₂O₂ during the first 25,000 bed volumes of water treated, but then further deterioration to beyond 100,000 bed volumes was minimal. The loss of reactivity was due mostly to exposure to the natural water, with continuous exposure to H₂O₂ having little impact, suggesting that the reaction with H₂O₂ may be catalytic whereas the GAC becomes fouled by natural organic matter or other constituents in the natural water. The six GACs exhibited different reaction rates with H₂O₂, suggesting that GAC type might be an important consideration for process design.

Key words | advanced oxidation, granular activated carbon, hydrogen peroxide

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INTRODUCTION

The use of ultraviolet light coupled with hydrogen peroxide (UV/H₂O₂) as an advanced oxidation treatment for drinking water is an emerging technology, with a new 380 MLD installation at the Lorne Park Water Treatment Facility in the Region of Peel (Ontario, Canada). A challenge with UV/H₂O₂ is that the majority of the applied H₂O₂ remains in the water following UV/H₂O₂ treatment, and must be removed prior to secondary disinfection since it exerts a strong chlorine demand (Dotson *et al.* 2010). The Lorne Park plant uses a granular activated carbon (GAC) contactor to quench the residual H₂O₂. GAC has been used for this purpose at several other plants previously, and is recognized as a viable treatment option (Cotton *et al.* 2010), but there is little published information about its performance, or its long-term ability to remain active in quenching H₂O₂.

The exact GAC-H₂O₂ reaction mechanism is not completely understood. Some studies have suggested that the

H₂O₂ decomposition reaction is catalyzed by GAC, with the formation of •OH and •OOH radicals as intermediates (Lücking *et al.* 1998; Oliveira *et al.* 2004; Castro *et al.* 2009; Kurniawan & Lo 2009; Aguinaco *et al.* 2011). Bach & Semiat (2011), however, observed that the process was not truly catalytic, with evidence of a reduction in reaction rates when the GAC was repeatedly exposed to 0.25 M H₂O₂. The reaction is reportedly affected by GAC surface characteristics, with Khalil *et al.* (2001) demonstrating that activated carbon pre-impregnated with NH₄Cl was about six times more efficient in quenching H₂O₂ than activated carbons impregnated with H₃PO₄ at pH values between 4.9 and 9.5. Bach & Semiat (2011) explored the use of embedded iron oxide to promote catalytic H₂O₂ oxidation. Hydrogen or alkalinity pretreatment can reduce surface oxygenated functional groups, which introduces activated surface sites, promoting H₂O₂ reaction (Oliveira *et al.*

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2004; Kurniawan & Lo 2009). GAC surface structure with less developed graphene layers has been demonstrated to be more efficient (Rey *et al.* 2011). Interestingly, GAC porosity was reportedly not a major factor in H₂O₂ decomposition (Khalil *et al.* 2001).

The effects of natural organic matter (NOM), pH, temperature and various ions on the H₂O₂-GAC reaction have been investigated, but not in the context of quenching hydrogen peroxide in drinking water. Instead, the focus has been on enhancing catalytic H₂O₂ oxidation to generate •OH radicals using GAC for organic pollutant removal, such as 4-chlorophenol (Lücking *et al.* 1998; Huang *et al.* 2003a), 2-chlorophenol (Huang *et al.* 2003b), dye (Oliveira *et al.* 2004), and raw leachate (Kurniawan & Lo 2009). In these short-term experiments, the presence of specific organic compounds (e.g. phenol, dyes) had a negative effect on the decomposition of H₂O₂ by competing for reactive sites (Huang *et al.* 2003a; Bach & Semiat 2011). This suggests that NOM in drinking water may adversely affect the long-term ability of GAC to quench H₂O₂, but specific data are lacking. It is also possible that the reaction between H₂O₂ and GAC that has been in service for some time may be mostly between the H₂O₂ and the adsorbed NOM that is covering the GAC surface. Little information on this topic could be found in the literature.

Solution pH can influence the GAC-H₂O₂ reaction. H₂O₂ quenching is reportedly faster at a pH above 8, possibly due to the disassociation of H₂O₂ into OOH⁻ (pK_a = 11.6, Khalil *et al.* 2001) (Kurniawan & Lo 2009), however, the effect may be confounded by the impact of pH on the GAC surface characteristics as well (Rey *et al.* 2011). Increased temperature can promote the reaction rate (Aguinaco *et al.* 2011), and greater concentrations of buffering salts such as phosphates have been found to suppress the decomposition process (Khalil *et al.* 2001; Aguinaco *et al.* 2011).

In summary, previous research suggests that the ability of GAC to quench H₂O₂ may deteriorate with time as the GAC becomes fouled with NOM, and/or reacts with H₂O₂, but little quantitative information is available. There are several large drinking water treatment plants known to the authors to have installed GAC contactors for quenching H₂O₂. The Peter D. Binney Water Treatment Plant (Aurora, Colorado, USA) has used GAC since 2010 to quench

1–2 mg/L of H₂O₂ to below detection limits in biologically active GAC (1.8 m) and sand (0.3 m) with an empty-bed contact time (EBCT) of 15 minutes. The Andijk water treatment plant in the Netherlands was designed to remove as much as 15 mg/L H₂O₂ with an EBCT of 9 minutes (Kruithof *et al.* 2007), and currently quenches H₂O₂ from 6 mg/L to less than 0.1 mg/L following 6 years of operation with the original GAC (Martijn 2014). The Waterloo Greenbrook facility in Canada has been using the original GAC for 6 years to quench approximately 5 mg/L H₂O₂ using an upflow system to avoid the risk of oxygen entrainment, with an EBCT of 2–5 minutes (Walton 2014).

In this research, it is hypothesized that the performance of GAC to quench H₂O₂ may be affected by the carbon type, age (i.e. bed volumes of water treated and corresponding exposure to NOM) and exposure to H₂O₂. These factors are explored in this study. A pilot-scale test was undertaken at the Lorne Park Water Treatment Facility, coupled with laboratory bench-scale tests, to examine H₂O₂ quenching as a function of six different types of GAC, monitoring the performance over time.

The GAC contactor at the Lorne Park plant is not operated in a biological mode, with little biological activity detected (adenosine triphosphate concentrations below 20 ng/g on the GAC media). There is evidence that biofilm on the surface of GAC can enhance H₂O₂ quenching (Urfer & Huck 1997), but this mechanism is outside the scope of this study.

OBJECTIVES

The objective of this study was to investigate the impact of GAC ageing on its ability to quench H₂O₂, as well as to evaluate different types of GAC. Ageing was defined as exposure to increasing volumes of water, with an assumption that the ageing would be due to either NOM in the water and/or H₂O₂.

A secondary objective was to compare the accuracy of laboratory bench-scale tests to evaluate GAC performance for H₂O₂ quenching relative to pilot-scale tests, and to compare both bench- and pilot-scale work to a limited series of H₂O₂ quenching tests using GAC that had been aged at full-scale.

METHODS AND MATERIALS

The effect of ageing on the reaction rate between different GACs and H₂O₂ was evaluated experimentally using three tests: (1) an ‘accelerated ageing batch test’, (2) a ‘column ageing batch test’, and (3) a ‘pilot column test’. The details of each of these tests are described below, and the names of the tests are applied consistently when presenting the data to avoid confusion.

Accelerated ageing batch test

One aspect of this research was to determine the accuracy of simple and relatively quick bench-scale tests to assess the ability of different types of GAC to quench H₂O₂ over the long term. In brief, water from the Lorne Park plant would be directed through pilot scale GAC columns at accelerated flow rates, with EBCTs of approximately 20 seconds compared to the 4 minutes used at the full-scale Lorne Park treatment plant. The exposure would continue for a realistic number of treated water bed volumes: e.g. 40,000 bed volumes, representing approximately three months of operation, but taking only 7 days due to the faster flow rate. It was hypothesized that if GAC ageing in terms of H₂O₂ reactivity were due to a fouling mechanism that was fast relative to the flow rate of water through the column, such as a very fast adsorption of NOM onto the GAC surface, then the ageing of the GAC would be more strongly correlated to the total amount of water delivered through the column (i.e. bed volumes) than to the flow rate at which it was delivered. This would allow an experimenter to evaluate many different types of GAC quickly and accurately, in the order of weeks as opposed to months/years.

Six types of GAC were obtained from their local suppliers, as shown in Table 1. The GACs were selected based on their popularity in drinking water treatment, while also including two products marketed for H₂O₂ quenching (labelled ‘catalytic’ in Table 1), and reflecting a mix of base material. It is emphasized that this research is not intended to identify specific GACs that are ‘best’ for quenching H₂O₂: the limited scope of the conditions tested would preclude the ability to draw such conclusions. Instead, the aim is to determine whether there can be differences in

Table 1 | GAC characterization

GAC label	Material	Iodine no. (mg/g)	TCN ^a (mg/cc)	Apparent density (g/L)
A	Bituminous coal-based; catalytic	1,044	8.9	530
B	Hard coal-based; catalytic	956	8.1	485
C	Bituminous coal-based	847	10.5	501
D	Coal-based	931	10.1	539
E	Lignite coal-based; acid washed	601	1.5	421
F	Coconut-based	861	10.7	599

^aTCN = trace capacity number.

performance for different types of GAC, and if so, to give some indication of the possible range of differences. This information would help to advise consultants and utilities as to the need to test different GAC options when designing a GAC contactor to quench H₂O₂. Because of these considerations, the names of the GAC products are not used in this paper, and are instead labelled GACs ‘A’ to ‘F’. The GACs were prepared by the coning and quartering technique (ASTM D346: Harvey 2000) and washed with Milli-Q water, then dried in the oven at 105 °C overnight (Hindarso *et al.* 2001). The GACs were otherwise used as received from the suppliers. They were then aged for the test at the Lorne Park treatment plant by filling 2.5 cm diameter glass columns to a depth of 128 cm with the different GACs, and pumping plant-treated water through the columns at the desired EBCT. Treatment at the plant consists of prechlorination, ultrafiltration, and UV disinfection, drawing water from Lake Ontario (total organic carbon (TOC) ranged from 1.9 to 2.5 mg-C/L, and pH from 7.5 to 7.9). There was negligible chlorine remaining by the time the water was directed onto the GAC. The GAC columns were run to up to 45,000 bed volumes of treated water. TOC breakthrough was observed to occur at approximately 900–1,350 bed volumes depending on the carbon type, demonstrating that the GAC was aged to a significant degree. In a parallel setup and operated at the same time, the GAC samples were also aged with water containing a continuous concentration of 4 mg/L H₂O₂ to evaluate the effect of H₂O₂ exposure on the ageing process.

A sample of GAC from within the top 10 cm of these columns was then removed for each sampling event and subjected to bench-scale H₂O₂ reactivity tests. These tests were conducted in 1 L capped amber glass bottle reactors. The reactors were prepared by adding 0.250 g of the selected and dried GAC to 500 mL Milli-Q water and 2 mL of a 50 mM Na₂CO₃/NaHCO₃ buffer. The pH of the mixture was then adjusted to 7.00 ± 0.05 by HCl. The reaction was initiated by dosing H₂O₂ to 5.0 mg/L (Sigma Aldrich, Canada). The reactors were then shaken in an orbital shaker at room temperature. Samples for H₂O₂ residual analysis were collected every hour during the 5 hour experiment and analyzed by the I₃⁻ method according to Klassen et al. (1994) using a spectrophotometer (Agilent Tech, Canada). The minimum detection limit of this method was determined to be 0.02 mg/L. The pH of the mixture was measured by an Orion Star A111 pH meter (Thermo Scientific, ON, Canada). Duplicated experiments were performed for each type of carbon. A method blank was performed in the absence of GAC to ensure that there was no H₂O₂ demand from the reagents or glassware.

The H₂O₂ decay data were observed to follow pseudo first-order kinetics, so the data were fit to a first-order model to obtain the decay coefficient, k (min⁻¹), for each GAC. The average variation between the calculated k values from the duplicate runs was 11%.

Column ageing batch test

An array of 22 pilot-scale glass columns containing GAC was used for this test, as described in the previous section. The columns were each 2.5 cm in diameter, and contained 128 cm of GAC to simulate the GAC depth of the full-scale plant (Figure 1). The columns were exposed to membrane permeate water from the plant (the same water as in the previously described test) with a realistic EBCT of 4 min (as opposed to the 20 second EBCT previously described). The columns were operated in parallel in the absence and in the continuous presence of 4 mg/L H₂O₂, with water flowing in continuous down-flow operation with no provision for backwash, since the quality of the membrane permeate feed led to no observable accumulation of headloss over the 11 months of operation. The 22 columns did not allow for all conditions to be tested in

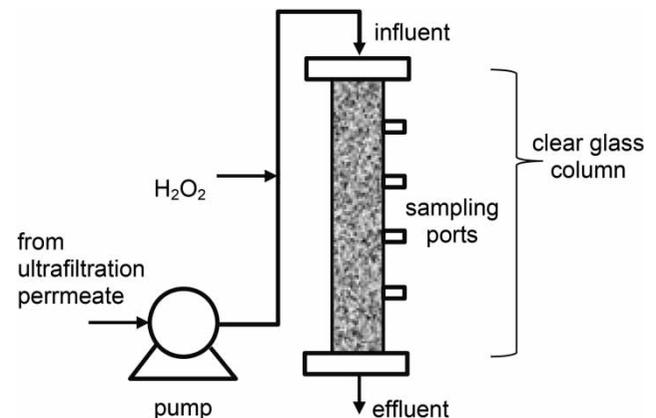


Figure 1 | Pilot-scale GAC column.

parallel (six GACs in duplicate, and with/without H₂O₂ = 24 conditions), so the duplicate columns for 25,000 and 45,000 bed volumes were run sequentially but within the same season. A comparison of the results between the duplicate series showed no differences (statistical analysis not shown). The water quality (TOC, pH) in Lake Ontario is quite stable throughout the year.

For the 'column ageing test', samples of GAC (less than 2 g) were removed from inside the top 10 cm of the columns and brought to the laboratory for a batch H₂O₂ reactivity test as described in the previous section. This way, the reactivity (pseudo first-order decay coefficient) could be compared for GACs aged in an 'accelerated' mode (fast flow rate) vs. a typical flow rate, but both for similar treated water bed volumes. The average variation between the calculated k values from the duplicate columns in this test was 15%.

Pilot column test

Several of the same 22 GAC pilot columns were also used for an *in situ* H₂O₂ breakthrough challenge. These tests were conducted immediately after the work described in this and the previous sections, and as such, were not performed on exactly the same water. Nevertheless, water quality parameters at the Lorne Park Plant (Lake Ontario) are very stable other than temperature. In this test, the H₂O₂ concentration was measured along the depth of the column when the influent water was temporarily spiked with 10 mg/L H₂O₂, which is the maximum H₂O₂ concentration that might be applied in practice at the plant. The

duration of the spiking event prior to sampling H₂O₂ breakthrough was approximately 2,000 bed volumes. H₂O₂ analysis for the pilot column test was performed onsite using a K-5543 H₂O₂ test kit (CHEMetrics, Virginia, US) and a Hach DR 2700™ portable spectrophotometer. This method is based on the ferric thiocyanate method (Boltz & Howell 1978). The minimum detection limit for this method was determined to be 0.04 mg/L. Due to logistical constraints, only a single column containing each GAC type could be tested in this way (i.e. no duplicates).

Full-scale monitoring

The pilot column test apparatus was also applied for GAC that had been collected from GAC contactors in use at the Lorne Park plant, to evaluate H₂O₂ quenching using GAC aged under real conditions as opposed to pilot conditions. The GAC contactors, which use GAC 'A', had been in service for approximately 1 year (130,000 bed volumes), 2 years (260,000 bed volumes), or 3 years (390,000 bed volumes). The contactors had only been exposed to H₂O₂ on one occasion: from September 2012 to November 2012 (approximately 32,000 bed volumes) with an average of 4 mg/L H₂O₂ during that period. GAC samples were collected from the contactors using a PVC sampling corer, and then transferred into the glass pilot columns while maintaining the same stratification as in the full-scale bed. The columns were then subjected to the same H₂O₂ breakthrough tests as previously described. Additional grab samples of GAC were collected from depths of 0, 60, and 128 cm in the contactors for batch H₂O₂ reactivity tests as described in the previous sections. These experiments were conducted at the same time as the work described in the Pilot column test section above.

RESULTS

The results for the three bench/pilot experiments are shown in Table 2.

Accelerated ageing batch test results

The decay of 5 mg/L H₂O₂ in the presence of 500 mg/L GAC aged either with NOM or with NOM + H₂O₂ in an

'accelerated' mode was monitored in the bench-scale batch reactors, with the pseudo first-order decay coefficients (k) shown in Table 2 (referring to the columns labelled '(1)' and '(4)' for this discussion).

The impact of ageing (bed volumes) on the decay rate (k) of the various GACs was determined by using a one-way analysis of variance (ANOVA). The ANOVA demonstrated that the ageing significantly reduced the k values (95% significance level) for GACs A, C, D, and E, but that B and F did not demonstrate statistically significant ageing. This trend held true for ageing in the presence of NOM only (column (1) in Table 2) and in the presence of NOM + H₂O₂ (column (4) in Table 2). A further analysis of the four GACs that were affected by ageing using Tukey's post hoc Honestly Significant Difference test demonstrated that most of the differences in the k values as a function of ageing were between the virgin GAC compared to aged GAC, but with no differences among the different amounts of ageing (i.e. 25,000–45,000 bed volumes). In other words, the four GACs experienced a rapid drop in H₂O₂ reactivity between virgin GAC and 25,000 bed volumes, but then the reactivity tended to remain the same from 25,000 to 45,000 bed volumes.

A Student t -test was applied to compare the k values for GAC aged in the presence of H₂O₂ to the k values for GAC aged in the absence of H₂O₂. From Table 2 (column (1) vs. column (4)), H₂O₂ exposure caused the k values to change by less than 46% in all cases, and usually by less than 30%. These impacts were not statistically significant at the 95% level.

The six types of GAC in this study are made from several types of materials, and have various physical and chemical properties (Table 1). The performances of the six GACs were compared and are summarized in Table 3, with rankings shown for both virgin GAC and for aged GAC by pooling and taking weighted (by volume of water treated) average k values for all aged GACs. Among the six types of GAC tested, activated carbon B had relatively good performance both before and after ageing, while C showed the poorest performance in these accelerated ageing batch tests. Interestingly, B had the poorest performance in terms of TOC removal (data not shown). It is possible that this rendered B the least affected by NOM fouling as a mechanism of deterioration in H₂O₂ quenching ability, but no quantitative data were collected to properly support this hypothesis.

Table 2 | Pseudo first-order H₂O₂ decay coefficients

GAC	Ageing history (bed volumes)	<i>k</i> (aged with NOM), min ⁻¹			<i>k</i> (aged with NOM + H ₂ O ₂), min ⁻¹		
		Accelerated ageing batch test (1)	Column ageing batch test (2)	Pilot column test (3)	Accelerated ageing batch test (4)	Column ageing batch test (5)	Pilot column test (6)
A	0	0.0026 ^a	0.0026	1.54	0.0026	0.0026	1.54
	25,000	0.0013	0.0009	0.92	0.0019 (+46%) ^b	0.0010 (+7%)	0.92 (+0%)
	35,000	0.0014	–	–	0.0013 (–7%)	–	–
	45,000	0.0016	0.0008	0.72	0.0014 (–13%)	0.0007 (–3%)	0.69 (–3%)
	100,000	–	0.0009	0.77	–	0.0007 (–21%)	0.98 (+21%)
B	0	0.0033	0.0033	1.50	0.0033	0.0033	1.50
	25,000	0.0024	0.0014	1.69	0.0024 (0.0%)	0.0013 (–9%)	1.12 (–57%)
	35,000	0.0024	–	–	0.0024 (0.0%)	–	–
	45,000	0.0024	0.0011	1.27	0.0024 (0.0%)	0.0013 (+16%)	1.73 (+46%)
	100,000	–	0.0014	1.37	–	0.0014 (–1%)	1.49 (+12%)
C	0	0.0020	0.0020	1.34	0.0020	0.0020	1.34
	25,000	0.0012	0.0009	1.31	0.0014 (+17%)	0.0006 (–34%)	0.52 (–79%)
	35,000	0.0015	–	–	0.0011 (–27%)	–	–
	45,000	0.0013	0.0008	1.55	0.0011 (–15%)	0.0005 (–37%)	0.54 (–101%)
	100,000	–	0.0008	1.14	–	0.0006 (–27%)	0.77 (–37%)
D	0	0.0043	0.0043	1.63	0.0043	0.0043	1.63
	25,000	0.0019	0.0013	1.24	0.0021 (+10%)	0.0010 (–29%)	0.66 (–58%)
	35,000	0.0020	–	–	0.0020 (0.0%)	–	–
	45,000	0.0017	0.0012	1.43	0.0019 (+12%)	0.0010 (–19%)	1.10 (–33%)
	100,000	–	0.0011	1.34	–	0.0010 (–10%)	1.40 (+6%)
E	0	0.0024	0.0024	1.47	0.0024	0.0024	1.47
	25,000	0.0015	0.0012	1.31	0.0020 (+33%)	0.0007 (–29%)	0.75 (–56%)
	35,000	0.0014	–	–	0.0017 (+21%)	–	–
	45,000	0.0014	0.0009	0.97	0.0016 (+14%)	0.0005 (–45%)	0.65 (–32%)
	100,000	–	0.0008	1.14	–	0.0005 (–31%)	1.00 (–14%)
F	0	0.0021	0.0021	1.28	0.0021	0.0021	1.28
	25,000	0.0017	0.0008	0.69	0.0020 (+18%)	0.0007 (–14%)	0.61 (–8%)
	35,000	0.0016	–	–	0.0016 (0.0%)	–	–
	45,000	0.0014	0.0008	0.66	0.0014 (0.0%)	0.0005 (–29%)	0.58 (–8%)
	100,000	–	0.0007	0.76	–	0.0005 (–26%)	0.99 (+24%)

^aValues shown for *k* in Columns #1,2,4,5 are the average of experimental duplicates, which exhibited an average difference between duplicates of 12%. *k* values in Columns 3 and 6 are obtained from single experiments.

^bNumber in brackets is percent difference between aged with peroxide vs. without peroxide.

Table 3 | Ranking of *k* values (from Table 2) for the six GACs. The number in the bracket is the percentage *k* value relative to the best-performing GAC in that category

GAC	Virgin GAC	Weighted average ^a <i>k</i> (aged with NOM)			Weighted average <i>k</i> (aged with NOM + H ₂ O ₂)		
		Accelerated ageing batch test	Column ageing batch test	Pilot column test	Accelerated ageing batch test	Column ageing batch test	Pilot column test
A	3 (60%)	5 (64%)	4 (68%)	5 (62%)	4 (71%)	3 (64%)	3 (62%)
B	2 (77%)	1 (100%)	2 (96%)	1 (100%)	2 (99%)	1 (100%)	1 (100%)
C	6 (47%)	6 (57%)	5 (61%)	3 (98%)	6 (55%)	5 (47%)	6 (47%)
D	1 (100%)	2 (97%)	1 (100%)	2 (98%)	1 (100%)	2 (90%)	2 (77%)
E	4 (56%)	4 (65%)	3 (71%)	4 (81%)	3 (75%)	4 (50%)	4 (58%)
F	5 (49%)	3 (66%)	6 (59%)	6 (54%)	5 (70%)	5 (47%)	5 (53%)

^aWeighted average of all *k* values from non-virgin GAC.

Column ageing batch test

This test was similar to the one described in the previous section, except that the GACs were aged in columns subjected to a typical flow rate (EBCT = 4 min) instead of the ‘accelerated’ flow of the previous test (EBCT = 20 seconds). Overall, the k values obtained in the batch H₂O₂ decay tests were consistently lower for the GAC that was aged under normal flow rates compared to accelerated flows, for the same total bed volumes (i.e. columns (2) vs. (1) and (5) vs. (4) in Table 2). Since ageing in the pilot columns under realistic flow rates is assumed to be more representative of the full-scale system, this implies that the accelerated ageing process introduces an error, leading to estimates that the GAC remains more reactive with H₂O₂ than would actually be the case. However, the accelerated ageing process was performed at a different time of year than the ageing process at normal flow rate (winter as opposed to spring/summer). As such, a direct quantitative comparison may be inappropriate. Instead, the general trends can be compared. The ageing process in this column ageing batch test led to statistically significant reductions in H₂O₂ reaction rates for all six GAC tested, both in the presence and absence of H₂O₂ in the flow. This is similar to the results obtained for the accelerated ageing tests, except that the GAC B and F ageing in the accelerated process were not statistically significant. Also, similar to the accelerated results, the H₂O₂ reaction rates were reduced when comparing virgin GAC to any of the aged GAC, but there was no statistically significant difference among the different levels of ageing for any of the GACs. Thus, the GAC ages quickly between virgin and 25,000 bed volumes of water treated (with or without H₂O₂ present), but then the rate of ageing slows down.

The ranking of H₂O₂ reactivity for the aged GACs (Table 3) is also very similar between the GAC aged under normal flow conditions and the accelerated flow conditions, with GACs B and D performing significantly better than the other four, which all exhibit similar performances. Overall, therefore, there is some evidence to conclude that the accelerated ageing process maintains a relative comparison between the degree of loss of H₂O₂ reactivity for different GAC types, but that the quantitative change in the rate of H₂O₂ reaction with GAC may not be accurately simulated in the accelerated ageing process.

Pilot column test

H₂O₂ reactivity with GAC was also measured by periodically applying a 10 mg/L H₂O₂ dose to the flow entering the GAC pilot columns, and then measuring the H₂O₂ at five sampling ports along the depth of the 128 cm column (data not shown). The relationship between $\ln[(\text{H}_2\text{O}_2)/(\text{H}_2\text{O}_2)_0]$ and time (where time was calculated based on the distance of the sampling port from the top of the GAC and the flow velocity) yielded a virtually linear relationship ($R^2 > 0.9$), implying that a first-order H₂O₂ decay kinetic model could be applied and a k value derived to represent H₂O₂ reactivity with the GAC in the pilot columns. These k values are reported in Table 2, columns (3) and (6). It is stressed that these k values are not comparable to the other k values shown in Table 2 for the batch experiments, since the ratio of the amount of H₂O₂ to GAC is very different between the batch experiments and the columns tests. Nevertheless, the trends in k values as a function of the different variables can be compared qualitatively. In these pilot column tests, it was again observed that the GAC aged very quickly between virgin GAC and the earliest time of testing, 25,000 bed volumes. After that, the reactivity with H₂O₂ tended to stabilize (in contrast with the batch tests, no statistical analysis of the significance of these effects was conducted since the measurements were not replicated, so the data are too few to provide statistical power). The relative rankings of the six GACs are also somewhat similar between the pilot column tests and the two batch tests, with GACs B and D always ranking among the best, and the others generally exhibiting lower reactivity with H₂O₂. Note that GAC B is a coal-based ‘catalytic’ GAC that is specifically designed to reduce H₂O₂, and therefore its consistent good performance might be expected, however the other catalytic GAC (A) did not perform well. The other consistent good performer, GAC (D), was a ‘normal’ coal-based product commonly used in drinking water treatment. The lignite and coconut-based GACs (E and F) performed approximately equally well as the other two coal-based products (A and C). As such, there does not appear to be any useful generalization that can be made about the types of GAC and their ability to quench H₂O₂.

The impact of H₂O₂ on the ageing process is difficult to identify from the data from this pilot column test, with no clear consistent trend.

Full-scale monitoring of GAC A

The Lorne Park plant uses GAC A contactors to quench residual H₂O₂, so it was useful to compare the H₂O₂ reactivity of the aged full-scale GAC to the GAC that was aged artificially in the pilot columns. GAC was collected from contactors at the plant that had been in operation for 130,000, 260,000, and 390,000 bed volumes (approximately 1, 2 and 3 years, respectively). The GAC was sampled at various depths for batch H₂O₂ reactivity tests as previously described, or used to fill a 128 cm pilot column while maintaining the same stratification as in the full-scale contactor, for an H₂O₂ breakthrough test.

In the ‘column ageing batch test’, GAC A that was aged to 100,000 bed volumes had a pseudo first-order k coefficient for reactivity with H₂O₂ ranging from 0.007 to 0.0010 min⁻¹ for the different degrees of ageing (Table 2). At full-scale (Table 4), the equivalent k coefficient for 130,000 bed volumes was in the order of 0.005 to 0.0011 min⁻¹, which is quite similar to the value derived from the column ageing batch tests. When the same full-scale GAC core sample was inserted into a 128 cm column and subjected to 10 mg/L H₂O₂, the resulting profile of residual H₂O₂ vs. depth (expressed as time) yielded a pseudo first-order k value of 0.74 min⁻¹ (Table 4), which compares to a value of 0.8–1.0 min⁻¹ when the H₂O₂ was performed in the pilot columns with GAC A aged to 100,000 bed volumes (Table 2). This suggests that the pilot-scale ageing process simulates full-scale ageing quite accurately. The pilot column k values in Table 4 also demonstrate that the GAC A collected from the full-scale

contactor has experienced very little ageing between 1 and 3 years of operation, with the k values remaining consistently in the range of 0.6–0.7 min⁻¹, compared to the virgin GAC A which had a k value of 1.5 min⁻¹. This corroborates the trend observed for all other experiments in this study, with a rapid initial loss of H₂O₂ reactivity, followed by little further deterioration. Recall that the GAC A collected from the full-scale plant had been exposed to very little H₂O₂ in its history, so the ageing is due mainly to exposure to NOM and other natural constituents.

The k values in Table 4 show a trend of greatest H₂O₂ reactivity with GAC at the top surface, with decreasing performance at depth. This is perhaps counterintuitive, as one might expect the top surface of the GAC to age more quickly due to higher exposure to NOM, H₂O₂, or other foulants. The reason for this trend is not known. One theory may relate to the role of biofilm on H₂O₂ decomposition, as previously mentioned (Urfer & Huck 1997). While there was no evidence of biofilm on the GAC based on adenosine triphosphate measurements, it is conceivable that even a small amount of biofilm can enhance H₂O₂ reactivity. Biofilm would be expected to be at highest concentrations near the GAC surface due to the maximum dissolved oxygen and nutrient loading at the top of the GAC bed. This hypothesis should be investigated in future research.

CONCLUSIONS

This research demonstrated that different GACs exhibit different reaction rates with H₂O₂, both for virgin GAC and for GAC aged up to 100,000 bed volumes (the maximum tested in this work). It was not the intent of this study to identify a preferred type of GAC, and it is plausible that a GAC that did not perform well under the conditions of this study might work well under other conditions. Instead, the demonstration that there is variability among GACs for quenching H₂O₂ suggests that it is worthwhile to test different products when selecting one for the purpose of quenching H₂O₂. This study provides evidence that an ‘accelerated ageing’ test, in which columns of GAC are exposed to water using faster than normal flow rates, might maintain the same qualitative order of performance of different GACs, although the absolute reaction rates may not be accurate. The presence of

Table 4 | k values for full-scale GAC A contactors at different depths

Full-scale Centaur	Depth (cm)	Batch reactor k value (min ⁻¹)	Pilot column k value (min ⁻¹) ^a
130,000 bed volumes	0	0.0011	0.74
	60	0.0006	
	128	0.0005	
260,000 bed volumes	0	0.0009	0.61
	60	0.0005	
	128	0.0005	
390,000 bed volumes	0	0.0008	0.62
	60	0.0005	
	128	0.0003	

^aVirgin GAC A had a pilot column k value of 1.5 min⁻¹.

H₂O₂ did not seem to be an important factor in ageing the GAC in the batch tests, suggesting that such a test could be done in the absence of H₂O₂.

It was consistently demonstrated at bench- and pilot-scales that GAC tends to lose a significant degree of reactivity with H₂O₂ during the first 25,000 bed volumes of operation (approximately four months for a typical plant), but then performance tends to stabilize. Similarly, the full-scale GAC exhibited similar stable H₂O₂ reactivity between 130,000 and 390,000 bed volumes. This corroborates the full-scale experience from the Greenbrook, Andijk, and Binney water treatment plants, where GAC has been effective for over 6 years without requiring replacement. The role of biological activity at these plants, however, is unknown. In this study, biological activity was presumed to be minimal as evidenced by very low adenosine triphosphate readings.

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