Quenching $\text{H}_2\text{O}_2$ Residuals After UV/ $\text{H}_2\text{O}_2$ Drinking Water Treatment Using Granular Activated Carbon

by

Jinghong Li

A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science

Graduate Department of Civil Engineering
University of Toronto

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ABSTRACT

The ability of six types of granular activated carbon (GAC) to quench H\textsubscript{2}O\textsubscript{2} was evaluated by bench-scale H\textsubscript{2}O\textsubscript{2} decomposition kinetics tests and pilot-scale H\textsubscript{2}O\textsubscript{2} breakthrough tests. Bench-scale studies showed that carbon ageing significantly reduced the performance of H\textsubscript{2}O\textsubscript{2} quenching by the GAC, but that the greatest impacts occurred within the first 25 000 bed volumes of water treated, with performance tending to stabilize afterwards. Pilot-scale studies suggested that both H\textsubscript{2}O\textsubscript{2} exposure and exposure to natural organic matter were important factors in GAC ageing, with exposure to oxygen also suspected of being important. A continuously stirred tank reactor (CSTR)-in-series model was proposed for the prediction of H\textsubscript{2}O\textsubscript{2} breakthrough in a GAC column.
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6.1 SUMMARY AND CONCLUSION

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GLOSSARY

AOP advanced oxidation process
C concentration
°C degrees Celsius
Cl₂ chlorine
cm centimeter (1 cm = 10⁻² m)
DBPs disinfection by-products
DO dissolved oxygen
D_p pore diffusivity based on pore void fraction
D_s surface diffusion coefficient
eV electron volts (1 eV = 1.6 x 10⁻¹⁹ J)
EBCT empty bed contact time
Fe iron
GAC granular activated carbon
H₂O₂ hydrogen peroxide
k pseudo first-order kinetics rate constant
k_f film transfer diffusion coefficient
L liter
m meter
MDL minimum detection level
mg/L milligram per liter
m/s meter per second
mol mole
NOM natural organic matter
O₂ oxygen
O₃ ozone
OH⁻ hydroxide ion
OH· hydroxyl radical
\( q_e \)  
adsorbent phase concentration in equilibrium with influent concentration

\( R \)  
adsorbent radius

TOC  
total organic carbon

UV/H\(_2\)O\(_2\)  
ultraviolet light coupled with hydrogen peroxide

WTP  
water treatment plant

\( \varepsilon \)  
porosity of the GAC

\( \varepsilon \)  
fraction of volumetric space in reactor unoccupied by adsorbent

\( \varepsilon_p \)  
fraction of volumetric space in adsorbent phase unoccupied by adsorbent on the pore volume fraction

\( \emptyset \)  
sphericity of the GAC

\( \rho_a \)  
adsorbent density which includes pore volume

\( \tau \)  
retention time
1 INTRODUCTION AND RESEARCH OBJECTIVES

1.1 INTRODUCTION

The use of ultraviolet light coupled with hydrogen peroxide (UV/H$_2$O$_2$) as an advanced oxidation treatment for taste and odor control during drinking water treatment is an emerging technology, with a new installation at the Lorne Park Water Treatment Facility in the Region of Peel (Ontario, Canada). A challenge with UV/H$_2$O$_2$ is that the majority of the applied H$_2$O$_2$ remains in the water following UV/H$_2$O$_2$ treatment, and must be removed prior to secondary disinfection since it exerts a strong chlorine demand (Dotson et al., 2010). The Lorne Park plant is using a granular activated carbon (GAC) contactor to quench the residual H$_2$O$_2$. GAC has been used for this purpose at several other plants previously (e.g. Aurora, Colorado, and Andijk in the Netherlands), but there is little published information about its performance.

The fundamental chemistry of H$_2$O$_2$ decomposition in the presence of GAC has been reported in some previous laboratory studies (Huang et al., 2003a; Castro et al., 2009; Rey et al., 2011), however, none of these studies were based on water treatment applications. Metz et al. (2011a) reported that GAC can quench excess H$_2$O$_2$ while removing unexpected degradation products in drinking water treatment, however, the quenching process or mechanism was not investigated. Whether the GAC may gradually lose its H$_2$O$_2$ quenching ability over time, or what factors may affect the quenching rate, are largely unknown.

It is hypothesized that the performance of GAC to quench H$_2$O$_2$ will be affected by the carbon type, age (i.e., bed volumes of natural water treated) and exposure to H$_2$O$_2$. These factors are explored in this study.

1.2 RESEARCH OBJECTIVES

The study addressed the following objectives:

1. To evaluate the impact of carbon ageing (25 000, 35 000 and 45000 bed volumes of water treated) and H$_2$O$_2$ exposure (0mg/L and 4 mg/L) on the performance of GAC for quenching H$_2$O$_2$ (six types of GAC) by bench-scale H$_2$O$_2$ decomposition kinetics tests.
2. To investigate the \( \text{H}_2\text{O}_2 \) (10 mg/L in the influent) breakthrough profile under different operating conditions (in the presence or absence of \( \text{H}_2\text{O}_2 \) during the ageing process for 25 000 and 45 000 bed volumes of water treated) at pilot-scale.

3. To compare the performance of six different types of GAC to quench \( \text{H}_2\text{O}_2 \) through both bench-scale \( \text{H}_2\text{O}_2 \) decomposition kinetics tests and pilot-scale \( \text{H}_2\text{O}_2 \) breakthrough tests results.

4. To develop a GAC contactor model that will predict effluent \( \text{H}_2\text{O}_2 \) concentrations as a function of influent \( \text{H}_2\text{O}_2 \), empty bed contact time (EBCT), bed volumes of water containing natural organic matter (NOM) treated, and an empirical reaction kinetic parameter.

1.3 DESCRIPTION OF CHAPTERS

- Chapter 2 provides background information about previous research related to this study, including fundamentals of ultraviolet light/hydrogen peroxide (UV/\( \text{H}_2\text{O}_2 \)) and granular activated carbon (GAC), heterogeneous catalysis of GAC for quenching ozone and chlorine, and the quenching of \( \text{H}_2\text{O}_2 \) using GAC.

- Chapter 3 evaluates the quenching of \( \text{H}_2\text{O}_2 \) that is aged artificially in columns with different exposures to \( \text{H}_2\text{O}_2 \), to examine the impact of \( \text{H}_2\text{O}_2 \) exposure on the kinetics of quenching, for different carbon types.

- Chapter 4 essentially repeats the work of Chapter 3, but uses a more realistic pilot-scale set-up at the Lorne Park Water Treatment Facility. Results from pilot-scale tests are compared to bench-scale test results in Chapter 3.

- Chapter 5 puts forward a simplified continuous stirring tank reactor (CSTR)-in-series model to study the \( \text{H}_2\text{O}_2 \) residual concentration in a column.

- Chapter 6 summarizes the key findings of this research and provides recommendations for future work.
1.4 REFERENCES


Dotson, A., Corwin, C., Rowley, C., Downs, M., Linden, K., 2010. Dynamic bench-scale quenching of H₂O₂ by GAC. Savannah, Georgia, USA: AWWA WQTC.


2 LITERATURE REVIEW

2.1 FUNDAMENTALS OF ULTRAVIOLET LIGHT / HYDROGEN PEROXIDE

2.1.1 Background

Ultraviolet light coupled with hydrogen peroxide (UV/H$_2$O$_2$) can be used as an advanced oxidation process (AOP) in drinking water or wastewater treatment. The UV/H$_2$O$_2$ mechanism to generate hydroxyl radicals has been summarized by Crittenden et al. (1999) as:

\[ H_2O_2 + hv \rightarrow 2HO^\bullet \]  

(2-1)

\[ H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet \]  

(2-2)

\[ HO_2^\bullet + H_2O_2 \rightarrow H_2O + O_2 + HO^\bullet \]  

(2-3)

\[ 2 HO_2^\bullet \rightarrow H_2O_2 + O_2 \]  

(2-4)

2.1.2 The Need to Quench Hydrogen Peroxide Residuals

A typical UV/H$_2$O$_2$ process might employ up to 10 mg/L H$_2$O$_2$, with only 5-20% of the applied hydrogen peroxide undergoing photolysis (Watts et al., 2012). The remaining hydrogen peroxide is not believed to be carcinogenic to human beings (CAS, 1995), however, eye or skin irritation, or damage to the respiratory system may occur by inhalation or ingestion of high concentrations (NOISH, 2010). Moreover, H$_2$O$_2$ exerts a chlorine demand that inhibits the maintenance of the secondary chlorine residual. The H$_2$O$_2$ reaction with chlorine is very fast (in the order of seconds) and occurs at approximately the stoichiometric ratio of 2.1 mg free chlorine per 1 mg H$_2$O$_2$ (Dotson et al., 2010). H$_2$O$_2$ reacts more slowly with chloramines, with a second-order rate constant of $2.76 \times 10^{-2}$ M$^{-1}$s$^{-1}$ (McKay et al., 2013). This suggests that 1 mg/L of monochloramine would have a half-life in the order of 50 hours in the presence of 1 mg/L H$_2$O$_2$, which may still be significant from the perspective of maintaining a chloramine residual in large distribution systems. Formation of biofilm in the distribution system can be promoted as well (Pantin, 2009). The Aurora Reservoir Water Purification Facility (Aurora, Colorado, US) and the Andijk water treatment plant (WTP) in the Netherlands installed granular activated carbon (GAC) contactors after UV/H$_2$O$_2$ AOP to quench H$_2$O$_2$ residuals (Kruithof et al., 2007; Pantin, 2009). In the full-scale practice at Andijk, GAC filtration was reported to successfully quench H$_2$O$_2$ from 6 mg/L to less than 0.1 mg/L over more than 2 years of operation (Kruithof et al., 2007).
2.2 Fundamentals of Granular Activated Carbon (GAC)

GAC is an effective method for removing a wide range of contaminants by adsorption. GAC can also serve as a catalyst or catalyst support for hydrogen peroxide decomposition (Calgon Carbon Corporation, 1987). The catalytic activity was found to increase with gradually increasing temperature (from 423 – 573K) (Szymański et al., 2002). The strength and accessibility of surface acidic groups are important influencing factors, with less surface acidity but higher accessibility to acidic groups leading to stronger catalytic activity (Szymański et al., 2002).

2.3 Heterogeneous Catalysis of GAC for Quenching Ozone and Cl₂

2.3.1 Reaction of Chlorine Decomposition Using GAC

GAC was used for dechlorination in England since 1910 (Hung et al., 2007). The reaction between GAC and chlorine was firstly assumed to be simple adsorption. However, Suidan et al. (1977) proposed a mathematical model to predict the removal of aqueous chlorine with GAC involving the formation of carbon oxides on the GAC surface during the chlorine decomposition process. A detailed description of the model is presented by Suidan et al. (1977), but the general chlorine decomposition process is:

\[ C^* + HOCl \leftrightarrow CHOCl^* \]  \hspace{1cm} (2-5)
\[ CHOCl^* \rightarrow CO^* + H^+ + Cl^- \]  \hspace{1cm} (2-6)

where CHOCl* represents the HOCl molecule on the carbon surface and CO* represents the carbon oxides.

The model combined both a surface reaction model and a pore diffusion model. Semi-batch reactor and closed batch reactor experiments were conducted to solve the reaction constants in the process and then a model to predict fixed-bed performance for F400 GAC was developed (Suidan et al., 1977).

The reaction of chlorine removal was considered as a very fast reaction compared to the removal of organics with GAC, in the order of seconds (Desilva, 2000). Later, the decomposition process was further studied and described as a first-order reaction by Skibinski et al. (2009), with a lab-scale reaction rate constant of between 0.106 and 0.113 s⁻¹ for the catalytic activated carbon used. Unlike conducting semi-batch reactor and closed batch reactor experiments and then
evaluating surface reaction rate constants numerically by Suidan et al. (1977), Skibinski et al. (2009) determined the reaction rate constant using activation energies from experiments.

The model and reaction kinetics studies developed for chlorine removal using GAC provides clues for the quenching of \( \text{H}_2\text{O}_2 \). It is logical to assume a similar oxidation reaction occurring on the GAC surface, resulting in the formation of carbon oxides on the surface.

2.3.2 GAC for Ozone Decomposition

The capability of activated carbon to accelerate ozone decomposition was investigated by Jans and Hoigné (1998). In their study, ozone was observed to decompose three times faster in the presence of a small amount of activated carbon (at the mg/L level). Activated carbon promoted ozone decomposition by accelerating the transformation of ozone into the more reactive hydroxyl radicals (Jans and Hoigné, 1998). Later, a completed model describing the reaction mechanism pathway with GAC as an initiator was proposed by Álvarez et al. (2006). In the model, a portion of dissolved ozone transferred from the external GAC surface to the internal pore surface, while the remainder occupied the pore sites by physical adsorption. Then with suitable GAC surface composition and under proper operating conditions, ozone decomposed into more reactive hydroxyl radicals and peroxide radicals, with the formation of \( \text{H}_2\text{O}_2 \) in aqueous solution. \( \text{H}_2\text{O}_2 \) was then disassociated to \( \text{HO}_2^- \) or transformed into OH radicals depending on solution pH (Alvárez et al., 2006).

The influencing factors of this process were investigated in many studies (Dussert and Kovacic, 1997; Jans and Hoigné, 1998; Jans and Hoigné, 2000; Sánchez-Polo and Rivera-Utrilla 2003; Sánchez-Polo et al., 2005; Sánchez-Polo et al., 2006; Alvárez et al., 2006), including the surface characteristics of GAC (Alvárez et al., 2006; Sánchez-Polo et al., 2006), the solution pH (Alvárez et al., 2006), and the presence of hydroxyl radical scavengers (Sánchez-Polo et al., 2005; Sánchez-Polo et al., 2006 ). The experimental conditions in different studies are shown in Table 2.1.

In general, textural and chemical characteristics of GAC were found to govern the effect on ozone decomposition (Alvárez et al., 2006; Sánchez-Polo et al., 2006). With higher basicity and less acidic surface groups, the promoting activity of GAC increases (Alvárez et al., 2006). In addition, GAC with larger surface area is more effective (Sánchez-Polo et al., 2006). Secondly, the promoting activity of GAC is favored at neutral or basic pH (Alvárez et al., 2006). Thirdly, OH radical generation was enhanced with the presence of \( \text{HCO}_3^- \) and DOC, which are OH
radical scavengers, because HCO$_3^-$ may be neutralized with the acidic surface groups on GAC and DOC could be reduced by adsorption (Dussert and Kovacic, 1997; Sánchez-Polo et al., 2006).

In some studies (Jans and Hoigné 1998; Alvárez et al., 2006), H$_2$O$_2$ was detected during the ozone decomposition process in the presence of activated carbon. However, Jans and Hoigné (1998) found that activated carbon did not remove this part of H$_2$O$_2$ while dissociation of H$_2$O$_2$ was reported by Alvárez et al. (2006). The conflicting results may be because of different pH in the two studies according to Alvárez et al. (2006), because H$_2$O$_2$ tended to disassociate by itself at high pH (pKa = 11.6).

The GAC is affected by reaction with ozone. According to Dussert and Kovacic (1997), the chemical properties of GAC changed after exposure to ozone, with the formation of acidic surface groups, but the oxidation states of the surface were not changed. Jans and Hoigné (1998) also found that the activity of activated carbon with respect to ozone decomposition did not change upon pre-exposure to higher concentrations of ozone. However, others reported that if exposed to ozone for a longer time, there would be more surface oxygen groups formed on the carbon surface, consequently leading to a decrease in carbon promoting capability (Sánchez-Polo et al., 2005; Alvárez et al., 2006).
Table 2.1: Experimental Conditions in Aqueous GAC-Ozone Studies

<table>
<thead>
<tr>
<th>GAC/AC</th>
<th>Experimental Conditions</th>
<th>Findings</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>F400</td>
<td>Milli-Q system; O₃ generated on site, at a flow rate of 1L/min; GAC mass = 130g; GAC EBCT = 11min; flow rate: 25 mL/min; run time = 6 months</td>
<td>(1) Oxygen on GAC surface increased via chemical adsorption (2) GAC surface chemistry changed after ozonation with decrease in iodine number (3) Initial reaction of GAC and ozone could form C-O surface complex</td>
<td>Dussert and Kovacic, 1997</td>
</tr>
<tr>
<td>TL9592 (Chemviron) Pre-ozonized</td>
<td>Water with pH 7.8 and DOC 1.3 mg/L; Experiment under pH 5 and 7.5; 4 mg/L AC and 2-100 µM [O₃]₀</td>
<td>(1) Extended pre-ozonation did not further change GAC chemical characteristics (2) H₂O₂ formed during the process was not depleted by GAC (3) Small amount of GAC can accelerate ozone decomposition</td>
<td>Jans and Hoigné, 1998</td>
</tr>
<tr>
<td>F400; F10 and F120: ozone exposure for 10min and 120min, respectively;</td>
<td>Fixed-bed reactor; 2g GAC at flow rate = 76 mg/min; NTS ozonation: 45 mg/L NTS and 0.5g AC</td>
<td>(1) The electronic density on AC deceased after preozonation (2) The AC promote ozonation for NTS degradation and TOC removal, but the catalytic capacity of AC decreased with increased preozonation time</td>
<td>Sánchez-Polo and Rivera-Utrilla, 2003</td>
</tr>
<tr>
<td>Oliver stone PAC</td>
<td>Milli-Q system in a 100ml batch reactor at pH 7; [O₃]₀ = 20 mg/L</td>
<td>(1) Hydroxyl radicals were generated (2) Preozonation did not affect AC performance for promoting ozone decomposition</td>
<td>Guiza et al., 2004</td>
</tr>
<tr>
<td>F400</td>
<td>Water with alkalinity = 2.6×10⁻³ M as HCO₃⁻ and DOC 1.4 mg/L; pH = 7</td>
<td>Ozonation with the presence of AC could remove DOC and HCO₃⁻</td>
<td>Sánchez-Polo et al., 2005</td>
</tr>
<tr>
<td>F400; Witco W; W-U (more basic surface groups)</td>
<td>Milli-Q water system with free O₃ or OH radicals-depleting impurities in 1L bottle reactor; GAC with pre-ozonation for 10mins and 120mins; GAC preloaded with organic matter</td>
<td>(1) AC surface with higher basicity and larger surface areas AC worked better (2) Pre-ozonation with longer time led to decrease in AC active sites (3) Pre-adsorption of low concentrations of DOC did not affect AC promoting activity</td>
<td>Sánchez-Polo et al., 2006</td>
</tr>
<tr>
<td>GAC from cherry stones CS; Hydraffin P110; Darco 20x40; Chemviron SS4P and AQ40</td>
<td>Milli-Q system in batch reactor; 7–8 mg/L [O₃]₀ and 0-5g/L GAC with pH 7 buffered, 5 mM TBA solution;</td>
<td>(1) Proposed mechanism of O₃ decomposition with GAC (2) The promoting effect was in favor of neutral or basic pH (3) H₂O₂ was formed and released during reaction (4) Increased surface basicity and hydroxyl SOG could increase GAC promoting activity</td>
<td>Álvarez et al., 2006</td>
</tr>
</tbody>
</table>
2.4 Quenching of Hydrogen Peroxide by GAC

2.4.1 Quenching Mechanism

Alternatives for quenching hydrogen peroxide in drinking water treatment have been studied. Liu et al. (2003) reported that catalase has a high efficiency with a 0.2 mg/L dose able to quench 145 mg/L H$_2$O$_2$. Some inorganic chemicals, such as sodium hypochlorite, sodium thiosulfate and sodium sulfite also react with H$_2$O$_2$ stoichiometrically according to redox reactions (Liu et al., 2003). Dose pacing when applying reducing agents, however, has reportedly been difficult to achieve when the H$_2$O$_2$ residual concentration is unstable (Cotton et al., 2010).

To solve these problems from a practical perspective, GAC is gaining more attention due to its heterogenic catalytic ability to quench H$_2$O$_2$ (Cotton et al., 2010). However, based on previous studies related to H$_2$O$_2$ decomposition using GAC, the quenching mechanism is not fully understood (Khalil et al., 2001; Huang et al., 2003a; Rey et al., 2011; Aguinaco et al., 2011). Two major hypotheses have been put forward to understand the quenching mechanism. Some studies suggested that the reaction occurs via generating •OH radicals and •OOH radicals as intermediates (Lücking et al., 1998; Oliveira et al., 2004; Castro et al., 2009; Kurniawan and Lo, 2009; Aguinaco et al., 2011). Other researchers proposed another pathway involving functional group transfer between GAC and H$_2$O$_2$ on the GAC surface in basic medium (Rey et al., 2009; Bach and Semiat, 2011).

The first hypothesis can be expressed as (Kurniawan and Lo, 2009):

$$AC + H_2O_2 \rightarrow AC^+ + OH^- + •OH$$  \hspace{1cm} (2-7)

$$AC^+ \rightarrow AC + H^+ + •OOH$$  \hspace{1cm} (2-8)

In this hypothesis, if H$_2$O$_2$ is in excess in basic medium, a chain reaction would follow to decompose H$_2$O$_2$ and slow down the oxidation process, with the formation of less reactive HO$_2^-$ and O$_2^-$ ion (Kurniawan and Lo, 2009). The chain reaction can be quoted as (Khalil et al., 2001):

$$H_2O_2 + •OH \rightarrow H_2O + HO_2^-$$  \hspace{1cm} (2-9)

$$HO_2^- \leftrightarrow H^+ + O_2^-$$  \hspace{1cm} (2-10)

$$O_2^- + H_2O_2 \rightarrow O_2 + OH^- + •OH$$  \hspace{1cm} (2-11)

To prove the formation of OH radicals, experiments of radical scavenger removal, such as dye (Gomes et al., 2011) or tert-butanol (Aguinaco et al., 2011) were conducted.
For the second hypothesis, the reaction was proposed as (Bach and Semiat, 2011):

\[
H_2O_2 \leftrightarrow H^+ + OO\cdot \quad (pK_a = 11.6) \quad (2-12)
\]

\[
AC-OH + H^+ 0O\cdot \rightarrow AC-OO\cdot + H_2O \quad (2-13)
\]

\[
AC-OO\cdot + H_2O_2 \rightarrow AC-OH + O_2 + H_2O \quad (2-14)
\]

This mechanism was supported by the observation that higher doses of GAC led to increased decomposition of \( H_2O_2 \), by forming surface peroxide.

The disagreement between the two hypotheses might be caused by three major influencing factors in experiments: (1) GAC characteristics (e.g. surface chemical and textural composition) (Huang et al., 2003; Gomes et al., 2011); (2) water matrix (e.g. pH, temperature, presence or absence of NOM) (Kurniawan and Lo, 2009; Aguinaco et al., 2011; Bach and Semiat, 2011); and (3) reactants (e.g. \( H_2O_2 \) concentration, GAC dose) (Kurniawan and Lo, 2009). The experimental conditions and basic information of the related studies are shown in Table 2.2.

The surface characteristics of GAC were widely investigated and proven to be a principal factor contributing to the hydrogen peroxide decay in various studies (Khalil et al., 2001; Huang et al., 2003a; Rey et al., 2011; Aguinaco et al., 2011). According to Khalil et al. (2001), the chemical nature of GAC can be determined by surface functional groups, mainly including the basic or acidic oxides. The formation of oxides depends on activation mode and precursors. Results showed that GAC with acidic functional groups, which formed after impregnation with \( H_3PO_4 \) (Khalil et al., 2001) or oxidation with \( HNO_3 \) under heat treatment (Huang et al., 2003a; Rey et al., 2011), tended to slow the \( H_2O_2 \) decay. This might be due to the blockage of reaction sites by surface oxygen groups (Rey et al., 2011). In contrast, activated carbon pre-impregnated with \( NH_4Cl \) showed about six times higher efficiency than activated carbons impregnated with \( H_3PO_4 \) at pH values between 4.9 and 9.5 (Khalil et al., 2001). In addition, the surface oxygenated functional groups were reduced by hydrogen (Oliveira et al., 2004) or alkalinity pretreatment (Kurniawan and Lo, 2009), with the introduction of more activated sites. However, a recent study by Aguinaco et al. (2011) disagreed with previous studies, with the evidence that Chemviron SSP-4 activated carbon, which has an acidic nature, decomposed hydrogen peroxide faster than HydrafhinP110, which has basic characteristics. The authors explained that the metal on Chemviron SSP-4 could be the reason for this conflict, since Fenton reactions occurred (Aguinaco et al., 2011). The promoting effect for \( H_2O_2 \) decay with metal ion was observed and
mentioned by Castro et al. (2009) as well. Thus, when comparing the surface nature of different GAC, the presence of metal on the GAC surface should be considered as well.

In addition to surface functional groups, surface structure is another important factor, with GAC having a more disorganized structure being more efficient (Rey et al., 2011). The decomposition process is also in favor of more π-electrons on its graphenic layers (Kurniawan and Lo, 2009). Unlike during adsorption processes, the porosity of GAC is not a predominant factor for H$_2$O$_2$ decomposition, because GAC with large pore volumes or wider pores did not speed the process (Khalil et al., 2001).

The effects of NOM, pH, temperature and existing ions on H$_2$O$_2$-GAC reaction have been investigated, but not directly in the context of hydrogen peroxide quenching. Instead, the focus has been on enhancing catalytic H$_2$O$_2$ oxidation using GAC for organic pollutant removal, such as 4-CP (Lücking et al., 1998; Huang et al., 2003a), 2-CP (Huang et al., 2003b), dye (Oliveira et al., 2004), raw leachate (Kurniawan and Lo, 2009). In these short-term experiments, the presence of organic compounds showed a negative effect on the decomposition of H$_2$O$_2$ by competing for reactive sites. The decomposition rate of H$_2$O$_2$ decreased while the removal rate of organics increased (Huang, Lu et al., 2003a; Bach and Semiat, 2011). If GAC is saturated by organics, the catalytic capability would decline dramatically. Bach and Semiat (2011) reported that the decomposition rate of H$_2$O$_2$ with GAC that is 80% saturated by phenol is twice slower than virgin GAC, due to the decrease in micropores. It indicates that with the presence of NOM in treated water, long term fouling would have an adverse effect on the quenching process.

Solution pH can influence the quenching process mainly via affecting the stability of H$_2$O$_2$ and surface characteristics of GAC (Aguinaco et al., 2011). H$_2$O$_2$ quenching is found to be faster at high pH, especially higher than 8 (Kurniawan and Lo, 2009), reportedly because of the disassociation of H$_2$O$_2$ into OOH$^-$ (Khalil et al., 2001). However, the effect of pH may be confounded since both pH of the GAC surface and solution pH may have an impact on the H$_2$O$_2$ decomposition (Rey et al., 2011). Increased temperature can also promote the decomposition efficiency (Aguinaco et al., 2011). Ions in buffering salts, such as phosphorus, have been found to suppress the decomposition process (Khalil et al., 2001; Aguinaco et al., 2011).

While the decomposition rate varies with different GAC, GAC itself is oxidized by H$_2$O$_2$ in the quenching process. To understand how GAC changes during the process is fundamental for optimization in drinking water treatment. Acidic functional groups or other oxides form on
the GAC surface during the reaction and thus reduce the catalytic efficiency (Huang et al., 2003a). The surface area of micropores, where the catalytic activity mainly occurs, has been reported to decrease 23.5% after \( \text{H}_2\text{O}_2 \) oxidation compared to virgin GAC (Bach and Semiat, 2011). However, the carbon activity showed good stability with 135 hours of \( \text{H}_2\text{O}_2 \) exposure (Quintanilla et al., 2010).
Table 2.2: Experimental Conditions in GAC-H$_2$O$_2$ Studies

<table>
<thead>
<tr>
<th>GAC/AC type</th>
<th>Experimental Conditions</th>
<th>Findings</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>coal-based F300 (Calgon); coal-based Darco GCW (Norit); peat-based ROW 0.8 Supra (Norit); peat-based and impregnated with iron hydroxide RFZ 1 (Norit)</td>
<td>(1) 1g/L 4-CP dissolved in batch reactor with DI water at 30°C; (2) For flow experiment, retention time = 26 min at flow rate 3.51 ml/h under pH = 3; 5.3g/L $[\text{H}_2\text{O}_2]_0$ and 1.0g/L GAC</td>
<td>(1) Virgin F300 had slowest removal rate in both situations (2) Surface characteristics of AC is important (3) $\text{H}_2\text{O}_2$ decomposition rate decreased with 4-CP</td>
<td>Lücking et al., 1998</td>
</tr>
<tr>
<td>F300 (Chemiron); F300 pre-impregnation with $\text{H}_3\text{PO}_4$; F300 pre-impregnation with $\text{NH}_4\text{Cl}$</td>
<td>20 mg AC with slurry pH 4.9-9.5 and 0.8mg/L $[\text{H}_2\text{O}_2]_0$ at 30°C in a glass cell with two way connection</td>
<td>(1) Proposed mechanism of oxonium-hydroxyl group exchange on carbon surface (2) With higher slurry pH, $\text{H}_2\text{O}_2$ decomposed faster (3) Higher T enhanced catalytic activity (4) P inhibited reaction (5) Carbon activated with $\text{NH}_4\text{Cl}$ or Steamed were better</td>
<td>Khalil et al., 2001</td>
</tr>
<tr>
<td>F300 (Calgon); GAC1; GAC2 oxidized with $\text{H}_2\text{O}_2$; GAC3 oxidized with $\text{HNO}_3$</td>
<td>1000 mg/L GAC and 20mM $[\text{H}_2\text{O}_2]_0$ with / without 4-CP/2-CP in batch reactor</td>
<td>(1) Higher pH$_{pzc}$ increased $\text{H}_2\text{O}_2$ decomposition (2) Surface reaction dominated mass transfer rate (3) Acidic functional groups slowed catalytic activity</td>
<td>Huang et al., 2003a; Huang et al., 2003b</td>
</tr>
<tr>
<td>Aldrich Darco G60 (Norit) treated with $\text{H}_2$ under 450-800 °C during 1h</td>
<td>30 mg AC in 7 ml 3mol/L $\text{H}_2\text{O}_2$ solution</td>
<td>(1) Treatment with $\text{H}_2$ on AC promoted catalytic action by creating reducing site; (2) Proposed radical pathway</td>
<td>Oliveira et al., 2004</td>
</tr>
<tr>
<td>Commercial ACM (Merck); ACR produced from spent coffee ground with iron oxide</td>
<td>30 mg AC in 7 ml 3mol/L $\text{H}_2\text{O}_2$ solution</td>
<td>(1) Proposed radical mechanism with phenol experiment (2) AC from residue is more active than commercial one</td>
<td>Castro et al., 2009</td>
</tr>
<tr>
<td>coconut shell-based GAC modified with NaOH</td>
<td>0.5 to 5.0 g/L $[\text{H}_2\text{O}_2]_0$ and 5 g/L GAC at pH 8.0 in the raw leachate samples</td>
<td>(1) Excessive $\text{H}_2\text{O}_2$ can expand chain reaction; (2) pH 8–9 has best COD removal efficiency with $\text{H}_2\text{O}_2$ and GAC</td>
<td>Kurniawan and Lo, 2009</td>
</tr>
<tr>
<td>Commercial GAC (Merck)</td>
<td>2.5 g AC and $[\text{H}_2\text{O}_2]<em>0$ 5g/L with pH$</em>{inlet}$ 3.5 in a trickle-bed reactor with pure $\text{O}<em>2$ at 127 °C and 8 atm Q$</em>{\text{O}_2}$ = 91.6mL/min</td>
<td>Carbon activity had good stability (after time = 135h)</td>
<td>Quintanilla et al., 2010</td>
</tr>
<tr>
<td>GAC/AC type</td>
<td>Experimental Conditions</td>
<td>Findings</td>
<td>Source</td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
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</tr>
</tbody>
</table>
| PAC: CM (Merck); Row 0.8 Supra (Norit); Centaur HSL (Chemviron Carbon); 12 others from three original | 0.5g/L PAC and 500mg/L [H₂O₂]₀ at 50°C under pH=3; stirring velocity: 200rpm              | (1) H₂O₂ decay decreased with the increase of acidic functional groups  
(2) Surface structure with more electron-rich centers can promote the catalytic activity | Rey et al., 2011          |
| Hydraulflin P110; Chemviron SSP-4 (acidic nature) | 1g AC and [H₂O₂]₀ 7.7mg /L at 25°C under pH₀ = 4.8 in a batch reactor with O₃ generated on site | (1) OH radicals reaction mechanism was confirmed by Tert-butanol  
(2) Chemviron SSP-4 showed higher capacity  
(3) Metal content in AC can promote the catalytic activity | Aguinaco et al., 2011 |
| Charcoal activated GAC; Purchased GAC with high temperature scheme and high pH; Saturated or partly loaded GAC by phenol | a: [H₂O₂]₀ = 8250 mg/L; b: [H₂O₂]₀ = 6500 mg/L without TOC in water system | (1) Without TOC, catalytic activity raised with the increase of pH;  
(2) Virgin GAC has twice efficiency comparing with saturated GAC | Bach and Semiat, 2011 |
Only a few studies (Kruithof et al., 2007; Doom, 2008; Collins et al., 2010; Dotson et al., 2010; Metz et al., 2011a) investigated GAC treatment after UV/H₂O₂ in drinking water treatment. The synergetic effect of GAC and H₂O₂ can prevent DBP formation (Collins et al., 2010; Metz et al., 2011a). As for the quenching process, H₂O₂ breakthrough was found in a GAC rapid small-scale column test with an EBCT of less than 4 minutes (Doom, 2008; Dotson et al., 2010).

There are two drinking water treatment plants known to the author to have installed GAC contactors for the purpose of quenching H₂O₂. One is the Aurora Reservoir Water Purification Facility (Aurora, Colorado, US) and the Andijk water treatment plant in the Netherlands (Kruithof et al., 2007; Pantin, 2009). Andijk uses GAC after UV/H₂O₂ AOP to remove H₂O₂, as well as AOC and nitrite (Kruithof et al., 2007). The GAC is reported to be able to quench 15 mg/L H₂O₂ with an EBCT less than 5 minutes (Kruithof et al., 2007). Over the long-term, it has been found that 6 mg/L H₂O₂ can be quenched to less than 0.1 mg/L following 2-years of operation (Kruithof et al., 2007). Information about pilot-scale and full-scale GAC studies is shown in Table 2.3.
Table 2.3: GAC-H₂O₂ Studies in Drinking Water Applications

<table>
<thead>
<tr>
<th>GAC</th>
<th>EBCT/min</th>
<th>Experimental set-up</th>
<th>Findings</th>
<th>Source</th>
</tr>
</thead>
</table>
| Norit ROW 2CAT       | 40       | 2 step GAC filter after UV/H₂O₂ with full-scale installation in Andijk WTP           | (1) 15 mg/L H₂O₂ could be removed within 5 minutes  
(2) GAC could remove 6 mg/L H₂O₂ to less than 0.1 mg/L for 2 years  
(3) AOC was reduced from 45–142 Ac C to 3–31 Ac C eq/L  
(4) Biofilm formation rate was lower than recommended value | Kruithof et al., 2007 |
| Not mentioned        | 1,2,4    | (1) Jar Tests  
(2) RSSCTs with 4 carbon sizes and 3 carbon ages with high and low TOC in water | (1) H₂O₂ breakthrough happened with EBCT less than 4 minutes  
(2) The presence of TOC and carbon size had no impact on quenching kinetics | Doom, 2008                  |
| Catalytic 1,2; Coal-based; Coconut-based | 5        | Loading rate = 12 gpm/ft² and [H₂O₂]₀ = 7 mg/L                                      | (1) H₂O₂ complete quenching with an EBCT < 2 min  
(2) The process increased headloss and required pumping  
(3) DBP precursors were reduced | Collins et al., 2010 |
| Not mentioned        | 4×1min in series of 1×11min | RSSCT with UV/H₂O₂ using water from coagulated and filtered Boulder Reservoir and [H₂O₂]₀ about 2 mg/L | (1) UV/H₂O₂ yielded more DBPs  
(2) With an EBCT = 1 min can get > 60% quenching of H₂O₂  
(3) With an EBCT = 4 min, 100% quenching of H₂O₂ | Dotson et al., 2010 |
| thermally reactivated GAC filter | 15-20    | A-year UV/H₂O₂ pilot study;  
[TOC]_in_ave = 1.9 mg/L;  
[TOC]_eff = 0.9 mg/L and [H₂O₂]₀ = 10 mg/L | (1) GAC filter before or after UV/H₂O₂ can both decrease the formation of DBPs  
(2) GAC can quench excess H₂O₂ when used after AOP | Metz et al., 2011a          |
| Coal-based GAC       | 15       | UV/H₂O₂ pilot study with 10 mg/L [H₂O₂]₀                                             | (1) GAC could remove TOC efficiently  
(2) Total AOC concentration was 40% lower with GAC after UV/H₂O₂ | Metz et al., 2011b          |
2.4.2 Kinetics of the Quenching Process

From previous studies discussed in Section 2.4.1, the reaction between GAC and H₂O₂ is likely not governed by physical adsorption, but a chemical redox reaction. Thus, the kinetics of H₂O₂ decomposition is also in need of consideration, along with the thermodynamics. Different variables have been studied, including the concentrations of H₂O₂ and GAC (Huang et al., 2003a; Aguinaco et al., 2011; Bach and Semiat, 2011). It has been proven that the surface reaction controls the overall efficiency via comparison of total molar flux (Huang et al., 2003a), while internal diffusion mass transfer resistance is considered not negligible according to Mears’ criterion (Aguinaco et al., 2011). Jar tests characterizing mass transfer mechanisms conducted by Doom (2008) showed that both external and internal reactions are important in the quenching process. Huang et al. (2003a) reported that the rate constant of H₂O₂ decomposition decreased with the increase in initial H₂O₂. To further investigate the process, a modified Langmuir-Hinshelwood kinetic rate model, which is typically used to describe heterogenic catalytic reactions, was applied to find the rate constant (Huang et al., 2003a). The model can be expressed as (Huang et al., 2003a):

\[
R_H = -\frac{d[H_2O_2]}{dt} = \frac{k[catalyst][H_2O_2]}{1 + k_H[H_2O_2]} \tag{2-15}
\]

where \(k_H\) is the binding constant and \(k\) is the reaction rate constant.

The first order kinetics law was used in several studies (Oliveira et al., 2004; Kurniawan and Lo, 2009; Rey et al., 2011), with a coefficient correlation fit of over 0.99. Huang et al. (2003a) found that the kinetic rate constant is related to the presence of organics. In the absence of organics, the reaction followed first order kinetics, while second order kinetics was chosen in the presence of 2-CP (Huang et al., 2003b). However, Bach and Semiat (2011) showed that second-order kinetics was more suitable even in the absence of TOC, with a set of experiments involving different GAC doses. Details about different studies are shown in Table 2.4. According to Bach and Semiat (2011), the reaction rate expression can be quoted as:

\[
r_{H_2O_2} = -\frac{d[H_2O_2]}{dt} = k_n[GAC][H_2O_2] = k_{H_2O_2}[H_2O_2] \tag{2-16}
\]

where \(k_n\) is the mass normalized rate coefficient.

This expression is inconsistent with the Huang et al. (2003b) equation with the presence of 2-CP, as well as another study by Huang et al. (2003a) applying the modified L-H kinetics
model. The difference in kinetic models may result from various GAC doses, initial \(H_2O_2\) concentrations, pH and the presence of organic matter.

### Table 2.4: Information of Experimental Set-up in Related Studies

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Rate constant k</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without 4-CP (GAC without modification)</td>
<td>pH about 7.0; ([H_2O_2]_0=4–30mM;) GAC =1000mg/L</td>
<td>Applied L-H model; (k= 5.93\times10^{-3}/min;) (kH = 2.33\times10^{-2}/mM;) (k) increased with the increase of (kH)</td>
</tr>
<tr>
<td>Without 2-CP</td>
<td>([H_2O_2]_0=20mM; T=30'C;) GAC =0.5 g/L</td>
<td>First order rate constant</td>
</tr>
<tr>
<td>With 2-CP</td>
<td>([2-CP]=1.13mM;) ([H_2O_2]_0=20mM; T=30'C;) GAC = 0.5 g/L</td>
<td>Second order rate constant</td>
</tr>
<tr>
<td>Without organics, original AC</td>
<td>AC: 30 mg in 7 ml solution of (H_2O_2) (3 mol/L)</td>
<td>First order rate constant (k = 0.015/min)</td>
</tr>
<tr>
<td>In leachate sample</td>
<td>Total reaction time: 60 min (pH = 8.0;) COD = 8000 mg/L GAC dose = 15 g/L</td>
<td>First order rate constant 30% (H_2O_2: k= 6.6\times10^{-3}/min;) 15% (H_2O_2: k= 1.24\times10^{-1}/min)</td>
</tr>
<tr>
<td>Without TOC</td>
<td>([H_2O_2]_0=8250 mg/l; GAC from 5 to 60 g/L)</td>
<td>Follows a first order and kinetic rate expression with respect to (H_2O_2) concentration</td>
</tr>
<tr>
<td></td>
<td>([H_2O_2]_0=6500 mg/L ; pH about 7)</td>
<td>GAC concentration affects (H_2O_2) decomposition rate; Second order rate constant</td>
</tr>
</tbody>
</table>

### 2.5 SUMMARY

According to previous studies concerning GAC-\(H_2O_2\) reaction (Lücking et al., 1998; Oliveira et al., 2004; Castro et al., 2009; Kurniawan and Lo, 2009; Rey et al., 2009; Aguinaco et al., 2011; Bach and Semiat, 2011), the reaction mechanism was hypothesized to be either through a hydroxyl radical pathway (Lücking et al., 1998; Oliveira et al., 2004; Castro et al., 2009; Kurniawan and Lo, 2009; Aguinaco et al., 2011), or by exchanging surface functional groups between GAC and \(H_2O_2\) (Rey et al., 2009; Bach and Semiat, 2011). The disagreement between the two pathways was resulted from the differences of GAC characteristics (Huang et al., 2003a; Gomes et al., 2011), water matrix (Kurniawan and Lo, 2009; Aguinaco et al., 2011; Bach and Semiat, 2011), and reactants (Kurniawan and Lo, 2009) in the studies. The GAC-\(H_2O_2\) reaction was found to be in favor of high temperature (Aguinaco et al., 2011), basic medium
(Kurniawan and Lo, 2009), and GAC with basic surface functional groups (Khalil et al., 2001, Rey et al., 2011). The Aurora Reservoir Water Purification Facility (Aurora, Colorado, US) and the Andijk water treatment plant in the Netherlands (Kruithof et al., 2007; Pantin, 2009) are known to have installed GAC contactor after UV/H₂O₂ AOP in drinking water treatment. In full-scale practice, GAC can effectively quench H₂O₂ residuals following 2-year operation (Kruithof et al., 2007).

Nevertheless, most of the laboratory studies related to GAC-H₂O₂ reaction were not in the context of drinking water treatment. How the performance of GAC for quenching H₂O₂ would be affected by long-term use, and which factors might affect that performance are not elucidated. This led to the uncertainty on how to design and operate a GAC system for quenching H₂O₂ following advanced oxidation process in drinking water treatment. In this work, how the efficiency of this quenching process is affected by carbon type, age (i.e., bed volumes of natural water) and other factors (e.g., exposure to H₂O₂) would be investigated by both bench-scale and pilot-scale experiments.
2.6 REFERENCES


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3  BENCH-SCALE ANALYSIS OF THE EFFECT OF H₂O₂ EXPOSURE AND CARBON TYPE ON H₂O₂ QUENCHING USING GAC

ABSTRACT

The performance of six types of granular activated carbon (GAC) to quench H₂O₂ was evaluated by bench-scale H₂O₂ decomposition kinetics tests. The objective of this study was to investigate the effect of carbon ageing and the addition of H₂O₂ during the ageing process on the GAC performance. The GAC samples in this study were aged by exposure to approximately 2000%, 3000% and 4000% total organic carbon (TOC) saturation levels. X-ray photoelectron spectroscopy (XPS) analysis and scanning electron microscopy (SEM) imaging were applied to understand the changes to the GAC surface characteristics.

The study showed that carbon ageing significantly reduced the kinetics of H₂O₂ quenching by the GAC, but that the greatest impacts occurred at the beginning of the ageing process, with performance tending to stabilize with longer ageing. The addition of H₂O₂ in the ageing process did not have as great an effect on the quenching performance as the addition of natural organic matter (NOM). The catalytic carbon, ADCAT, had the most stable performance among the six GACs when aged with either H₂O₂ exposure or exposure to NOM.
3.1 INTRODUCTION

The application of ultraviolet light coupled with hydrogen peroxide (UV/H$_2$O$_2$) as an advanced oxidation process (AOP) in drinking water treatment to control taste and odour-causing compounds is a new and emerging technique. In this process, only approximately 5-20% of the H$_2$O$_2$ is consumed, and the excess H$_2$O$_2$ will exert chlorine and chloramine demand on the distribution system (Dotson et al., 2010; Watts. et al., 2012; McKay et al., 2013). To quench the H$_2$O$_2$ residuals prior to application of a secondary disinfectant, the Aurora Reservoir Water Purification Facility (Aurora, Colorado, US) and the Andijk water treatment plant (WTP) in the Netherlands (Kruithof et al., 2007; Pantin, 2009) have installed granular activated carbon (GAC) contactors after UV/H$_2$O$_2$ AOP.

With more than two years full-scale practice at Andijk, GAC was reported to be capable of quenching H$_2$O$_2$ from 6 mg/L to less than 0.1 mg/L (Kruithof et al., 2007), however, studies related to H$_2$O$_2$ quenching using GAC in drinking water treatment are limited. Previous studies (Lücking et al., 1998; Huang et al., 2003; Huang, Lu et al., 2003; Oliveira et al., 2004; Kurniawan and Lo, 2009) have reported the enhanced catalytic H$_2$O$_2$ oxidation using GAC for organic pollutant removal, such as 4-CP (Lücking et al., 1998; Huang et al., 2003), 2-CP (Huang, Lu et al., 2003), dye (Oliveira et al., 2004), raw leachate (Kurniawan and Lo, 2009), but not in the context of drinking water treatment. It remains unclear how the performance of GAC for quenching H$_2$O$_2$ would be affected by long-term use, and which factors might affect that performance.

NOM fouling is hypothesized to be one of the potential factors affecting H$_2$O$_2$ quenching by GAC. To investigate the effect of NOM, virgin GAC was exposed to natural water (containing NOM) collected from the Lorne Park water treatment plant (Peel Region, Ontario), immediately downstream of ultrafiltration membranes. The Lorne Park plant employs ultrafiltration followed by UV-H$_2$O$_2$ for taste and odour control, with GAC contactors to quench residual H$_2$O$_2$. The water used for this study therefore represents the water from the full-scale plant at the point of full-scale GAC application.

According to Snoeyink and Summers (1999), GAC will be saturated by NOM (i.e. influent TOC equal to effluent TOC) after several thousand bed volumes of water treated. To study the long-term performance of GAC, the ageing process was conducted by exposure to
three different levels of bed volumes treated after NOM saturation (i.e. approximately 2000%, 3000% and 4000% of NOM saturation).

Since the reasons that cause degradation of $\text{H}_2\text{O}_2$ quenching ability by GAC are not well understood, $\text{H}_2\text{O}_2$ exposure during the ageing process was proposed as another potential affecting factor. Another set of ageing was conducted to investigate the impact of $\text{H}_2\text{O}_2$ exposure by spiking $\text{H}_2\text{O}_2$ into the water during the ageing process (i.e., ageing the GAC with NOM+$\text{H}_2\text{O}_2$).

A bench-scale $\text{H}_2\text{O}_2$ decomposition kinetics test was selected to study the quenching process between GAC and $\text{H}_2\text{O}_2$. Initially, the suitability of a bench-scale test to accurately represent full-scale performance was unknown. One of the objectives of this work was to generate bench-scale test data that could then be compared to similar larger (pilot) scale data (described in Chapter 4), to determine whether fast and inexpensive bench-scale tests to evaluate GAC effectiveness to quench $\text{H}_2\text{O}_2$ are appropriate.

Six types of GAC were used in this study to explore differences in their ability to quench $\text{H}_2\text{O}_2$.

### 3.2 Objective

The main objective was to evaluate the performance of granular activated carbon (GAC) to quench $\text{H}_2\text{O}_2$ residuals after the UV/$\text{H}_2\text{O}_2$ process. The specific objectives included the following:

1. To investigate the effect of carbon ageing (2000%, 3000% and 4000% of NOM saturation) and $\text{H}_2\text{O}_2$ exposure (0mg/L and 4 mg/L) during the ageing process on the GAC performance to quench $\text{H}_2\text{O}_2$, using bench-scale $\text{H}_2\text{O}_2$ decomposition kinetics tests.

2. To study the changes of GAC surface characteristics after the ageing process (aged with NOM, and with NOM+$\text{H}_2\text{O}_2$) by X-ray photoelectron spectroscopy (XPS) analysis and scanning electron microscopy (SEM) imaging.

3. To compare the performance of six GACs (Centaur, ADCAT, F300, GAC300, HD3000 and TN5) for the quenching of $\text{H}_2\text{O}_2$. 

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3.3 MATERIAL AND METHODS

3.3.1 Carbon Preparation

3.3.1.1 Activated Carbons

Six types of GAC (Centaur, F300 and TN5 from Calgon; HD3000 and GAC 300 from Norit Canada; ADCAT from CarboTech) were tested. All carbons were received from manufacturers with a particle size of 8×30 US sieve size. Pulverized activated carbon (95% under 325 US sieve size) was prepared in the lab (in the Department of Mechanical and Industrial Engineering at the University of Toronto) by using a ball mill (Fisher Scientific, OH, US) and measured with a Mastersizer 2000 particle size analyzer (Malvern instruments, Worcestershire, UK).

3.3.1.2 Carbon Ageing, Drying and Preservation

Carbon samples with six different pre-exposure histories were prepared at the Lorne Park Water Treatment Plant using 1-inch glass columns through which plant membrane permeate water flowed. Twenty grams of representative carbon samples were selected by the coning and quartering technique (ASTM D346) and washed with Milli-Q water, then dried in the oven at 105°C overnight in order to remove impurities (Calgon Carbon Corporation, 1987). After that the GACs were packed at the bottom of the column (7.5 cm) and continuously loaded with membrane permeate at a flow rate of 158 mL/min (equivalent to an EBCT of 0.24 min).

During the pre-exposure process, both influent and effluent of the GAC columns were collected for TOC analysis to determine the bed volumes of water treated to NOM saturation as defined by no TOC reduction across the GAC column. According to Figure 3.1, NOM saturation (i.e. greater than 70% TOC breakthrough in this study) on all types of GAC was observed after approximately 1200 bed volumes of pre-loading. To study the long-term performance of GAC, the ageing process was conducted by exposure to 25 000, 35 000 and 45 000 bed volumes treated after NOM saturation (i.e. approximately 20, 30, and 40 times longer than time to NOM saturation), which are equivalent to up to six months service duration. Another potential affecting factor, H₂O₂ exposure, was studied by adding the average H₂O₂ concentration during the full-scale daily operation at the Lorne Park Water Treatment Facility, 4 mg/L, into the membrane permeate. A new set of representative virgin GAC samples was pre-exposed to the
membrane permeate with H$_2$O$_2$ for the same bed volumes of water treated as the ones without H$_2$O$_2$. Operating conditions for the pre-exposure process are shown in Table 3.1.

![Figure 3.1: TOC Breakthrough Profile (C: effluent TOC; C$_0$: influent TOC)](image)

**Table 3.1: Carbon Pre-Exposure Operating Conditions**

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>Carbon weight (g)</th>
<th>Pre-exposure histories</th>
<th>Water information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td></td>
<td>Aged with NOM:</td>
<td></td>
</tr>
<tr>
<td>F300</td>
<td></td>
<td>1. 25 000 bed volumes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. 35 000 bed volumes</td>
<td></td>
</tr>
<tr>
<td>GAC300</td>
<td>20.000</td>
<td>3. 45 000 bed volumes</td>
<td>Ultrafiltration membrane permeate</td>
</tr>
<tr>
<td>ADCAT</td>
<td></td>
<td>Aged with NOM + 4 mg/L H$_2$O$_2$:</td>
<td>(TOC: 1.9-2.4mg/L)</td>
</tr>
<tr>
<td>HD3000</td>
<td></td>
<td>1. 25 000 bed volumes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. 35 000 bed volumes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. 45 000 bed volumes</td>
<td></td>
</tr>
<tr>
<td>TN5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After pre-exposure to the natural water and H$_2$O$_2$, carbon samples were collected from the columns and kept at 4°C until freeze dried (Andrews, 1990) in 20 mL vials in a freeze drier (Dura-Dry MP, US) located in the Industrial BioDevelopment laboratory of the MaRs Centre (Toronto, Ontario, Canada). The freeze-drying process involved an initial freeze for 1 hour, and then the vacuum was turned on and the samples were freeze-dried for at least 96 hours. After freeze-drying, carbon samples were collected in amber HDPE bottles (Fisher Scientific, ON,
and sealed with Teflon tape, then stored in a desiccator at room temperature. Procedures for freeze-drying are shown in Appendix A.3.

### 3.3.2 Carbon Characterization

#### 3.3.2.1 Carbon Property Tests

The iodine number, trace capacity number (TCN), and apparent density were measured for each activated carbon. Results from triplicate experiments are shown in Table 3.2. The experimental set-up and operating procedures are provided in Appendix A.1.

<table>
<thead>
<tr>
<th>GAC type</th>
<th>Material</th>
<th>Iodine NO. (mg/g)</th>
<th>TCN (mg/g)</th>
<th>Apparent Density (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>Bituminous coal-based; catalytic</td>
<td>1044</td>
<td>7.8</td>
<td>530</td>
</tr>
<tr>
<td>ADCAT</td>
<td>Hard coal-based; catalytic</td>
<td>956</td>
<td>7.8</td>
<td>485</td>
</tr>
<tr>
<td>F300</td>
<td>Bituminous coal-based</td>
<td>847</td>
<td>5.5</td>
<td>501</td>
</tr>
<tr>
<td>GAC300</td>
<td>Coal-based</td>
<td>931</td>
<td>7.9</td>
<td>539</td>
</tr>
<tr>
<td>HD3000</td>
<td>Lignite coal-based; acid washed</td>
<td>601</td>
<td>9.6</td>
<td>421</td>
</tr>
<tr>
<td>TN5</td>
<td>Coconut-based</td>
<td>861</td>
<td>7.1</td>
<td>599</td>
</tr>
</tbody>
</table>

#### 3.3.2.2 X-ray photoelectron spectroscopy (XPS) Analysis

The surface characteristics of GAC, including surface structures and elements, were investigated using X-ray photoelectron spectroscopy (XPS, in the Department of Chemical Engineering at the University of Toronto) and scanning electron microscopy (SEM, in the Department of Earth Science at the University of Toronto).

XPS analysis was conducted to study the elemental composition and functional groups on the GAC surface. Carbon samples after freeze-drying were collected and run on the Thermo Scientific Theta Probe XPS spectrometer (ThermoFisher, E. Grinstead, UK) located at the University of Toronto.

The samples were run in standard mode (i.e. all angles collected for spectra). A monochromatic Al Kα X-ray source was used with a spot area of 400 μm. Where necessary,
charge compensation was provided utilizing the combined e-/Ar+ flood gun. The position of the energy scale was adjusted to place the main C 1s feature (C-C) at 284.6 eV. A survey spectrum was obtained at low resolution (pass energy = 200 eV) as well as for the regions of interest. The C 1s region was also obtained at high-energy resolution (pass energy = 30 eV). The instrument and all data processing were performed using the software (Avantage) provided with the instrument.

3.3.2.3 Scanning Electron Microscopy (SEM) Imaging

The surface morphology of the GAC was investigated by the JSM-6610LV scanning electron microscope (JEOL, MA, US) located in the Department of Earth Sciences at the University of Toronto. Carbon samples after freeze-drying were coated with gold to improve the image quality before scanning. The SEM was operated in secondary electron imaging (SEI) mode with a spot size of 33 mm. The images were captured with different magnifications and compared.

3.3.3 H$_2$O$_2$ Decomposition Kinetics Tests in the Presence of GAC

The H$_2$O$_2$ decomposition kinetics tests in the presence of GAC were conducted in 1L capped amber glass bottles. Virgin and six types of GAC aged by different conditions were tested in the kinetics tests. The reactors were prepared by adding 0.2500 g of selected representative carbon sample to 500 mL Milli-Q water with 50 mM Na$_2$CO$_3$/NaHCO$_3$ buffer, and then the pH of the mixture was adjusted to 7.00±0.05. The reaction was initiated by adding H$_2$O$_2$. After that the reactors were shaken in an orbital shaker at room temperature. Samples for H$_2$O$_2$ residual analysis were collected every hour during the 5-hour experiment and analyzed by the I$_3^-$ method according to Klassen et al. (1994) using a UV-Vis spectrometer (Agilent Tech, ON, 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 conducted for each type of carbon. Table 3.3 shows experimental conditions for the H$_2$O$_2$ decomposition kinetics tests.

After conducting the tests, the data were fitted to a kinetics reaction rate model and the reaction rate constant k was calculated. Based on results from a preliminary test (Appendix C.3), with the current GAC dose and H$_2$O$_2$ initial concentration, the GAC-H$_2$O$_2$ reaction followed
pseudo-first order kinetics as the GAC concentration was at an excess level compared to $\text{H}_2\text{O}_2$. Thus, $k$ was calculated as (Connors, 1991):

$$\frac{d[H_2O_2]}{dt} = -k[H_2O_2] \quad (3-1)$$

where $k$ is the pseudo-first order reaction rate constant, L/(mg·min).

**Table 3.3: Experimental Conditions for the $\text{H}_2\text{O}_2$ Kinetics Test in the Presence of GAC**

<table>
<thead>
<tr>
<th>GAC</th>
<th>Temperature (°C)</th>
<th>Stirring speed (RPM)</th>
<th>pH</th>
<th>Carbon dose (g)</th>
<th>Initial $\text{H}_2\text{O}_2$ conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>Room Temperature, 21±2°C</td>
<td>Moderate, around 180±10</td>
<td>7.00±0.05, buffered with 50 mM Na$_2$CO$_3$/NaHCO$_3$; adjusted by HCl</td>
<td>0.2500</td>
<td>5</td>
</tr>
<tr>
<td>ADCAT F300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HD3000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Results and Discussion

#### 3.4.1 Effect of Carbon Age on the Quenching of $\text{H}_2\text{O}_2$

Results of bench-scale $\text{H}_2\text{O}_2$ decomposition kinetics tests using GAC aged with NOM are shown in Figure 3.2 to Figure 3.7. It was hypothesized that the reactivity between GAC and $\text{H}_2\text{O}_2$ might slow down as the GAC continued to be exposed to water containing NOM, despite being essentially exhausted as measured by TOC removal. To explore this, the number of bed volumes treated to exhaustion in terms of TOC removal was first determined (1200 bed volumes), and then the GAC samples were aged for approximately 20, 30, and 40 times longer. This led to three different ageing levels of 25 000 bed volumes, 35 000 bed volumes and 45 000 bed volumes. The pseudo-first order reaction rate constant $k$ was determined as the slope of the experimental data linear regression equation and then compared among the GACs and treatments. A one-way ANOVA was applied to evaluate the impact of carbon age on the GAC performance for the quenching of $\text{H}_2\text{O}_2$. Results from the ANOVA are shown in Table 3.4.
Figure 3.2: Comparison of virgin Centaur and Centaur aged with NOM

Figure 3.3: Comparison of virgin ADCAT and ADCAT aged with NOM

Figure 3.4: Comparison of virgin GAC300 and GAC300 aged with NOM
Figure 3.5: Comparison of virgin F300 and F300 aged with NOM

Figure 3.6: Comparison of virgin HD3000 and HD3000 aged with NOM

Figure 3.7: Comparison of virgin TN5 and TN5 aged with NOM
Table 3.4: One-way ANOVA Results for the Effect of Carbon Age

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>F value</th>
<th>F critical (0.05)</th>
<th>F critical (0.01)</th>
<th>Reject or accept the null (0.01)</th>
<th>Reject or accept the null (0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>100.5659</td>
<td>6.5914</td>
<td>16.6943</td>
<td>Reject</td>
<td>Reject</td>
</tr>
<tr>
<td>ADCAT</td>
<td>5.8344</td>
<td>6.5914</td>
<td>16.6943</td>
<td>Accept</td>
<td>Accept</td>
</tr>
<tr>
<td>F300</td>
<td>7.8779</td>
<td>6.5914</td>
<td>16.6943</td>
<td>Accept</td>
<td>Reject</td>
</tr>
<tr>
<td>GAC300</td>
<td>127.5693</td>
<td>6.5914</td>
<td>16.6943</td>
<td>Reject</td>
<td>Reject</td>
</tr>
<tr>
<td>HD3000</td>
<td>13.838</td>
<td>6.5914</td>
<td>16.6943</td>
<td>Accept</td>
<td>Reject</td>
</tr>
<tr>
<td>TN5</td>
<td>4.6615</td>
<td>6.5914</td>
<td>16.6943</td>
<td>Accept</td>
<td>Accept</td>
</tr>
</tbody>
</table>

*Null hypothesis H₀: no difference among k values for virgin and various aged GACs (α =0.05 and 0.01)

According to the ANOVA results in Table 3.4, the effect of ageing on GAC performance was significant for Centaur and GAC300 with 99% statistical confidence. For HD3000 and F300 the impact is significant at the 95% significance level. Tukey’s post hoc test was then used to compute the honestly significant difference (HSD) for the ones showing “Reject” in the one-way ANOVA. Then, differences between selected two groups (virgin, 25 000 bed volumes, 35 000 bed volumes and 45 000 bed volumes) were calculated and compared to the HSD. If the difference was greater than the HSD, the difference was considered to be significant at the selected significance level. The results from Tukey’s post hoc test are shown in Table 3.5.

Table 3.5: Tukey’s Post-hoc Test Results for HSD Analysis

<table>
<thead>
<tr>
<th>GAC</th>
<th>virgin - 25000</th>
<th>virgin - 35000</th>
<th>virgin - 45000</th>
<th>25000 - 25000</th>
<th>25000 - 35000</th>
<th>25000 - 45000</th>
<th>35000 - 45000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>F300</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>GAC300</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>ADCAT</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

After calculating the honestly significance difference, most of the differences come from virgin GAC compared to aged GAC. Only Centaur GAC shows a difference among the three ageing levels at the 95% statistical significance level. All the other types of GAC did not show distinct differences after the GAC had become saturated by NOM. In other words, the degree of ageing (25 000 vs. 35 000 vs. 45 000 bed volumes) did not affect the rate of H₂O₂ reaction significantly, except for the Centaur GAC.
Overall, these data suggest that GAC rapidly loses some ability to react with H₂O₂ after being exposed to the water (within 25000 bed volumes), presumably through NOM loading, but that the rate of deterioration quickly slows and stabilizes.

### 3.4.2 Effect of the Addition of H₂O₂ during the Ageing Process

The previous tests evaluated the rate of H₂O₂ quenching by GAC as the GAC was aged through exposure to plant membrane permeate water containing NOM. It was also hypothesized that exposure to H₂O₂, in addition to NOM, would cause the GAC to age and the reaction with H₂O₂ to slow. Tests were therefore undertaken where the membrane permeate water was spiked with 4 mg/L H₂O₂, and then the GAC was aged through 25000, 35000, and 45000 bed volumes as before. The data are shown in Figure 3.8 to Figure 3.13.

**Figure 3.8: Comparison of virgin Centaur and Centaur aged with NOM+H₂O₂**

**Figure 3.9: Comparison of virgin ADCAT and ADCAT aged with NOM+H₂O₂**
Figure 3.10: Comparison of virgin F300 and F300 aged with NOM+H₂O₂

Figure 3.11: Comparison of virgin GAC300 and GAC300 aged with NOM+H₂O₂

Figure 3.12: Comparison of virgin HD3000 and HD3000 aged with NOM+H₂O₂
A Student t-test was applied to compare the pseudo first-order reaction rate constant k for GAC aged in the presence of H₂O₂ to the k value for GAC aged in the absence of H₂O₂, as shown in Table 3.6. From Table 3.6, the H₂O₂ exposure caused the k values to change by less than 46% in all cases, and usually by less than 30%. This impact may not be statistically significant, but it should be taken into consideration.

Table 3.6: Results of the Effect of H₂O₂ Addition during the Ageing Process

<table>
<thead>
<tr>
<th>GAC</th>
<th>Ageing history (bed volumes)</th>
<th>k (aged with NOM)</th>
<th>k (aged with NOM+H₂O₂)</th>
<th>P-value (Two-tail)</th>
<th>95% significance (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>25000</td>
<td>0.0013</td>
<td>0.0019 (+46.2%)</td>
<td>0.0148</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>35000</td>
<td>0.0014</td>
<td>0.0013 (-7.1%)</td>
<td>0.0367</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>45000</td>
<td>0.0016</td>
<td>0.0014 (-12.5%)</td>
<td>0.1056</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.0024</td>
<td>0.0024 (0.0%)</td>
<td>0.6985</td>
<td>N</td>
</tr>
<tr>
<td>ADCAT</td>
<td>35000</td>
<td>0.0024</td>
<td>0.0024 (0.0%)</td>
<td>1.0000</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>45000</td>
<td>0.0024</td>
<td>0.0024 (0.0%)</td>
<td>0.6985</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.0012</td>
<td>0.0014 (+16.7%)</td>
<td>0.9982</td>
<td>N</td>
</tr>
<tr>
<td>F300</td>
<td>35000</td>
<td>0.0015</td>
<td>0.0011 (-26.7%)</td>
<td>0.8887</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>45000</td>
<td>0.0013</td>
<td>0.0011 (-15.4%)</td>
<td>0.3746</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.0019</td>
<td>0.0021 (+10.5%)</td>
<td>0.8083</td>
<td>N</td>
</tr>
<tr>
<td>GAC300</td>
<td>35000</td>
<td>0.0020</td>
<td>0.0020 (0.0%)</td>
<td>1.0000</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>45000</td>
<td>0.0017</td>
<td>0.0019 (+11.8%)</td>
<td>0.1101</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.0015</td>
<td>0.0020 (+33.3%)</td>
<td>0.0565</td>
<td>N</td>
</tr>
<tr>
<td>HD3000</td>
<td>35000</td>
<td>0.0014</td>
<td>0.0017 (+21.4%)</td>
<td>0.0256</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>45000</td>
<td>0.0014</td>
<td>0.0016 (+14.3%)</td>
<td>0.3333</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>25000</td>
<td>0.0017</td>
<td>0.0020 (+17.6%)</td>
<td>0.0995</td>
<td>N</td>
</tr>
<tr>
<td>TN5</td>
<td>35000</td>
<td>0.0016</td>
<td>0.0016 (0.0%)</td>
<td>1.0000</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>45000</td>
<td>0.0014</td>
<td>0.0014 (0.0%)</td>
<td>0.8442</td>
<td>N</td>
</tr>
</tbody>
</table>

*Values in the () indicate the difference between k for GAC aged with NOM+H₂O₂ and k for GAC aged with NOM.
A two-way ANOVA was conducted to determine whether the ageing duration (i.e. 0, 25 000, 35 000, or 45 000 bed volumes) or H$_2$O$_2$ exposure (i.e. k values in the presence or absence of H$_2$O$_2$) in the ageing process dominates the impact on the GAC performance for quenching H$_2$O$_2$. The results are shown in Table 3.7.

<table>
<thead>
<tr>
<th>GAC</th>
<th>Source of variance</th>
<th>Carbon age</th>
<th>The addition of H$_2$O$_2$</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>95% significance (Yes/No)</td>
<td>95% significance (Yes/No)</td>
<td>95% significance (Yes/No)</td>
</tr>
<tr>
<td>Centaur</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>ADCAT</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>F300</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>GAC300</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>HD3000</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>TN5</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td></td>
</tr>
</tbody>
</table>

*Null hypothesis H$_0$: no difference among the groups tested

The results demonstrated that the presence of H$_2$O$_2$ had only a marginal impact on the deterioration in GAC quenching ability, relative to the impact of carbon age (i.e. exposure to natural water for longer duration). In the table, the impact of carbon age was significant for all types of GAC with 95% statistical confidence, while the impact of H$_2$O$_2$ exposure was significant for HD3000 only. On the whole, the ageing process was controlled by the exposure to natural water, presumably (but not conclusively) the NOM in the water.

### 3.4.3 Comparison of the six GACs

As shown in Table 3.2, the six types of GAC in this study are made from several types of materials, and have various physical and chemical properties. The performances of the six GACs were compared and are shown in Table 3.8. Among the six types of GAC tested, ADCAT had relatively good performance both before and after ageing, while the F300 showed the poorest performance. Interestingly, ADCAT has the poorest performance in terms of TOC removal (Figure 3.1). It is possible that this rendered ADCAT the least affected by NOM fouling as a mechanism of deterioration in H$_2$O$_2$ quenching ability.
Table 3.8: Comparison of H$_2$O$_2$ Quenching Performance among six GACs

<table>
<thead>
<tr>
<th>GAC</th>
<th>Virgin carbon</th>
<th>Average k for aged with NOM</th>
<th>Average k for aged with NOM+H$_2$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>ADCAT</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>F300</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>GAC300</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HD3000</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>TN5</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

3.4.4 Changes to GAC Element Composition and Surface Functional Groups

To better understand the changes to the GAC surface during the ageing process, samples before and after treatment were analyzed using XPS for more information on element composition and surface functional groups. To compare different elemental components among samples, the abundance of other elements were normalized to the carbon abundance on each sample, i.e., abundance of C = 1.0. Results of the elemental analysis on the GAC surface are shown in Figure 3.14. The normalized oxygen (O) component of aged GAC increased 65% to 250% compared to the virgin GAC for most of the GACs. The normalized nitrogen (N) components on aged GAC are 2-7 times of the virgin GACs. The binding of O or N with C could occupy the “free” activated space of carbon and thus result in a decrease in quenching performance. The XPS was then used in a high-resolution scanning mode to study the carbon functional groups. Spectra of virgin and aged Centaur using XPS are shown as an example in Figure 3.15 and Figure 3.16.
From Figure 3.15 and Figure 3.16, the peak due to C-C binding occurs at the binding energy of 284.6 eV. However, comparing Figure 3.16 to Figure 3.15, the C-C peak has a deflection due to other elements binding to the carbon. The shifts of the C-C peak are then analyzed and quantified for surface functional group information according to binding energy (Lee, 1993), with results shown in Table 3.9. It is observed that the ratio of unoccupied carbon (i.e., -C- and -C-C- bonding) decreased after GAC was aged with NOM for 45 000 bed volumes, while other functional groups involving carbon-oxygen binding increased for most of the GAC analyzed. According to Rey et al. (2011), the bonding of O with carbon could compete for electron-rich sites where H$_2$O$_2$ decomposition reaction mainly occurs, resulting in a decrease in the H$_2$O$_2$ decay rate.
Figure 3.15: Spectrum of High-resolution Scanning for Carbon Bonding - Virgin Centaur

Figure 3.16: Spectrum of High-resolution Scanning for Carbon Bonding - Centaur Aged with NOM at 45 000 Bed Volumes
Table 3.9: Surface Functional Groups Analysis from XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>-C- At%</th>
<th>-C-O-C At%</th>
<th>-C=C- At%</th>
<th>O-C-O or RCOR At%</th>
<th>R₂O(C=O)OR₂ At%</th>
<th>O-C=O At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur-virgin</td>
<td>54.38</td>
<td>12.8</td>
<td>7.34</td>
<td>7.31</td>
<td>9.38</td>
<td>3.94</td>
</tr>
<tr>
<td>Centaur aged with NOM 45 000 BV</td>
<td>51.10</td>
<td>20.44</td>
<td>7.18</td>
<td>10.3</td>
<td>4.12</td>
<td>3.64</td>
</tr>
<tr>
<td>F300-virgin</td>
<td>53.43</td>
<td>10.97</td>
<td>11.24</td>
<td>7.38</td>
<td>8.72</td>
<td>3.68</td>
</tr>
<tr>
<td>F300-aged with NOM 45 000 BV</td>
<td>50.75</td>
<td>20.11</td>
<td>7.48</td>
<td>10.67</td>
<td>3.46</td>
<td>3.79</td>
</tr>
<tr>
<td>GAC300-virgin</td>
<td>57.62</td>
<td>11.81</td>
<td>8.04</td>
<td>6.45</td>
<td>8.03</td>
<td>3.44</td>
</tr>
<tr>
<td>GAC300-aged with NOM 45 000 BV</td>
<td>51.96</td>
<td>18.69</td>
<td>8.06</td>
<td>10.59</td>
<td>3.95</td>
<td>3.51</td>
</tr>
<tr>
<td>ADCAT-virgin</td>
<td>60.28</td>
<td>12.11</td>
<td>5.93</td>
<td>6.94</td>
<td>6.53</td>
<td>3.35</td>
</tr>
<tr>
<td>ADCAT-aged with NOM 45 000 BV</td>
<td>56.10</td>
<td>17.71</td>
<td>6.27</td>
<td>8.73</td>
<td>4.71</td>
<td>3.03</td>
</tr>
<tr>
<td>HD3000-virgin</td>
<td>58.35</td>
<td>11.84</td>
<td>7.53</td>
<td>6.71</td>
<td>7.53</td>
<td>3.81</td>
</tr>
<tr>
<td>HD3000-aged with NOM 45 000 BV</td>
<td>59.65</td>
<td>11.72</td>
<td>9.75</td>
<td>7.31</td>
<td>5.38</td>
<td>6.19</td>
</tr>
<tr>
<td>TN5-virgin</td>
<td>62.34</td>
<td>9.15</td>
<td>9.39</td>
<td>8.04</td>
<td>5.76</td>
<td>5.33</td>
</tr>
<tr>
<td>TN5-aged with NOM 45 000 BV</td>
<td>60.92</td>
<td>12.52</td>
<td>8.69</td>
<td>10.01</td>
<td>2.3</td>
<td>5.56</td>
</tr>
</tbody>
</table>

* At% = atom percentage

3.4.5 SEM Images

SEM images for six virgin GACs and six GAC aged with NOM at 45 000 bed volumes are shown in Figure 3.17 to Figure 3.22.

![Figure 3.17: SEM images for Centaur (a) virgin Centaur (b) Centaur aged with NOM at 45 000 bed volumes](image-url)
Figure 3.18: SEM images for ADCAT (a) virgin ADCAT (b) ADCAT aged with NOM at 45 000 bed volumes

Figure 3.19: SEM images for F300 (a) virgin F300 (b) F300 aged with NOM at 45 000 bed volumes

Figure 3.20: SEM images for GAC300 (a) virgin GAC300 (b) GAC300 aged with NOM at 45 000 bed volumes
The virgin GACs appeared to have more disordered surfaces, with a clear porous structure, while the surface of aged GACs were more flat. The hypothesis in this study would be that NOM fouling created a film on the GAC surface, resulting in the blockage of some active sites. The observation of film forming on GAC surface after ageing was also reported in Yu et al. (2009). However, this hypothesis lacks additional evidence.

### 3.5 Summary and Conclusion

Factors that may influence GAC performance for quenching H$_2$O$_2$, including carbon age and the addition of H$_2$O$_2$ during the ageing process, were studied. Six types of GAC were aged and evaluated by H$_2$O$_2$ decomposition kinetics tests, XPS analysis and SEM imaging.

The H$_2$O$_2$ decomposition rate decreased when GAC was aged both by membrane permeate water (containing NOM), as well as when the same water was spiked with 4 mg/L of H$_2$O$_2$. Interestingly, the addition of H$_2$O$_2$ had only a small to negligible impact on GAC
performance compared to exposure to the water (containing NOM) only. Furthermore, the amount of ageing (25 000 vs. 35 000 vs. 45 000 bed volumes) did not have a great impact on GAC performance, but all ageing levels showed significant deterioration in performance relative to virgin GAC. This suggests that GAC performance deteriorates upon installation (within 25 000 bed volumes), but then the rate of deterioration slows considerably. Among the six types of GAC tested, ADCAT showed relatively good performance both before and after ageing, while the F300 showed the poorest performance.

XPS analysis and SEM imaging provided semi-quantitative and qualitative assessments of both virgin and aged GAC. After exposure to 45 000 bed volumes of water, F300 had the highest oxygen to carbon ratio, with the corresponding lowest k. For all aged GAC, the increase of C-O bonding is theorized to lead to a decrease in H$_2$O$_2$ quenching performance.

### 3.6 Recommendations for Future Work

This bench-scale study demonstrated the potential impact of ageing on the performance of GAC to quench H$_2$O$_2$. However, all the H$_2$O$_2$ decomposition kinetics tests were conducted at neutral pH and room temperature. Repeating this work at different pH and temperatures would be useful to be more representative of the full range of treatment plant conditions. Moreover, in this study, all types of GAC were aged with membrane permeate water from the Lorne Park Water Treatment Plant, which had a relatively low TOC. The impact of different sources and levels of NOM is still unknown and thus worthy of more investigation. In addition, all GAC in this study was received from manufacturers with the same US sieve size of 8×30. The potential influence on H$_2$O$_2$ quenching caused by particle size and its distribution should be studied as well.
3.7 REFERENCES


Calgon Carbon Corporation, 1987. Granular activated carbon used as catalyst or catalyst support.


Klassen, N.V., Marchington, D., McGowan, H.C.E., 1994. \( \text{H}_2\text{O}_2 \) determination by the \( \text{I}_3^- \) method and by \( \text{KMnO}_4 \) titration. Analytical Chemistry 66 (18), 2921-2925.


4 PILOT-SCALE STUDY FOR THE QUENCHING OF H₂O₂ USING GAC

ABSTRACT

The performance of six types of granular activated carbon (GAC) to quench H₂O₂ was evaluated by pilot-scale H₂O₂ breakthrough tests and bench-scale H₂O₂ decomposition kinetics tests. The objectives of this study were to investigate the effect of carbon ageing and H₂O₂ exposure during the ageing process on the GAC performance by pilot-scale column tests, and to validate bench-scale H₂O₂ decomposition kinetics test results as introduced in Chapter 3. The GAC samples in this study were aged by exposure to a cumulative flow that was the equivalent of 25 to 45 times the treated water bed volumes required to achieve total organic carbon (TOC) saturation levels in pilot-scale columns. X-ray photoelectron spectroscopy (XPS) analysis and scanning electron microscopy (SEM) imaging were applied to understand the changes to the GAC surface characteristics.

The impact of carbon ageing was carbon-type specific. Only TN5 and Centaur showed breakthrough in the pilot-scale H₂O₂ breakthrough tests columns after 45 000 bed volumes when aged with natural water only. The presence of H₂O₂ had an impact on the deterioration in GAC quenching ability compared to exposure to natural water only, as indicated by a higher (more than 10%) H₂O₂ breakthrough in the effluents, than that of GAC aged without H₂O₂, except ADCAT. The impact of H₂O₂ exposure appeared to be stronger at the beginning of the ageing duration, but then the rate of deterioration slowed with longer ageing. The bench-scale quenching kinetics results for the GACs tested using accelerated ageing tests (as introduced in Chapter 3) may overestimate the quenching performance of GAC based on pilot-scale studies.

The normalized oxygen and nitrogen abundance on the surface of GAC from pilot-scale columns increased by 22% to 1246% compared to virgin GACs after ageing with natural water only. When H₂O₂ was applied to the water, the normalized O and N abundance showed a decrease compared to the GAC aged with natural water only.

Bench-scale H₂O₂ decomposition tests using Centaur from the Lorne Park Water Treatment Plant’s full-scale contactor (operated by down-flow) showed that the sample from the
2-year old contactor had approximately a 20% slower quenching rate compared to the one with 1-year operation. Samples of the GAC from the contactor’s top layer had the best performance, while GAC from the bottom layer had the worst.
4.1 INTRODUCTION

In Chapter 3, the effect of GAC ageing (exposure to natural water with and without H2O2) on the reaction rate with H2O2 was explored. The ageing process, however, was somewhat artificial. A small column (7.5 cm) containing GAC was exposed to a 158 mL/min flow for up to 45 000 bed volumes. The empty bed contact time (EBCT) of this process was around 0.24 minutes, while the EBCT of the full-scale GAC contactors at the Lorne Park Water Treatment Facility is 4.12 minutes. Therefore, the accelerated ageing process may not be representative of ageing of GAC in the full-scale contactors.

To provide a more realistic simulation of a full-scale GAC contactor, the work in Chapter 3 was reproduced at pilot-scale. If the pilot-scale results match the same trends as were observed in the bench-scale tests, then it would indicate that the bench-scale tests adequately simulated large-scale GAC performance for H2O2 quenching, and could be used in the future for exploring other aspects of quenching without the time and expense associated with pilot tests. A case study using GAC samples from the full-scale contactors at the Lorne Park Water Treatment Facility (Mississauga, Ontario, Canada) was also conducted to validate pilot-scale and bench-scale results.

4.2 OBJECTIVE

The main objective was to evaluate the performance of GAC for the quenching of H2O2 using pilot-scale columns. The specific objectives included the following:

(1) To evaluate the H2O2 quenching performance of six GACs (Centaur, ADCAT, F300, GAC300, HD3000 and TN5) after different levels of ageing with NOM (25 000 bed volumes and 45 000 bed volumes), and after ageing with NOM+4 mg/L H2O2.
(2) To compare the H2O2 decomposition kinetics tests results using GAC samples from pilot-scale columns with the ones using accelerated aged GAC (as introduced in Chapter 3) for validation of bench-scale tests.
(3) To study the changes of GAC surface characteristics after the ageing process (aged with NOM, and with NOM+H2O2 to 25 000 bed volumes, 45 000 bed volumes) by X-ray photoelectron spectroscopy (XPS) analysis and scanning electron microscopy (SEM) imaging.
(4) To evaluate the impact of ageing with natural water containing NOM using GAC from the
full-scale contactors and to investigate the differences in quenching performance using GAC sampled from different depths of the contactor.

4.3 Material and Methods

4.3.1 Pilot-Scale Set-up

4.3.1.1 Column design

To simulate full-scale GAC contactors, 22 pilot-scale glass columns were installed at the Lorne Park Water Treatment Facility (Mississauga, Ontario, Canada). Glass columns were selected to prevent any reaction between the GAC and the interior wall of the column. The columns were 1 inch in diameter. While this diameter is smaller than traditionally recommended for pilot filter columns (Mehta and Hawley, 1969), the GAC pilot contactors were not designed for backwash, and preliminary testing proved that the flow through the columns was completely plug flow, which are the main considerations when designing pilot filter columns for conventional media filtration. The other dimensions and the operating parameters of the pilot-scale columns were identical to the full-scale GAC contactors in the plant (Table 4.1). Four sampling ports were located along the columns to allow observation of the H₂O₂ quenching along the contactor depth (Figure 4.1). The detailed pilot column design is shown in Appendix D.3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-sectional area (m²)</td>
<td>107</td>
</tr>
<tr>
<td>Average flow rate (L/day)</td>
<td>47 500 000</td>
</tr>
<tr>
<td>Media volume (m³)</td>
<td>136.01</td>
</tr>
<tr>
<td>Media depth (m)</td>
<td>1.27</td>
</tr>
<tr>
<td>EBCT (min)</td>
<td>4.12</td>
</tr>
<tr>
<td>Approach velocity (m/hr)</td>
<td>18.36</td>
</tr>
</tbody>
</table>
4.3.1.2 Source Water and Carbon Preparation

The source water for this pilot study was ultrafiltration membrane permeate pumped from the Lorne Park Water Treatment Facility. Water quality details are shown in Table 4.2. Six types of GAC were used, as shown in Table 3.2. Representative GAC samples were obtained by the coning and quartering method (ASTM D346) and washed with Mill-Q water before use.
Table 4.2: Water Quality of Membrane Permeate

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total organic matter (mg/L)</td>
<td>2.2</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.018</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>98</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.116</td>
</tr>
</tbody>
</table>

4.3.1.3 Running Conditions

Twenty-two columns were run to investigate the ageing effect on GAC for H₂O₂ quenching. The conditions for the 22 columns are shown in Table 4.3. After being aged to the desired NOM saturation level (e.g., at 25 000 bed volumes), the top layer of GAC sample (approximately the top 2-3 cm) in each column was collected, freeze-dried and preserved for H₂O₂ decomposition tests, as described in part 4.3.2.

Table 4.3: Pilot-scale Columns Ageing Conditions

<table>
<thead>
<tr>
<th>GAC type</th>
<th>Ageing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>Aged with NOM to 25 000, 45 000 and 100 000 bed volumes, respectively (in duplicate); 6 columns in total</td>
</tr>
<tr>
<td>ADCAT</td>
<td>Aged with NOM+ 4 mg/L H₂O₂ to 25 000, 45 000 and 100 000 bed volumes, respectively (in duplicate); 6 columns in total</td>
</tr>
<tr>
<td>F300</td>
<td>Aged with NOM to 100 000 bed volumes (25 000 bed volumes and 45 000 bed volumes had 1 run breakthrough test respectively); 5 columns in total</td>
</tr>
<tr>
<td>GAC300</td>
<td>Aged with NOM+ 4mg/L H₂O₂ to 100 000 bed volumes (25 000 bed volumes and 45 000 bed volumes had 1 run breakthrough test respectively); 5 columns in total</td>
</tr>
<tr>
<td>HD3000</td>
<td></td>
</tr>
<tr>
<td>TN5</td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Tests to Study Quenching Performance

The ability of the GAC to quench H₂O₂ was evaluated using two tests: a pilot-scale H₂O₂ breakthrough test, and a bench-scale H₂O₂ decomposition kinetics test. The pilot-scale breakthrough test was simply a measurement of the H₂O₂ concentration profile along the depth of the column when the influent water was temporarily spiked with 10 mg/L H₂O₂, which is plausibly the maximum H₂O₂ concentration that might be applied in practice (note that the normal exposure to H₂O₂ during the GAC ageing process was 4 mg/L, as per Table 4.3). The duration of the spiking event prior to sampling H₂O₂ breakthrough was approximately 2 000 bed volumes. The bench-scale decomposition test was as described in Chapter 3, and involved
collecting GAC samples from the top of pilot column after the breakthrough tests on-site, and brought to the laboratory for batch H$_2$O$_2$ quenching kinetics tests.

H$_2$O$_2$ analysis for the breakthrough tests was performed using a K-5543 H$_2$O$_2$ test kit (CHEMetrics, Virginia, US) and a Hach DR 2700™ portable spectrophotometer. This method is based on the ferric thiocyanate method (Boltz and Howell, 1978). The minimum detection limit of this method was determined to be 0.04 mg/L. Dissolve oxygen level was measured by an YSI 550A DO meter (Yellow Springs Inc., Ohio, US).

4.4 RESULTS AND DISCUSSION

4.4.1 H$_2$O$_2$ Breakthrough Tests

H$_2$O$_2$ breakthrough tests with an initial H$_2$O$_2$ concentration of 10 mg/L were conducted at 25 000 bed volumes (Figure 4.2 and Figure 4.3) and 45 000 bed volumes (Figure 4.4 and Figure 4.5) in pilot-scale columns. The differences between GAC aged with NOM and GAC aged with NOM+H$_2$O$_2$ at all four sampling ports and effluents are shown in Table 4.4. The impact of carbon age and H$_2$O$_2$ exposure, carbon performance at different depths in the column, and comparison of six GACs would be discussed accordingly.

![Graph](image.png)

**Figure 4.2: H$_2$O$_2$ Breakthrough, GAC aged with NOM (25 000 bed volumes)**
Figure 4.3: \( \text{H}_2\text{O}_2 \) Breakthrough, GAC aged with NOM+4mg/L \( \text{H}_2\text{O}_2 \) (25 000 bed volumes)

Figure 4.4: \( \text{H}_2\text{O}_2 \) Breakthrough, GAC aged with NOM (45 000 bed volumes)

Figure 4.5: \( \text{H}_2\text{O}_2 \) Breakthrough, GAC aged with NOM+4mg/L \( \text{H}_2\text{O}_2 \) (45 000 bed volumes)
Table 4.4: H$_2$O$_2$ Difference (mg/L) between GAC Aged with/without H$_2$O$_2$

<table>
<thead>
<tr>
<th>Ageing history</th>
<th>Column depth (cm)</th>
<th>Difference of H$_2$O$_2$ residual conc. for GAC aged with/without H$_2$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Centaur</td>
<td>ADCAT</td>
</tr>
<tr>
<td>25000 bed volumes</td>
<td>25</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>-0.56</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>0.23</td>
</tr>
<tr>
<td>45000 bed volumes</td>
<td>25</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>-0.27</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td><strong>0.16</strong></td>
</tr>
</tbody>
</table>

*Difference = H$_2$O$_2$ concentration for GAC aged with NOM and H$_2$O$_2$ – H$_2$O$_2$ concentration for GAC aged with NOM at selected depth.

The impact of carbon age on the performance of GAC was studied by comparing the effluent H$_2$O$_2$ breakthrough at 25 000 bed volumes with 45 000 bed volumes, when aged with natural water only. Comparing Figure 4.2 with Figure 4.4, Centaur showed a 5.1% higher effluent breakthrough at 45 000 bed volumes, while F300 and HD3000 showed better performance (i.e. no breakthrough), compared to that of 25 000 bed volumes. ADCAT and GAC300 showed good performance to quench H$_2$O$_2$ to the level below detection limit (0.15 mg/L) at both 25 000 bed volumes and 45 000 bed volumes. TN5 showed similar breakthrough under both circumstances. Therefore, after NOM saturation on GAC, the impact of carbon age on GAC is relatively slight.

When the pilot columns were aged by natural water that also contained 4 mg/L of H$_2$O$_2$, the performance deteriorated relative to ageing in the presence of water without the H$_2$O$_2$. From Table 4.4, GAC aged with H$_2$O$_2$ during the ageing process showed a higher (more than 10%) H$_2$O$_2$ breakthrough at all depths, than that of GAC aged without H$_2$O$_2$, for both 25 000 and 45 000 bed volumes. The impact of H$_2$O$_2$ exposure appeared to be stronger at the beginning of the ageing (25 000 bed volumes), with the effect of H$_2$O$_2$ exposure diminishing at 45 000 bed volumes.

It would be interesting to compare the impact of H$_2$O$_2$ to the impact of NOM fouling on the GAC ageing process, however, the experimental design did not allow this comparison to be made explicitly. Instead, case study examples could be used from the data shown in Figures 4.2 to 4.5 to semi-quantitatively compare the importance of H$_2$O$_2$ to NOM. For example, when using
the GAC300 data from Figures 4.2 and 4.3, if it were a design goal to reduce the H$_2$O$_2$ concentration to 2 mg/L, then it would take 60 cm of GAC depth to achieve the treatment goal at 25,000 bed volumes when the GAC300 was aged with natural water only, while it would take 80 cm (20 cm more GAC) when aged with H$_2$O$_2$ present in the water. This suggests that the presence of H$_2$O$_2$ in the water that is flowing through the GAC contactor has a measurable, but perhaps not overwhelming impact on the required bed depth to treat the water. Further research is required in this area.

The overall performance (i.e. effluent H$_2$O$_2$ concentration) of each GAC is ranked in Table 4.5. Catalytic ADCAT had the most stable performance under all circumstances, while the coconut-based TN5 showed overall poorest performance for the quenching of H$_2$O$_2$.

Table 4.5: Ranking of GAC Performance for the Quenching of H$_2$O$_2$

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Centaur</th>
<th>ADCAT</th>
<th>F300</th>
<th>GAC300</th>
<th>HD300</th>
<th>TN5</th>
</tr>
</thead>
<tbody>
<tr>
<td>25,000 bed volumes with NOM</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>25,000 bed volumes with NOM+H$_2$O$_2$</td>
<td>2</td>
<td>1</td>
<td>6</td>
<td>4</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>45,000 bed volumes with NOM</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>45,000 bed volumes with NOM+H$_2$O$_2$</td>
<td>3</td>
<td>1</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

*Same ranking indicates same effluent concentration for comparison. Rank “1” also indicates no breakthrough detected.

4.4.2 Validation of Bench-scale H$_2$O$_2$ Decomposition Kinetics Tests

Bench-scale H$_2$O$_2$ decomposition kinetics tests (introduced in Chapter 3) were reproduced with GAC samples collected from pilot-scale columns. Results from the tests were compared to the ones in Chapter 3 and shown in Table 4.6. The number in the parenthesis shows the percentage difference between the k value for GAC from pilot-scale columns (Chapter 4) and the k value from the accelerated ageing GAC test of Chapter 3.
According to Table 4.6, the k values for pilot-scale GAC samples were 25%-65% smaller than the ones obtained by using the accelerated ageing test GAC described in Chapter 3, suggesting that the H₂O₂ quenching process at pilot scale was significantly slower than predicted when using the bench-scale batch tests. A Student’s t-test (Table 4.7) indicated that these differences were almost all significant at the 95% level when comparing the pilot-scale versus bench-scale test results for GAC aged with NOM and H₂O₂, but that only 5 out of 12 tests where the GAC was aged only with NOM were significantly different at the 95% level (although, as per Table 4.6, the average trend was universal). This suggests that the difference between the pilot-scale and bench-scale tests is greater when ageing occurs by both NOM and H₂O₂.

### Table 4.6: Comparison of Pilot-scale GAC and Accelerated Ageing Test GAC

<table>
<thead>
<tr>
<th>GAC</th>
<th>Average k for pilot-scale GAC</th>
<th>Average k for accelerated ageing test GAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25000 bed volumes 45000 bed volumes</td>
<td>25000 bed volumes 45000 bed volumes</td>
</tr>
<tr>
<td></td>
<td>NOM NOM+H₂O₂ NOM NOM+H₂O₂</td>
<td>NOM NOM+H₂O₂ NOM NOM+H₂O₂</td>
</tr>
<tr>
<td>Centaur</td>
<td>0.0009 0.001 (-30.8%) 0.0007 0.0007 (-50.0%)</td>
<td>0.0013 0.0019 0.0016 0.0014</td>
</tr>
<tr>
<td>ADCAT</td>
<td>0.0014 0.0013 0.0011 0.0013 (-41.7%) 0.0013 (-45.8%)</td>
<td>0.0024 0.0024 0.0024 0.0024</td>
</tr>
<tr>
<td>F300</td>
<td>0.0008 0.0006 0.0008 0.0005 (-33.3%) 0.0006 (-38.5%) 0.0005 (-45.8%)</td>
<td>0.0012 0.0014 0.0013 0.0011</td>
</tr>
<tr>
<td>GAC300</td>
<td>0.0013 0.0009 0.0012 0.0009 (-31.6%) 0.0011 (-37.1%) 0.0010 (-29.4%) 0.0009 (-52.6%)</td>
<td>0.0019 0.0021 0.0017 0.0019</td>
</tr>
<tr>
<td>HD3000</td>
<td>0.0011 0.0007 0.0010 0.0005 (-26.7%) 0.0006 (-65.0%) 0.0008 (-28.6%) 0.0005 (-68.8%)</td>
<td>0.0015 0.002 0.0014 0.0016</td>
</tr>
<tr>
<td>TN5</td>
<td>0.0008 0.0007 0.0008 0.0005 (-52.9%) 0.0007 (-65.0%) 0.0005 (-42.9%) 0.0004 (-64.3%)</td>
<td>0.0017 0.002 0.0014 0.0014</td>
</tr>
</tbody>
</table>

### Table 4.7: Student t-test Results for k Values Different between Pilot-scale and Accelerated Ageing Test GAC

<table>
<thead>
<tr>
<th>GAC</th>
<th>k value different between pilot-scale and accelerated ageing test GAC (95% significance) (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25000 bed volumes 45000 bed volumes</td>
</tr>
<tr>
<td></td>
<td>NOM NOM+H₂O₂</td>
</tr>
<tr>
<td>Centaur</td>
<td>Y Y Y Y</td>
</tr>
<tr>
<td>ADCAT</td>
<td>N Y N Y</td>
</tr>
<tr>
<td>F300</td>
<td>N Y N Y</td>
</tr>
<tr>
<td>GAC300</td>
<td>Y Y Y Y</td>
</tr>
<tr>
<td>HD3000</td>
<td>N Y N Y</td>
</tr>
<tr>
<td>TN5</td>
<td>N Y Y Y</td>
</tr>
</tbody>
</table>
The ranking of quenching performance for the six GACs from the pilot-scale columns was compared to the ranking from the bench-scale tests of Chapter 3. Figure 4.6 shows the comparison using GAC aged with NOM only at both 25 000 and 45 000 bed volumes, while Figure 4.7 demonstrates results using GAC aged with NOM+H₂O₂.

**Figure 4.6: Comparison of Ranking between Pilot-scale Test and Accelerated Aged Test GAC**

(GACs aged with NOM only)

**Figure 4.7: Comparison of Ranking between Pilot-scale Test and Accelerated Aged Test GAC**

(GACs aged with NOM+H₂O₂)
According to Figure 4.6, the ranking from accelerated aged tests GAC only provided 1/4 accurate predictions compared to that of pilot-scale tests GAC when aged with natural water only. With the addition of H$_2$O$_2$ during ageing process, the accuracy of the ranking prediction was 50% (Figure 4.7). Therefore, the accelerated aged test result may not be sufficient to predict pilot-scale test results.

For the kinetics test result using pilot-scale GAC samples (Table 4.6 left side), the ADCAT performed the best after ageing in the pilot-scale column, which is consistent with the bench-scale test results of Chapter 3. In the previous TOC removal study (Figure 3.1), ADCAT had the poorest performance in terms of TOC removal, so it is plausible that this leads to a smaller fouling effect in terms of H$_2$O$_2$ quenching. For the other five types of GAC, the NOM fouling effect was relatively close.

For the impact of H$_2$O$_2$ exposure on the quenching performance of GAC samples from pilot-scale columns in H$_2$O$_2$ decomposition kinetics tests, Student t-tests were conducted to compare pilot-scale column samples aged with NOM, and with NOM+H$_2$O$_2$ (Table 4.8). Three types of GAC indicate that the H$_2$O$_2$ was significantly affecting the GAC performance with 95% confidence at 25 000 bed volumes. But at 45 000 bed volumes, only one GAC showed a significant difference with 95% confidence. This may indicate that the impact of H$_2$O$_2$ exposure may be strong at the beginning, and then becomes weaker as the ageing process continues.

<table>
<thead>
<tr>
<th>GAC</th>
<th>k value different between GAC aged with/without H$_2$O$_2$ from pilot-scale columns (95% significance) (Yes/No)</th>
<th>25000 bed volumes</th>
<th>45000 bed volumes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>ADCAT</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>F300</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>GAC300</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>HD3000</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>TN5</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
</tr>
</tbody>
</table>

4.4.3 XPS Analysis

Samples aged with NOM and with NOM+H$_2$O$_2$ were analyzed by XPS for surface element composition (Figure 4.8 and Figure 4.9) and surface functional group information (Table
to observe whether either could be correlated directly to changes in H$_2$O$_2$ quenching performance.

**Figure 4.8:** XPS Analysis for GAC Aged with NOM, and NOM+H$_2$O$_2$ (25000 bed volumes)

**Figure 4.9:** XPS Analysis for GAC Aged with NOM, and with NOM+H$_2$O$_2$ (45 000 bed volumes)

Compared to virgin GACs, the normalized oxygen and nitrogen abundance on aged GACs (i.e. aged with NOM, or NOM+H$_2$O$_2$ to 25 000 and 45 000 bed volumes) from pilot-scale
columns appeared to increase, as shown in Table 4.9, by 22% to 1246%. For the impact of H₂O₂ exposure during the ageing process, the normalized O and N abundance showed a decrease for most GACs aged with NOM+H₂O₂ compared to the ones aged with natural water only. The hypothesis in this study would be that the reaction between H₂O₂ and NOM in the presence of GAC led to the mineralization of NOM, presumably by the hydroxyl radicals generated on GAC surface. According to Huang et al. (2003b), the removal of organic pollutant, 2-CP, was increased when with both H₂O₂ and GAC, compared to with GAC only. It is likely that with less NOM adsorbed on the GAC surface during this equilibrium, compared with GAC aged without H₂O₂, the normalized O and N abundance subsequently decreased. But this hypothesis should be further explored to be able to better understand the mechanism of GAC ageing.

The analysis of surface functional groups with carbon binding is shown in Table 4.11 and Table 4.12. Compared to virgin GACs, the surface functional group containing a carbon-oxygen double bond (R₁O(C=O)OR₂) on aged GACs at 45 000 bed volumes had a sharp decrease (73%-92%), while the surface functional group containing carbon-oxygen single bond (-C-O-C or O-C-O) increased. According to Rey et al. (2011), H₂O₂ decomposition on activated carbon surfaces occurs predominantly on electron-rich sites. Therefore, a change from carbon-oxygen double bonds to single bonds could lead to a decrease in the performance of quenching H₂O₂.

<table>
<thead>
<tr>
<th>Ageing conditions</th>
<th>Centaur (%)</th>
<th>ADCAT (%)</th>
<th>F300 (%)</th>
<th>GAC300 (%)</th>
<th>HD300 (%)</th>
<th>TN5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with NOM 25 000 BVs</td>
<td>161 O 1507 N 105 O 410 N</td>
<td>202 O 989 N 67 O 279 N</td>
<td>194 O 1246 N 243 O 616 N</td>
<td>145 O 1031 N 132 O 520 N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with NOM+H₂O₂ 25 000 BVs</td>
<td>221 O 1158 N 519 O 862 N</td>
<td>152 O 1012 N 190 O 534 N</td>
<td>166 O 908 N 307 O 805 N</td>
<td>178 O 1008 N 338 O 997 N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>with NOM 45 000 BVs</td>
<td>192 O 815 N 61 O 483 N</td>
<td>166 O 908 N 23 O 415 N</td>
<td>166 O 908 N 307 O 805 N</td>
<td>143 O 707 N 22 O 556 N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.10: Surface Functional Group Analysis from XPS (25 000 bed volumes)

<table>
<thead>
<tr>
<th>GAC type</th>
<th>-C-</th>
<th>-C-O-C</th>
<th>-C-C*</th>
<th>O-C-O or RCOR</th>
<th>O-C=O</th>
<th>dummy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
</tr>
<tr>
<td>Centaur-NOM</td>
<td>55.9</td>
<td>16.3</td>
<td>11.9</td>
<td>9.1</td>
<td>4.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Centaur-NOM+H_2O</td>
<td>53.1</td>
<td>19.6</td>
<td>11.0</td>
<td>8.4</td>
<td>4.4</td>
<td>3.6</td>
</tr>
<tr>
<td>ADCAT-NOM</td>
<td>65.9</td>
<td>9.7</td>
<td>10.8</td>
<td>8.7</td>
<td>3.5</td>
<td>1.9</td>
</tr>
<tr>
<td>ADCAT-NOM+H_2O</td>
<td>67.0</td>
<td>6.8</td>
<td>10.9</td>
<td>7.6</td>
<td>3.0</td>
<td>4.7</td>
</tr>
<tr>
<td>F300-NOM</td>
<td>63.1</td>
<td>8.2</td>
<td>11.1</td>
<td>12.8</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>F300-NOM+H_2O</td>
<td>62.9</td>
<td>8.3</td>
<td>12.4</td>
<td>9.4</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>GAC300-NOM</td>
<td>57.9</td>
<td>11.9</td>
<td>13.2</td>
<td>11.6</td>
<td>0.8</td>
<td>4.6</td>
</tr>
<tr>
<td>GAC300-NOM+H_2O</td>
<td>62.0</td>
<td>10.6</td>
<td>10.6</td>
<td>7.3</td>
<td>6.3</td>
<td>3.1</td>
</tr>
<tr>
<td>HD3000-NOM</td>
<td>61.2</td>
<td>9.8</td>
<td>11.4</td>
<td>11.8</td>
<td>1.4</td>
<td>4.4</td>
</tr>
<tr>
<td>HD3000-NOM+H_2O</td>
<td>62.2</td>
<td>10.4</td>
<td>11.0</td>
<td>7.9</td>
<td>2.7</td>
<td>5.8</td>
</tr>
<tr>
<td>TN5-NOM</td>
<td>64.6</td>
<td>8.9</td>
<td>12.2</td>
<td>9.1</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>TN5-NOM+H_2O</td>
<td>62.5</td>
<td>9.4</td>
<td>12.3</td>
<td>9.2</td>
<td>1.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>

*At% = atom percentage; dummy indicates the corresponding binding energy cannot be defined as specific known surface functional group.

Table 4.11: Surface Functional Group Analysis from XPS (45 000 bed volumes)

<table>
<thead>
<tr>
<th>GAC type</th>
<th>-C-</th>
<th>-C-C*</th>
<th>-C-O-C</th>
<th>O-C-O or RCOR</th>
<th>O-C=O</th>
<th>R(O(C=O))OR_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
</tr>
<tr>
<td>Centaur-NOM</td>
<td>57.1</td>
<td>9.2</td>
<td>16.3</td>
<td>13.1</td>
<td>3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Centaur-NOM+H_2O</td>
<td>56.3</td>
<td>9.4</td>
<td>15.4</td>
<td>14.3</td>
<td>3.3</td>
<td>1.4</td>
</tr>
<tr>
<td>ADCAT-NOM</td>
<td>54.3</td>
<td>11.9</td>
<td>14.9</td>
<td>13.6</td>
<td>3.6</td>
<td>1.8</td>
</tr>
<tr>
<td>ADCAT-NOM+ H_2O</td>
<td>57.1</td>
<td>4.9</td>
<td>16.2</td>
<td>15.3</td>
<td>5.9</td>
<td>0.5</td>
</tr>
<tr>
<td>F300-NOM</td>
<td>48.9</td>
<td>12.7</td>
<td>15.1</td>
<td>17.1</td>
<td>4.1</td>
<td>2.2</td>
</tr>
<tr>
<td>F300-NOM+ H_2O</td>
<td>58.6</td>
<td>11.2</td>
<td>11.8</td>
<td>12.6</td>
<td>4.4</td>
<td>1.4</td>
</tr>
<tr>
<td>G300-NOM</td>
<td>48.1</td>
<td>10.2</td>
<td>16.7</td>
<td>19.1</td>
<td>4.5</td>
<td>1.5</td>
</tr>
<tr>
<td>G300-NOM+ H_2O</td>
<td>57.2</td>
<td>10.4</td>
<td>12.8</td>
<td>13.9</td>
<td>4.0</td>
<td>1.6</td>
</tr>
<tr>
<td>HD3000-NOM</td>
<td>55.6</td>
<td>7.6</td>
<td>14.9</td>
<td>17.2</td>
<td>3.5</td>
<td>1.1</td>
</tr>
<tr>
<td>HD3000-NOM+ H_2O</td>
<td>59.5</td>
<td>8.9</td>
<td>13.0</td>
<td>12.8</td>
<td>3.9</td>
<td>2.0</td>
</tr>
<tr>
<td>TN5-NOM</td>
<td>56.0</td>
<td>8.4</td>
<td>14.5</td>
<td>17.2</td>
<td>3.2</td>
<td>0.7</td>
</tr>
<tr>
<td>TN5-NOM+ H_2O</td>
<td>56.4</td>
<td>7.2</td>
<td>17.5</td>
<td>14.7</td>
<td>2.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*At% = atom percentage

4.4.4 SEM Imaging

SEM images for six GACs aged with NOM, and with NOM+H_2O at 45 000 bed volumes, are shown in Figure 4.10 to Figure 4.15.
Figure 4.10: SEM images for Centaur (a) aged with NOM (b) aged with NOM+ H$_2$O$_2$ at 45 000 bed volumes

Figure 4.11: SEM images for ADCAT (a) aged with NOM (b) aged with NOM+ H$_2$O$_2$ at 45 000 bed volumes

Figure 4.12: SEM images for F300 (a) aged with NOM (b) aged with NOM+ H$_2$O$_2$ at 45 000 bed volumes
Figure 4.13: SEM images for GAC300 (a) aged with NOM (b) aged with NOM+ H$_2$O$_2$ at 45,000 bed volumes

Figure 4.14: SEM images for HD3000 (a) aged with NOM (b) aged with NOM+ H$_2$O$_2$ at 45,000 bed volumes

Figure 4.15: SEM images for TN5 (a) aged with NOM (b) aged with NOM+ H$_2$O$_2$ at 45,000 bed volumes
The surfaces of the aged GACs tended to be flat, either with or without H₂O₂ exposure during the ageing process. As discussed in Chapter 3, the hypothesis in this study would be that NOM fouling created a film on the GAC surface, resulting in the blockage of some active sites. The observation of film forming on GAC surface after ageing was also reported by Yu et al. (2009).

### 4.4.5 Study of Full-scale GAC Samples

#### 4.4.5.1 Introduction

An additional study using GAC samples from two full-scale GAC contactors (GACCs) at the Lorne Park Water Treatment Facility was conducted. The two GACCs, with Centaur as media (US sieve size 8 × 30) have operated for either approximately 1 year (GACC2, equivalent to 130 000 bed volumes of water treated) or 2 years (GACC8, equivalent to 260 000 bed volumes of water treated). Both GACC2 and GACC8 were exposed to H₂O₂ on only one occasion, from September 2012 to November 2012 (approximately 32 000 bed volumes), with an average of 4 mg/L H₂O₂ during that period.

The specific objectives of this study included the following:

1. To evaluate the impact of ageing with natural water containing NOM by comparing GAC samples from the 1-year old and 2-year old full-scale GAC contactors.
2. To investigate the differences of H₂O₂ quenching performance at various depths along the contactor by comparing GAC samples from the bottom, middle and top layers.
3. To study the effect of influent H₂O₂ concentrations (4 mg/L and 10 mg/L) in the full-scale quenching process by conducting H₂O₂ decomposition kinetics tests using GAC samples after an H₂O₂ breakthrough test (4 mg/L and 10 mg/L).
4. To explore the surface characteristics of full-scale GAC samples (bottom, middle and top layer samples from GACC2) by X-ray photoelectron spectroscopy (XPS) analysis and scanning electron microscopy (SEM) imaging.

#### 4.4.5.2 Methods and Materials

GAC samples were collected from GACC2 and GACC8 by a PVC sampling corer. The 0 cm, 60 cm and 128 cm positions on the core were marked and approximately 5-10 grams of GAC around the marked line were collected for bench-scale H₂O₂ decomposition kinetics tests,
representing the top, middle and bottom layers, respectively. The rest of the samples were then transferred into the pilot columns with the same stratification. To be specific, samples from the top 1/3, middle 1/3 and bottom 1/3 of the core were unpacked from the core to clean sampling bags, and labeled as top, middle and bottom layer. Then samples were packed into the pilot-scale column with the same stratification. The samples for bench-scale kinetics tests were dried and preserved as introduced in Chapter 3. H$_2$O$_2$ decomposition kinetics tests were conducted to evaluate the quenching performance of the full-scale GAC samples.

4.4.5.3 H$_2$O$_2$ decomposition kinetics tests: Results and Discussion

Bench-scale H$_2$O$_2$ decomposition kinetics test results using samples from 1-year old and 2-year old contactors are shown in Figure 4.16. Samples from GACC2 at different depths were studied as well, as shown in Figure 4.17. The results showed that the sample from the 2-year old contactor had approximately a 20% slower quenching speed compared to the one with 1-year operation, but that the difference is not statistically significant at 95% confidence level according to a student t-test. This result was consistent with the kinetics tests results using accelerated aged tests GAC and pilot-scale tests GAC, that the performance of GAC tends to stabilize with longer ageing.

For the samples from three depths of one contactor, the GAC from the bottom of the contactor was less reactive with H$_2$O$_2$. This may be related to the dissolved oxygen (DO) level which was 32% higher at the bottom of the contactor than at the top. It is plausible that the H$_2$O$_2$ quenching in the top part of the contactor was generating DO that was washed downward toward the bottom and then reacted with the GAC lower down to cause ageing. Therefore, the hypothesis in this study would be that the oxygen was significantly affecting the GAC ageing process.
An additional batch test was performed to observe the \( \text{H}_2\text{O}_2 \) quenching rate of the two Centaur GACs (GACC2 and GACC8) compared to virgin Centaur GAC, while the GAC samples were collected after \( \text{H}_2\text{O}_2 \) breakthrough tests in pilot-scale columns, with either 4 mg/L or 10 mg/L initial \( \text{H}_2\text{O}_2 \) concentration for the breakthrough tests (i.e., with exposure to 4 mg/L or 10 mg/L \( \text{H}_2\text{O}_2 \) for approximately 2 000 bed volumes). Results are shown in Figure 4.18.
According to Figure 4.18, the aged Centaur GACs yielded reaction rate coefficients that were approximately 50% smaller than virgin Centaur, however, the difference between GACC2 and GACC8 activated carbon was not notable. This result is consistent with the previous observations whereby GAC quenching performance deteriorates rapid initially, but thereafter tends to stabilize. In this case, the GAC that had been in service for 1 year and 2 years exhibited similar H$_2$O$_2$ quenching speeds. Compared to Figure 4.16, which was from samples without H$_2$O$_2$ breakthrough tests, the k values for both contactors have approximately 30% decrease. Therefore, the H$_2$O$_2$ running in the breakthrough tests could have destroyed the GAC surface to a certain level to affect its performance for further quenching of H$_2$O$_2$. The potential reaction between NOM and H$_2$O$_2$ will need to be elucidated.

4.4.5.4 XPS Analysis for Full-scale GAC Samples

GAC samples from the 1-year old and 2-year old full-scale contactors were analyzed using XPS, with results shown in Figure 4.19. For each contactor, samples were collected from 3 depths. Compared to virgin Centaur, the full-scale samples had distinctly higher normalized oxygen and nitrogen abundance. Samples from the 1-year old contactor had a slightly lower oxygen to carbon ratio than those from the 2-year old contactor. The data show that exposure to water leads to more O and N on the surface, which we believe is correlated to a lower reactivity
with H₂O₂. The bottom layers have higher normalized oxygen and nitrogen abundance, and also showed lower reactivity with H₂O₂ (Figure 4.17), which supports this theory.

![XPS Analysis for Full-scale GAC Samples at Different Depths](image)

**Figure 4.19: XPS Analysis for Full-scale GAC Samples at Different Depths**

4.4.5.5 SEM imaging of Full-Scale Samples

SEM images for GAC samples from top, middle, and bottom layer of GACC2 are shown in Figure 4.20. The surfaces of the full-scale GACs were much flatter than virgin Centaur. When comparing the samples from the top layer to the bottom and middle layers, the surface Centaur showed a less disordered structure.

![SEM image](image)
4.5 SUMMARY AND CONCLUSION

The effects of carbon age and H₂O₂ exposure during the ageing process were studied with a pilot-scale column installation at the Lorne Park Water Treatment Facility. To evaluate the performance of six GACs for the quenching of H₂O₂, pilot-scale H₂O₂ breakthrough tests in the columns were conducted.

The carbon ageing observed in the pilot column tests was not as fast as observed when using the bench-scale accelerated aged tests in Chapter 3. Even after 45 000 bed volumes of ageing with natural water, only TN5 and Centaur showed breakthrough in the pilot-scale H₂O₂ breakthrough tests.
The pilot column tests demonstrated that the performance of GAC for quenching H$_2$O$_2$ was affected by the presence of H$_2$O$_2$ more than would be predicted by the bench tests in Chapter 3, where the presence of H$_2$O$_2$ had only a negligible effect on ageing, as indicated by higher H$_2$O$_2$ breakthrough at all depths (except for the ADCAT). This disagreement may be due to the much smaller EBCT in the accelerated aged tests (0.24 min) compared to the EBCT of the pilot-scale columns (4.12 min), which shortened the time of GAC exposure to dissolved oxygen which is believed to impair the GAC’s ability to quench H$_2$O$_2$. In the H$_2$O$_2$ breakthrough tests, ADCAT had the best performance in both ageing conditions while the coconut-based TN5 showed overall poorest performance for the quenching of H$_2$O$_2$. The outstanding performance of ADCAT was correlated to the lowest TOC removal (reported in Chapter 3), suggesting that the ADCAT may have experienced less NOM fouling than the other GACs, leading to its superior H$_2$O$_2$ quenching.

To validate the bench-scale tests as introduced in Chapter 3, batch H$_2$O$_2$ decomposition kinetics tests using GAC taken from the pilot-scale columns were repeated. The k values for the GAC samples collected from the pilot columns were 25%-65% smaller than the ones obtained by using the accelerated aged GAC. Thus, the bench-scale kinetics results from accelerated aged tests may overestimate the performance of GAC from pilot-scale samples, especially with H$_2$O$_2$ exposure during the ageing process.

To study the changes of GAC surface characteristics after the ageing process, XPS analysis and SEM imaging were applied. Both the normalized oxygen and nitrogen abundance increased by 22% to 1246% compared to virgin GACs after ageing with natural water only (no H$_2$O$_2$). When H$_2$O$_2$ was applied to the water ageing the GAC, the normalized O and N abundance showed a decrease compared to the GAC aged with natural water only. This is believed to relate to a reaction between H$_2$O$_2$ and NOM in the presence of GAC, which might lead to the mineralization of NOM on GAC surface, presumably by the hydroxyl radicals generated. With less NOM adsorbed during this equilibrium, compared to the GAC aged without H$_2$O$_2$, the normalized O and N abundance was reduced. In addition, a change from carbon-oxygen double bonds to single bonds on the surface functional groups was observed, which is believed to lead to a decrease of the H$_2$O$_2$ quenching rate because H$_2$O$_2$ decomposition on activated carbon surfaces occurs predominantly on electron-rich sites.
A case study using Centaur GAC from the Lorne Park plant’s full-scale contactors was conducted to evaluate the impact of ageing with natural water containing NOM and to investigate the differences of quenching performance using GAC samples from different depths of the contactor by $\text{H}_2\text{O}_2$ decomposition kinetics tests. Results showed that the sample from the 2-year old contactor had approximately a 20% slower quenching speed compared to the one with 1-year operation, but the difference was not statistically significant at the 95% confidence level. This result is consistent with the kinetics tests results using accelerated aged tests GAC and pilot-scale tests GAC, where the performance of GAC tends to stabilize with longer ageing. $\text{H}_2\text{O}_2$ decomposition kinetics tests using samples from different depths showed that the top layer of GAC had the best performance, while the bottom had the worst. This may be related to the dissolved oxygen level, that the DO level on the bottom was 32% higher than that on the surface. It is plausible that the oxygen was significantly affecting the GAC ageing process.

4.6 **RECOMMENDATIONS FOR FUTURE WORK**

In this chapter, $\text{H}_2\text{O}_2$ addition during the GAC ageing process was demonstrated to have a strong impact on the deterioration of $\text{H}_2\text{O}_2$ quenching performance, as demonstrated by pilot-scale $\text{H}_2\text{O}_2$ breakthrough tests. The XPS analysis showed that the normalized oxygen and nitrogen abundance on the GAC surface decreased when aged with $\text{H}_2\text{O}_2$ exposure compared to that without $\text{H}_2\text{O}_2$. A reduction in surface abundance of O and N would tend to indicate a more reactive GAC for $\text{H}_2\text{O}_2$, which conflicts with the observed results. This contradiction should be further explored to be able to better understand the mechanism of GAC ageing. In the full-scale study, the bottom GAC was less reactive with $\text{H}_2\text{O}_2$ compared to GAC on the surface. The hypothesis in this study was that the oxygen could be a more significant factor for the GAC ageing process than exposure to NOM or $\text{H}_2\text{O}_2$. Experiments for a direct comparison of the magnitude of oxygen, $\text{H}_2\text{O}_2$ and NOM on GAC ageing for $\text{H}_2\text{O}_2$ quenching could be conducted. In addition, this study included only one water. To generalize the findings concerning the reaction among $\text{H}_2\text{O}_2$, GAC and NOM, and allow industry professionals to be able to predict, with much more confidence, how best to design and operate a GAC system for quenching $\text{H}_2\text{O}_2$ following advanced oxidation treatment, ageing with different types of natural waters could be conducted.
4.7 REFERENCES


5 MODELLING HYDROGEN PEROXIDE QUENCHING WITH GRANULAR ACTIVATED CARBON

ABSTRACT

A mathematical model to predict the performance of GAC to quench H$_2$O$_2$ residuals after the UV/H$_2$O$_2$ process was investigated. A CSTR-in-series model was develop to predict effluent H$_2$O$_2$ concentrations as a function of influent H$_2$O$_2$, EBCT, treated bed volumes, and an empirical reaction kinetic parameter. Experimental data from specific sites would be required for the application of the model since parameters used to develop the model were site-specific.

In the CSTR-in-series model the reaction kinetic parameter was correlated to bed volumes treated, the H$_2$O$_2$ exposure during the ageing process and the interaction of these two items, using the bench-scale H$_2$O$_2$ decomposition kinetics tests results for accelerated aged tests GAC. The model was tested by the pilot-scale H$_2$O$_2$ breakthrough tests results at 25 000 bed volumes and 45 000 bed volumes. The CSTR-in-series model provided a 50% accurate prediction for H$_2$O$_2$ breakthrough at four sampling ports and effluents (95% significance level, paired t-tests) for all the ageing conditions evaluated. When aged in the absence of H$_2$O$_2$, approximately 70% (95% significance level, paired t-tests) of the model predictions for H$_2$O$_2$ breakthrough at four sampling ports and effluents were not significantly different from the pilot-scale breakthrough tests results.
5.1 Introduction

A utility that uses GAC contactors to quench H$_2$O$_2$ would want to track their remaining service life to be able to anticipate the need for replacement of the GAC. At present, there are no tools available to guide this decision. It would be helpful if a model could be developed that could accept easily-obtained data, such as from actual full-scale performance or laboratory tests using GAC sampled from the contactor, and then predict the future performance of the contactor. In this chapter, a relatively simplistic model is developed using the bench-scale data obtained in Chapter 3 and is then validated against H$_2$O$_2$ data obtained from the pilot-scale columns.

5.2 Objectives

The objectives of this work were:
(1) To develop a GAC contactor model that would predict effluent H$_2$O$_2$ concentrations as a function of (a) influent H$_2$O$_2$, (b) EBCT, (c) time (treated bed volumes), and (d) empirical reaction kinetic parameter(s), using bench-scale H$_2$O$_2$ decomposition tests data from accelerated aged tests GAC.
(2) To determine the accuracy of the model by comparison to pilot-scale H$_2$O$_2$ breakthrough data (25 000 bed volumes and 45 000 bed volumes).

5.3 Model Description and Parameters

A continuous stirred tank reactor (CSTR)-in-series model was used to predict the H$_2$O$_2$ effluent breakthrough profile, based on the configuration of the pilot-scale columns described in Chapter 4. The column configuration is shown in Figure 5.1.

Assuming perfect mixing and only chemical reaction occurring in each CSTR in series, the basic CSTR model can be expressed as (Schmidt, 2004):

\[ \text{In} - \text{Out} + \text{Production} = \text{Accumulation} \]  

(5-1)
For the H₂O₂ decomposition in the reactor, a pseudo first order kinetics law is applied (Connors, 1991):

\[
\frac{d[H_2O_2]}{dt} = -k [H_2O_2] \tag{5-2}
\]

where \( k \) is the pseudo first order reaction rate constant, in L/(mg·min)

For the first CSTR (with depth \( h \)), by integration of Equation 2:

\[
[H_2O_2]_{\text{eff}} = \frac{[H_2O_2]_0}{1 + k \cdot t} = \frac{[H_2O_2]_0}{1 + k \cdot \frac{h}{H} \cdot \text{EBCT} \cdot \varepsilon} \tag{5-3}
\]

where \([H_2O_2]_0\) is the initial influent H₂O₂ concentration, mg/L;
k is the pseudo first-order reaction rate constant, L/(mg·min);
EBCT is the empty bed contact time of the full-scale GAC bed (4.12 min for this study according to the GAC contactor at the Lorne Park Water Treatment Facility);
ε is the porosity of the GAC (0.62 is chosen as per Clements and Haarhoff, 2004);
H is the total length of the GAC column, 128 cm in this study;
h is the height of one CSTR, 5 cm is chosen in this study.

For the $i^{th}$ CSTR, where $i \leq n$, the total number of conceptual CSTRs in series, the influent concentration of $\text{H}_2\text{O}_2$ is the effluent concentration of the $i-1^{th}$ CSTR. By iteration, for the $n^{th}$ CSTR,

$$n = \frac{H}{h}$$ (5-4)

$$[\text{H}_2\text{O}_2]_{\text{eff}} = \frac{[\text{H}_2\text{O}_2]_{\text{eff}}^{n-1}}{1+k\cdot t} = \frac{[\text{H}_2\text{O}_2]_{\text{eff}}^{n-1}}{1+k\cdot \text{EBCT} \cdot \varepsilon \cdot \frac{h}{H}}$$ (5-5)

Using Equations 5-2, 5-3, 5-4, 5-5, the effluent $\text{H}_2\text{O}_2$ concentration of the $n^{th}$ CSTR is solved as:

$$[\text{H}_2\text{O}_2]_n = \frac{[\text{H}_2\text{O}_2]_0}{(1+k\cdot \text{EBCT} \cdot \varepsilon \cdot \frac{h}{H})^n}$$ (5-6)

The Centaur GAC is taken as an example to show the development of the model. The $\text{H}_2\text{O}_2$ decomposition kinetic rate constant $k$ can be correlated to bed volumes of water treated and $\text{H}_2\text{O}_2$ exposure during the ageing process by a multiple linear regression model:

$$k = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1 X_2 + \varepsilon_0$$ (5-7)

where $k$ is the reaction rate constant, L/(mg·min);
$X_1$ is the bed volumes of water treated;
$X_2$ is the concentration of $\text{H}_2\text{O}_2$ exposure during ageing process, mg/L;
$X_1 X_2$ is the interaction of two factors (i.e. bed volumes of water treated and $\text{H}_2\text{O}_2$ exposure)
$\varepsilon_0$ is the standard error of the regression.
According to Chapter 3, k values from the H₂O₂ decomposition tests using accelerated aged test GAC appeared to decrease rapidly at the beginning and then tended to stabilize. To model this trend, the X₁, X₂ and X₁X₂ parameters in Equation 5-7 are transformed to \( e^{-\frac{X_1}{10000}} \), \( e^{-X_2} \) and \( e^{-\frac{X_1}{10000}-X_2} \). Then, multiple regression fitting was run in Excel. The results are shown in Table 5.1.

<table>
<thead>
<tr>
<th>Parameters in the regression</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e^{-\frac{X_1}{10000}} ), ( e^{-X_2} ) and ( e^{-\frac{X_1}{10000}-X_2} )</td>
<td>0.8592</td>
</tr>
<tr>
<td>( e^{-\frac{X_1}{10000}} ), ( e^{-X_2} )</td>
<td>0.8587</td>
</tr>
<tr>
<td>( e^{-X_2} ) and ( e^{-\frac{X_1}{10000}-X_2} )</td>
<td>0.4245</td>
</tr>
<tr>
<td>( e^{-\frac{X_1}{10000}} ) and ( e^{-\frac{X_1}{10000}-X_2} )</td>
<td>0.8590</td>
</tr>
</tbody>
</table>

With the highest \( R^2 \), regression with all three items is chosen. The regression equation is calculated to be:

\[
k = 0.001483373 + 0.001101402e^{-\frac{X_1}{10000}} - 1.79001 \times 10^{-5}e^{-X_2} - 5.28548 \\
\times 10^{-5}e^{-\frac{X_1}{10000}-X_2} + 0.000208978
\]

Equation 5-8 is plotted in Figure 5.2, with k values from bench-scale H₂O₂ decomposition tests using accelerated aged GAC shown in the graph.

![Figure 5.2: Comparison of k Value between Model prediction and Experimental Data](image-url)
To model the quenching process in a column, the k values from the prediction are proportionally adjusted, i.e., increased volumetrically by multiplying by the ratio of GAC percentage in a column and GAC in a batch reactor, according to Bach and Semiat (2011). The calculation for Centaur is shown in Table 5.2.

<table>
<thead>
<tr>
<th>GAC</th>
<th>Batch reactor</th>
<th>Pilot-scale column</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k value</td>
<td>volume percentage of GAC</td>
</tr>
<tr>
<td>Centaur</td>
<td>0.00264</td>
<td>0.094%</td>
</tr>
</tbody>
</table>

*volume percentage of GAC in a batch reactor = volume of GAC/volume of solution; volume percentage of GAC in a pilot-scale column = (mass of GAC/apparent density of GAC)/(mass of GAC/bed density)

With Equation 5-5 and 5-7, for Centaur, the effluent concentration of H$_2$O$_2$ is a function of sampling port depth, column depth, EBCT, bed volumes treated, initial concentration of H$_2$O$_2$ in the breakthrough test and the concentration of H$_2$O$_2$ exposure, as shown in Equation 5-9.

$$[H_2O_2]_n = f(C_0, h, EBCT, X_1, X_2, H)$$  \hspace{1cm} (5-9)

The development of the model for the other five types of GAC is shown in Appendix D.2.

### 5.4 Modeling Results and Discussion

#### 5.4.1 Prediction of H$_2$O$_2$ Effluent Breakthrough

H$_2$O$_2$ effluent breakthrough results for each type of GAC were predicted using the CSTR-in-series model. In the model, the H$_2$O$_2$ exposure during the ageing process was 4 mg/L, the same as the average influent concentration at the Lorne Park Water Treatment Facility. The influent H$_2$O$_2$ was 10mg/L.

Results for 25 000 bed volumes and 45 000 bed volumes are shown from Figure 5.3 to Figure 5.8. The prediction from the CSTR-in-series model was compared to pilot-scale breakthrough data at different depths. In all the figures, the dashed line indicates the model prediction.
Figure 5.3: Model Prediction and Pilot-scale Results-Centaur

(a): aged with NOM-25 000 bed volumes; (b): aged with NOM+H2O2 - 25 000 bed volumes; (c): aged with NOM - 45 000 bed volumes; (d): aged with NOM+H2O2 - 45 000 bed volumes.
Figure 5.4: Model Prediction and Pilot-scale Results - ADCAT

(a): aged with NOM - 25000 bed volumes; (b): aged with NOM+H2O2 - 25000 bed volumes; (c): aged with NOM - 45000 bed volumes; (d): aged with NOM+H2O2 - 45000 bed volumes.

(a)
Figure 5.5: Model Prediction and Pilot-scale Results - F300

(a): aged with NOM-25 000 bed volumes; (b): aged with NOM+H₂O₂-25 000 bed volumes; (c): aged with NOM-45 000 bed volumes; (d): aged with NOM+H₂O₂-45 000 bed volumes.
Figure 5.6: Model Prediction and Pilot-scale Results - GAC300

(a): aged with NOM-25 000 bed volumes; (b): aged with NOM+H₂O₂-25 000 bed volumes; (c): aged with NOM - 45 000 bed volumes; (d): aged with NOM+H₂O₂-45 000 bed volumes.

(a) HD3000 with NOM-prediction-25 000 bed volumes
(b) HD3000 with NOM-pilot-scale-25 000 bed volumes
Figure 5.7: Model Prediction and Pilot-scale Results -HD3000

(a): aged with NOM-25 000 bed volumes; (b): aged with NOM+H2O2 - 25 000 bed volumes; (c): aged with NOM - 45 000 bed volumes; (d): aged with NOM+H2O2 - 45 000 bed volumes.
Figure 5.8: Model Prediction and Pilot-scale Results - TN5

(a): aged with NOM-25 000 bed volumes; (b): aged with NOM+H2O2 - 25 000 bed volumes; (c): aged with NOM - 45 000 bed volumes; (d): aged with NOM+H2O2 - 45 000 bed volumes.
5.4.2 Evaluation of the Accuracy of the CSTR-in-Series Model

The accuracy of the CSTR-in-series model was evaluated by paired t-tests of the \( \text{H}_2\text{O}_2 \) breakthrough at five sampling depths (25 cm, 50 cm, 75 cm, 100 cm, 128 cm). The null hypothesis in the paired t-test was that no difference existed between the group of model prediction (all depths evaluated) and pilot-scale data.

The statistical difference of model prediction and pilot-scale data was analyzed with 95% significance level, and results are shown in Table 5.3.

| Table 5.3: Paired t-test Results for the Difference between Model Prediction and Pilot-scale Data |
|---------------------------------|--------|--------|--------|--------|--------|--------|--------|
| 95% significance (Y/N)         | Centaur| ADCAT  | F300   | GAC300 | HD3000 | TN5    |        |
| 25 000 bed volumes with NOM     | N      | N      | N      | N      | Y      | Y      |        |
| 25 000 bed volumes with NOM+H\(_2\text{O}_2\) | N      | N      | Y      | Y      | Y      | Y      |        |
| 45 000 bed volumes with NOM     | Y      | N      | N      | N      | N      | Y      |        |
| 45 000 bed volumes with NOM+H\(_2\text{O}_2\) | Y      | N      | Y      | N      | Y      | Y      |        |

According to Table 5.3, 50% of the predictions by the CSTR-in-series model were not statistically different from the pilot-scale breakthrough results (at the 95% significant level) under all ageing conditions. For ageing with natural water only, approximately 70% of the model predictions were not significantly different from pilot-scale breakthrough tests results. But with the presence of \( \text{H}_2\text{O}_2 \) during to ageing process, the accuracy dropped to around 33% and the predicted \( \text{H}_2\text{O}_2 \) effluent breakthrough was 1%-11% smaller than the pilot-scale results. Moreover, there are more significant model inaccuracies for the shallower depths in both ageing conditions by observation. Therefore, the CSTR-in-series model would be more suitable for \( \text{H}_2\text{O}_2 \) breakthrough prediction when the GAC contactor is not exposed to \( \text{H}_2\text{O}_2 \) during daily operation, but the observed inaccuracy for the shallower depths should also be considered.
5.5 SUMMARY AND CONCLUSION

In this chapter, a CSTR-in-series model was proposed to predict the H$_2$O$_2$ effluent breakthrough profile in column tests. The model is based on the correlation of a pseudo-first order kinetic rate constant $k$ to two major affecting factors in this study, the carbon age (bed volumes treated) and H$_2$O$_2$ exposure during the ageing process. $k$ values from bench-scale H$_2$O$_2$ decomposition kinetics tests using accelerated aged GAC (as introduced in Chapter 3) were applied to develop the CSTR-in-series model. The H$_2$O$_2$ breakthrough test results from pilot-scale tests at 25 000 bed volumes and 45 000 bed volumes were used to validate the model. From the comparison, 50% of the model predictions for H$_2$O$_2$ breakthrough at five sampling locations were not significantly different from the pilot-scale results (95% significance level, paired t-tests). The model prediction for H$_2$O$_2$ breakthrough at five sampling locations had approximately 70% accuracy when GACs were aged without H$_2$O$_2$.

5.6 RECOMMENDATIONS FOR FUTURE WORK

The model described in this chapter did not provide a very good prediction of H$_2$O$_2$ concentrations across the depth of the pilot columns. As discussed in Chapter 4, dissolved oxygen may be a significant factor affecting the GAC ageing process: a phenomenon that was not accurately modeled in the batch tests that generated the data for the models. To improve the model accuracy, methods should be developed to account for the impact of oxygen generated from H$_2$O$_2$ decomposition on ageing (i.e. the $k$ values) of the GAC.
5.7 REFERENCES


6 SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 SUMMARY AND CONCLUSION

The performance of six types of GAC to quench H₂O₂ was evaluated by bench-scale H₂O₂ decomposition kinetics tests using GAC from accelerated aged tests, and pilot-scale H₂O₂ breakthrough tests in columns. A CSTR-in-series model was proposed to predict the H₂O₂ breakthrough in the GAC contactor. The effects of carbon ageing and H₂O₂ exposure during the ageing process on the GAC performance were investigated. XPS analysis and SEM imaging were applied to understand the changes to the GAC surface characteristics.

In the bench-scale H₂O₂ decomposition kinetics tests using accelerated aged tests GAC, the addition of H₂O₂ had only a small to negligible impact on GAC performance compared to exposure to the water (containing NOM) only. Furthermore, the amount of ageing (25 000 vs. 35 000 vs. 45 000 bed volumes) did not have a great impact on GAC performance, but all ageing levels showed significant deterioration in performance relative to virgin GAC. This suggests that GAC performance rapidly deteriorates upon installation (within 25 000 bed volumes), but then the rate of deterioration tends to stabilize.

The pilot column tests demonstrated that the performance of GAC for quenching H₂O₂ was more affected by the presence of H₂O₂ than would be predicted by the bench tests in Chapter 3, where the presence of H₂O₂ had only a negligible effect on ageing, as indicated by a higher (more than 10%) H₂O₂ breakthrough in the effluents, than that of GAC aged without H₂O₂, except ADCAT. But whether the impact of H₂O₂ addition is more significant than the impact of NOM fouling is not elucidated. The carbon ageing observed in the pilot column tests was not as fast as observed when using the bench-scale accelerated aged tests in Chapter 3. Even after 45 000 bed volumes of ageing with natural water, only TN5 and Centaur showed breakthrough in the pilot-scale H₂O₂ breakthrough tests. It is possible that the presence of dissolved oxygen generated by the H₂O₂ caused more significant ageing in the pilot columns than would be experienced in the batch test, where much of the generated DO could have escaped from the system.

XPS analysis and SEM imaging showed that the increase of normalized oxygen and nitrogen abundances on the surface of aged GAC compared to virgin GACs, which was presumed to be caused by NOM saturation, could result in the decrease of the H₂O₂ quenching
performance by the GAC. When GAC was aged with H₂O₂, the normalized O and N abundance showed a decrease compared to the GAC aged with natural water only. In this study, the hypothesis would be that a reaction between H₂O₂ and NOM in the presence of GAC occurred, which might lead to the mineralization of NOM on GAC surface, presumably by the hydroxyl radicals generated.

An additional study about H₂O₂ decomposition using samples from different depths of the full-scale contactor at the Lorne Park Water Treatment Facility showed an interesting result, that the bottom GAC was less reactive than the top layer of GAC. It is plausible that the oxygen was significantly affecting the GAC ageing process, since the dissolved oxygen level on the bottom was 32% higher than that on the top layer.

A CSTR-in-series model was developed to predict effluent H₂O₂ concentrations as a function of influent H₂O₂, EBCT, treated bed volumes, and an empirical reaction kinetic parameter. The model was tested using the H₂O₂ breakthrough tests results from pilot-scale tests at 25 000 bed volumes and 45 000 bed volumes. 50% of the model predictions for H₂O₂ breakthrough at five sampling locations were not significantly different from the pilot-scale results (95% significance level, paired t-tests). When GAC was aged without H₂O₂, the model prediction for H₂O₂ breakthrough at five sampling locations could provide approximately 70% accurate prediction.

6.2 RECOMMENDATIONS FOR FUTURE WORK

The recommendations from this thesis are to:

- Reproduce bench-scale H₂O₂ decomposition kinetics tests at different pH and temperatures to be more representative of the full range of treatment plant conditions.
- Reproduce the ageing process with different types of natural waters.
- Conduct experiments for a direct comparison of the magnitude of oxygen, H₂O₂ and NOM on GAC ageing for H₂O₂ quenching.
- Conduct mesh size sieving to study the potential influence on H₂O₂ quenching caused by particle size and its distribution.
- Correlate the DO level with reaction rate constant to improve the accuracy of the CSTR-in-series model.
A: EXPERIMENTAL PROTOCOLS
A.1 CARBON PROPERTY DETERMINATION

A.1.1 Apparent density measurement
Set-up and method were obtained from Smith (2011), Appendix B.5.1 APPARENT DENSITY.

A.1.2 Iodine number test
Set-up and method were obtained from Smith (2011), Appendix B.6.1 IODINE NUMBER TEST.

A.1.3 Trace capacity number test
Set-up and method were obtained from Smith (2011), Appendix B.6.2 TRACE CAPACITY NUMBER.

A.2 TOTAL ORGANIC CARBON ANALYSIS
Method was obtained from Smith (2011), Appendix B.7 TOTAL ORGANIC CARBON.

A.3 CARBON DRYING
Method was obtained from Andrews (1990), Appendix I.4 Procedure for Freeze-Drying Granular Activated Carbon.

REFERENCE

B: PRELIMINARY TESTS
B.1 MODELING WITH AdDESIGNSTM

B.1.1 Introduction

This part aims to discuss the suitability of applying AdDesignSTM software to predict the capacity of a specific GAC (Calgon Centaur Carbon) for quenching H2O2. The porous and surface diffusion model (PSDM) incorporated in the software is selected to develop an H2O2 effluent concentration profile.

The detailed description of the PSDM can be found elsewhere (Zhang 2012). The model assumes a constant flow rate with local adsorption equilibrium existing between the solute and adsorbent particles. A linear driving force is used to describe the bulk phase mass flux at the exterior surface of the adsorbent, while the intraparticle mass flux is expressed by surface diffusion and pore diffusion. The Freundlich isotherm equation is used to model single compound adsorption equilibrium (Crittenden et al., 1987). Similar to the HSDM model, this model does not consider liquid-phase mass transfer resistance when estimating surface diffusion coefficients (Chakravort et al., 1974).

To determine the suitability of using this model, the first problem is whether the model can take into account both the chemical redox reaction and adsorption processes between H2O2 and GAC. The initial assumption made in this work is that the chemical oxidation rate of H2O2 adsorbed to the surface of GAC is fast relative to the adsorption rate. This allows the oxidation reaction to be ignored when modeling the removal of H2O2 from the water phase when using the AdDesignSTM software. The assumption will be tested subsequently in this work. Another assumption that is inherent in the AdDesignSTM software, that liquid-mass transfer resistance is negligible, can be proven by either calculating the surface Biot number, i.e. the ratio of the liquid-phase mass transfer rate to the intraparticle mass transfer rate (Hand et al., 1984), or conducting a completely mixed batch reactor (CMBR) experiment as described by Hand et al. (1983). The proof will be shown and discussed in section B.1.3. In addition, AdDesignSTM requires the input of Freundlich isotherm parameters. While adsorption isotherm tests can be performed using H2O2, since the removal of H2O2 is due to a combination of adsorption and chemical reaction on the surface of the activated carbon, the appropriateness of using a Freundlich adsorption isotherm model is unknown, and will be explored as part of this research.
B.1.2 Parameters Required in AdDesignSTM

Input for modeling by user

<table>
<thead>
<tr>
<th>Table B.1: User Input for Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water properties</strong></td>
</tr>
<tr>
<td><strong>Fixed bed properties</strong></td>
</tr>
<tr>
<td><strong>Adsorbent properties</strong></td>
</tr>
<tr>
<td><strong>Component properties</strong></td>
</tr>
<tr>
<td><strong>Freundlich isotherm parameters</strong></td>
</tr>
<tr>
<td><strong>Kinetics</strong></td>
</tr>
<tr>
<td><strong>Fouling of GAC</strong></td>
</tr>
</tbody>
</table>

*NB: Normal boiling point

H₂O₂ properties were generated from the StEPPSTM software database, which is incorporated in the AdDesignSTM software, or selected from reference (Nikitin et al., 1995). Details about input and calculated parameters are shown as following.

Parameters calculated by software

<table>
<thead>
<tr>
<th>Table B.2: Parameters Calculated by Software</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorbent dimensionless groups</strong></td>
</tr>
<tr>
<td><strong>Fixed bed properties</strong></td>
</tr>
<tr>
<td><strong>Kinetics parameters</strong></td>
</tr>
</tbody>
</table>

The correlation or equations to estimate or calculate parameters are shown in B.1.6.

B.1.3 Testing Model Assumptions

The Biot number, which is defined as the ratio of the liquid-phase mass transfer rate to the intraparticle mass transfer rate (Hand et al., 1984), was calculated to check the accuracy of the assumption that the liquid-phase mass transfer resistance is negligible. If Biot number increases, the liquid-phase mass transfer becomes faster and thus intraparticle mass transfer rate dominates the adsorption rate (Hand et al., 1984). AdDesignSTM was used to calculate the Biot number based on the input activated carbon and adsorbate parameters. From results shown in B.1.6, the surface Biot number of 63.9 is assumed to be great enough (more than 30) to conclude
that intraparticle mass transfer controls the adsorption process and therefore the liquid-phase mass transfer resistance can be neglected, as assumed (Hand et al., 1984). Thus, CMBR experiments will not be conducted.

In the AdDesignS™ software, the surface and pore diffusion flux ratio (SPDFR) and Freundlich parameters are input by the user. Therefore, these variables may have impact on the modeling results. To elucidate the effects, the PSDM were run with different values of parameters to compare the corresponding results.

According to Sontheimer et al. (1988), the mean SPDFR value is 6.58 with a 95% confidence interval of 4.60 to 8.56. The true SPDFR value for H₂O₂ on activated carbon is unknown, so a sensitivity analysis was performed by calculating the predicted bed volumes of water treated to 50% breakthrough while assuming SPDFR values over the entire expected range of 5 to 8. The results, shown Table B.3 (along with several other parameters describing breakthrough characteristics) indicate that the breakthrough of H₂O₂ is not supposed to be significantly affected by the assumed value of the SPDFR. As such, an average value of 6.58 (Hand et al., 1996) is used for the rest of the modeling if not mentioned specifically.

<table>
<thead>
<tr>
<th>SPDFR</th>
<th>5.0</th>
<th>6.0</th>
<th>6.58</th>
<th>7.0</th>
<th>7.25</th>
<th>7.3</th>
<th>7.5</th>
<th>7.95</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% breakthrough/days</td>
<td>68.18</td>
<td>67.83</td>
<td>67.80</td>
<td>67.79</td>
<td>/</td>
<td>67.76</td>
<td>67.75</td>
<td>67.71</td>
<td>/</td>
</tr>
<tr>
<td>BVT/(×10⁴ m³/m³)</td>
<td>2.03</td>
<td>2.03</td>
<td>2.04</td>
<td>2.05</td>
<td>/</td>
<td>2.06</td>
<td>2.06</td>
<td>2.07</td>
<td>/</td>
</tr>
</tbody>
</table>

*“/” indicates that the model returned an error when using the corresponding SPDFR

For Freundlich parameters, k and 1/n were doubled or half reduced to evaluate the influence of Freundlich parameter on the corresponding H₂O₂ effluent profiles. The results, shown in Table B.4 (along with several other parameters describing breakthrough characteristics) indicate that the model is sensitive to k and 1/n. By either increasing the k or 1/n respectively can both expand the bed volume treated and extend the 50% breakthrough days. But the length of mass transfer zone does not follow a distinct trend.
Table B.4: PSDM Results with Different Values of Freundlich Parameter

<table>
<thead>
<tr>
<th>k[(mg/g) * (L/mg)^1/n]</th>
<th>228.13</th>
<th>228.13</th>
<th>228.13</th>
<th>456.26</th>
<th>114.065</th>
<th>456.26</th>
<th>456.26</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/n</td>
<td>0.1342</td>
<td>0.2684</td>
<td>0.067</td>
<td>0.1342</td>
<td>0.1342</td>
<td>0.067</td>
<td>0.2684</td>
</tr>
<tr>
<td>50% breakthrough/days</td>
<td>66.75</td>
<td>90.41</td>
<td>57.01</td>
<td>133</td>
<td>/</td>
<td>114</td>
<td>181</td>
</tr>
<tr>
<td>BVT x 10^4 (m^3/m^3)</td>
<td>2.04</td>
<td>2.81</td>
<td>1.7</td>
<td>4.05</td>
<td>/</td>
<td>3.4</td>
<td>NA</td>
</tr>
</tbody>
</table>

*/// indicates that the model returned an error with the input values (may be out of the software operating range); data in bold is original Freundlich parameter values from Peel Region Report; to reduce software error, the value of SPDFR used here is 5.00

B.1.4 Results from the PSDM

AdDesignSTM estimates the diffusion coefficients by using correlations reported in other literature (Sontheimer et al., 1988). Details about these correlations and a discussion about parameter sensitivity are shown in Section B.1.6. By running the PSDM with and without the presence of NOM respectively, the predicted \( \text{H}_2\text{O}_2 \) effluent concentration profiles were generated. With the absence of NOM, as shown in Figure B.1, 50 % breakthrough occurred around 18100 bed volumes treated.

![Figure B.1: PSDM Result with Organic Free Water](image)

Peel Region conducted a pilot test to study the quenching of \( \text{H}_2\text{O}_2 \) by Centaur carbon in order to evaluate the service life of GAC. In the pilot test, 10mg/L \( \text{H}_2\text{O}_2 \) was injected into a GAC contactor and sampled at different time. In the result from this pilot test, as shown in Figure B.1-
2, the flow rate Q and EBCT is 2.59 L/min and 5.38min, respectively. Then the bed volume treated in this test can be calculated as (çezen and Aktaç 2011)

\[
\text{Bed Volume Treated (m}^3/\text{m}^3) = \frac{\text{Volume of water treated } V (m^3)}{\text{Flow rate Q (L/min)} \times \text{EBCT(min)} \times 10^{-3} m^3/L}
\] (B-1)

According to Figure B.1, it shows that less than 50% breakthrough was found within all the operating time, which demonstrated that 50% breakthrough occurs at more than 14870 bed volume treated.

In the model prediction, bed volume treated at 50% breakthrough is 18100, which is in the range of pilot scale results. However, the water matrix in the pilot test is not real UV/H\(_2\)O\(_2\) effluent, but membrane permeated water from another pilot site instead, which may contains more NOM and leads to the uncertainty of whether the two results are comparable.

In order to improve the accuracy of the PSDM in simulating the prediction of the H\(_2\)O\(_2\) effluent concentration profile, scenario with the presence of NOM was studied by operating the PSDM model with NOM fouling mode. Comparison of modeling results with and without the
presence of NOM is shown in Figure B.3. The \( \text{H}_2\text{O}_2 \) breakthrough occurs earlier with NOM fouling.

![Figure B.3: Effect of NOM Fouling on GAC](image)

Comparing with the pilot column test results in Figure B.2, the 50% breakthrough bed volumes treated predicted by PSDM is around 18000, which is also in the range of pilot scale results. Thus, the PSDM can predict the breakthrough accurately to the same magnitude level without considering the impact of NOM characteristics.

### B.1.5 Summary and Conclusions

#### Table B.5: Comparison of Pilot Scale Result and the PSDM Results

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Pilot scale</th>
<th>PSDM without NOM</th>
<th>PSDM with NOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% breakthrough/bed volume treated</td>
<td>&gt; 14870</td>
<td>18100</td>
<td>18000</td>
</tr>
</tbody>
</table>

From the results shown in Table B.5, it can be concluded that the PSDM incorporated in the AdDesignS\(^\text{TM}\) can accurately predict the \( \text{H}_2\text{O}_2 \) effluent concentration profiles to the same magnitude level. However, it is still not confident enough to draw a conclusion that the software can be used for the design of GAC contactor alone. One reason is the lacking of real matrix fouling parameters concerning specific compound and GAC used in this research. Another reason is that the AdDesignS\(^\text{TM}\) only takes into account the adsorption process, rather than both chemical reaction and adsorption in an \( \text{H}_2\text{O}_2 \)-quenching system using GAC. To better evaluate the feasibility of using AdDesignS\(^\text{TM}\) to design a GAC contactor for the quenching of \( \text{H}_2\text{O}_2 \)
residual, bench scale and pilot scale experiments, which are introduced in the next chapter, will be conducted for comparison and validation of the modeling results.

**B.1.6 Supplementary Information**

B.1.6.1 Information on Input and Output in AdDesignS™

(1) H₂O₂ properties:

![Figure B.4: H₂O₂ Properties](image)

*Solubility: since H₂O₂ is miscible in water, the solubility value is set using the maximum value available in the software. According to the identical results of different solubility trials, the solubility value input will not have effect on the H₂O₂ effluent concentration profiles developed by the software.*

(2) Fixed bed properties:

![Figure B.5: Fixed Bed Properties](image)
(3) Carbon properties:

![Figure B.6: Carbon Properties](image1.png)

(4) Polanyi parameters:

![Figure B.7: Polanyi Parameters Calculated by AdDesignS™](image2.png)

(5) Dimensionless groups

![Figure B.8: Dimensionless Groups Calculated by AdDesignS™](image3.png)
B.1.6.2 Calculation or Estimation of Parameters

(1) Dimensionless parameters calculated by AdDesignSTM can be expressed as: (Hand et al.,1984; Crittenden et al., 1987)

Stanton number

\[ St = \frac{k_f \tau (1 - \varepsilon)}{Re \phi} \]  \hspace{1cm} (B-2)

Surface solute distribution parameter

\[ Dg_s = \frac{\rho_a q_e (1 - \varepsilon)}{\varepsilon C_0} \]  \hspace{1cm} (B-3)

Pore solute distribution parameter

\[ Dg_p = \frac{\varepsilon_p (1 - \varepsilon)}{\varepsilon} \]  \hspace{1cm} (B-4)

Pore biot number

\[ Bi_p = \frac{St}{Ed_p} = \frac{k_f R(1 - \varepsilon)}{\varepsilon Dg_p D_p \phi} \]  \hspace{1cm} (B-5)
Surface biot number

\[ Bi_s = \frac{St}{Ed_s} = \frac{k_f R (1 - \epsilon)}{\epsilon D_g D_s \Phi} \]  \hspace{1cm} (B-6)

Pore diffusivity modulus

\[ Ed_p = \frac{D_p D_g p \tau}{R^2} \]  \hspace{1cm} (B-7)

Surface diffusivity modulus

\[ Ed_s = \frac{D_s D_g s \tau}{R^2} \]  \hspace{1cm} (B-8)

Where

- \( C_0 \) is initial influent concentration (kg/m\(^3\))
- \( D_p \) is pore diffusivity based on pore void fraction (m\(^2\)/s)
- \( D_s \) is surface diffusion coefficient (m\(^2\)/s)
- \( k_f \) is film transfer diffusion coefficient (m/s)
- \( q_e \) is adsorbent phase concentration in equilibrium with influent concentration (kg/kg)
- \( R \) is adsorbent radius (m)
- \( \epsilon \) is fraction of volumetric space in reactor unoccupied by adsorbent, or void fraction
- \( \epsilon_p \) is fraction of volumetric space in adsorbent phase unoccupied by adsorbent on the pore volume fraction
- \( \Phi \) is sphericity of adsorbent
- \( \rho_a \) is adsorbent density which includes pore volume (kg/m\(^3\))
- \( \tau \) is fluid residence time in packed bed, or packed bed contact time (s)

(2) Film transfer diffusion coefficient \( k_f \) (m/s)

It is estimated using the Gnielinski correlation (Sontheimer et al. 1988):

\[ k_f = \frac{[1 + 1.5 (1 - \epsilon)] D_L}{d_p} \left[ 2 + 0.644 \, Re^{1/2} \, Sc^{1/3} \right] \]  \hspace{1cm} (B-9)

Where

- \( d_p \) is the adsorbent particle diameter (m)
\(D_L\) is the adsorbate liquid phase diffusivity \(\text{(m}^2/\text{s})\)

\(\varepsilon\) is fraction of volumetric space in reactor unoccupied by adsorbent, or void fraction

\(\text{Re}\) is Reynolds numbers, calculated as \(\text{Re} = \frac{\rho_d \nu}{\mu}\); \(\rho\) is the liquid phase density \(\text{(kg/m}^3)\), \(\nu\) is liquid phase interstitial velocity \(\text{(m/s)}\), and \(\mu\) is the liquid phase viscosity \(\text{(kg/m/s)}\)

\(\text{Sc}\) is Schmidt numbers, calculated as \(\text{Sc} = \frac{\mu}{\rho D_L}\)

This correlation is valid when \(\text{Re}\) is within 1 to 100 and \(\text{Sc}\) is between 0.6 and 10000 (Sontheimer et al. 1988) and is generally used for activated carbon fixed-bed adsorbers.

### (3) Liquid diffusivity \(\text{(cm}^2/\text{s})\)

The correlation given by Hayduk and Laudie (1974) can be quoted as:

\[
D_L = \frac{13.26 \times 10^{-5}}{\mu^{1.4} V_b^{0.589}} \tag{B-10}
\]

Where

- \(V_b\) is the molar volume of the chemical at the normal boiling point \(\text{(cm}^3/\text{mol)}\)
- \(\mu\) is the liquid phase viscosity \(\text{(kg/m/s)}\)

This correlation was developed based on three previous correlations, from direct experimental result from the diffusivities of vinyl chloride monomer in water and used on 89 compounds to evaluate the accuracy.

### (4) Pore Diffusion Coefficient \(D_p\)

The pore diffusion coefficient is related to the adsorbate diffusivity and the intra-particle physical properties. The calculation can be expressed as (Sontheimer et al. 1988):

\[
D_p = \frac{D_L}{\tau_p} \tag{B-11}
\]

Where

- \(D_L\) is the adsorbate liquid phase diffusivity \(\text{(cm}^2/\text{s})\)
- \(\tau_p\) is the adsorbent tortuosity

This is a rough estimation of pore diffusion coefficient. It assumes that the diffusion of the adsorbate molecules in the pore liquid can describe the transport resistance within the adsorbent grain (Sontheimer et al., 1988).
(5) Surface Diffusion Coefficient \( D_s \)
The surface diffusion coefficient is obtained by relating the surface diffusion flux to the pore diffusion flux by a correlation factor, the surface to pore diffusion flux ratio (SPDFR). The surface diffusion coefficient can be calculated as (Sontheimer et al. 1988):

\[
D_s = \frac{D_L \varepsilon_p C_0}{\tau_p \rho a q_o} \times SPDFR
\]  \hspace{1cm} (B-12)

Where
- \( C_0 \) is initial influent concentration (mg/L)
- \( D_L \) is the adsorbate liquid phase diffusivity (cm\(^2\)/s)
- \( D_s \) is surface diffusion coefficient (cm\(^2\)/s)
- \( q_o \) is solid phase concentration in equilibrium with \( C_0 \) for a single-solute equilibrium (mg/g)
- \( \rho_a \) is adsorbent density which includes pore volume (g/L)
- \( \varepsilon_p \) is fraction of volumetric space in reactor unoccupied by adsorbent, or void fraction
- \( \tau_p \) is the adsorbent tortuosity

SPDFR is input by user. Tortuosity can be determined by user or using a correlation provided by software. When fouling is considered, pore diffusion is the predominant intraparticle mass transfer mechanism and the correlation of time and tortuosity is used. When \( t < 70 \) days, \( \tau_p = 1.0 \). When \( t \geq 70 \) days, \( \tau_p \) is estimated as (Sontheimer et al. 1988):

\[
\tau_p = 0.334 + 9.518 \times 10^{-3} \times t
\]  \hspace{1cm} (B-13)

Where
- \( t \) is the operating time (day)

(6) Discussion on the Sensitivity of Film Transfer Diffusion Coefficient \( k_f \) and Surface Diffusion Coefficient \( D_s \)

To determine the parameter sensitivity to PSDM, changes of effluent profile for \( \pm 25\% \) \( k_f \), \( D_s \), respectively and simultaneously are modeled in AdDesignSTM. Results are shown in Figure B.10.
According to the study of parameter sensitivity, it can be found that the changes of $k_f$ or $D_s$ did not have strong impact on the effluent concentration profiles. Thus, it is acceptable to estimate the coefficients by correlation.

B.1.6.3 Effect of Freundlich Parameter

![Figure B.10: H$_2$O$_2$ effluent concentration profiles with different $k_f$ and $D_s$](image)

(* Model cannot run if $k_f$ and $D_s$ are increased or decreased simultaneously)

Figure B.11: Bed Volume Treated at 50% Breakthrough with Different Freundlich Parameters
B.1.6.4 Effect of NOM Fouling

<table>
<thead>
<tr>
<th>Empirical Kinetic Constants for:</th>
<th>Rhine River, Germany, Anthropogenic Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>0.350</td>
</tr>
<tr>
<td>K2</td>
<td>6.15E-08</td>
</tr>
<tr>
<td>K3</td>
<td>0.650</td>
</tr>
<tr>
<td>K4</td>
<td>8.93E-05</td>
</tr>
</tbody>
</table>

Figure B.12: Empirical Kinetics Constants in NOM fouling Correlation

Details of empirical kinetics constants for NOM fouling in different water matrix can be found elsewhere (Jarvie et al., 2005). GAC adsorption capacity can be reduced due to the presence of background organic matter in surface and ground waters (Jarvie et al., 2005), represented by the reduction of Freundlich parameter $k$. Thus, an empirical equation was developed to describe this trend (Sontheimer et al., 1988):

$$\frac{K(t)}{K} = 0.01 \times [K1 - K2 \times t + K3 \times e^{-K4 \times t}]$$  \hspace{0.5cm} (B-14)

Where

- $K(t)$ is the Freundlich coefficient of a solute within a specific water matrix with NOM, at time $t$ of exposure to the NOM ($\mu$mol/g/[L/ $\mu$mol]$^{1/n}$)
- $t$ is the adsorber operation time (min)
- $K_i$ is the empirical kinetic constants specific to a given SOC, water matrix and GAC type ($i = 1,2,3,4$)

<table>
<thead>
<tr>
<th>Empirical Constants for:</th>
<th>Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.650</td>
</tr>
<tr>
<td>A2</td>
<td>0.350</td>
</tr>
</tbody>
</table>

Figure B.13: Empirical Constants for specific chemical group with reference of TCE

Since the empirical kinetics constants in equation 3-13 were determined using TCE, for other compounds, similar correlation of Freundlich parameter $K$ can be decided with the reference of TCE. The correlation is summarized by Jarvie et al. (2005):
Results for NOM fouling are shown in Figure B.14:

\[
\frac{K(t)}{K} = A1 \times \frac{K(t)}{K_{TCE}} + A2
\]  \hspace{1cm} (B-15)

![Figure B.14: Modeling results for NOM fouling](image-url)
B.1.7 References


B.2 INVESTIGATION OF THE GAC CAPACITY FOR QUENCHING H₂O₂

B.2.1 Pre-loading GAC with H₂O₂

H₂O₂ isotherm test was initially proposed to estimate the GAC service life for the quenching of H₂O₂ residuals after UV/H₂O₂ advanced treatment process. To evaluate the feasibility of conducting H₂O₂ isotherm test for Freundlich adsorption parameters, GAC was continuously loaded with certain amount of H₂O₂. Meanwhile, the H₂O₂ concentration at aqueous phase is measured every 24 hours to check whether the equilibrium between GAC and H₂O₂ reaches or not. If carbon stops quenching H₂O₂ at some point, then isotherm test can be conducted following loading experiment to estimate the service life of GAC using isotherm equation. If carbon can quench infinite amount of H₂O₂, then isotherm test will be replaced by H₂O₂ decomposition kinetics test.

All types of GAC were used in the preliminary test. In the test, GAC was repeatedly exposed to H₂O₂ with the same initial concentration every day. Grams of H₂O₂ quenched by per gram GAC during 24 hours time interval were recorded and cumulative H₂O₂ quenched were calculated. Figure B.15 shows the result using virgin GAC.

![Figure B.15: Cumulative H₂O₂ Quenched by Per Gram GAC](image)

As shown in the figure, the accumulated H₂O₂ quenched by per gram GAC is still increasing over five days. Thus, it is highly possible that there is no thermodynamic equilibrium between virgin GAC and H₂O₂, or such equilibrium will be difficult to reach in terms of real
application. Then it is hard or even impossible to conduct H\textsubscript{2}O\textsubscript{2} isotherm test with virgin GAC. Kinetics test for the quenching of H\textsubscript{2}O\textsubscript{2} using GAC will be conducted as substitute.

From Figure B.15, it can also be found that the amount of H\textsubscript{2}O\textsubscript{2} quenched by GAC during the 24-hour time interval is decreasing, which may because of the modification of GAC surface characteristics. The GAC surface could have some sites to be destroyed by H\textsubscript{2}O\textsubscript{2}. Therefore, the aim of the experiment was changed to find a suitable model to describe this reaction. Current catalytic reaction models cannot completely apply to this case.

The carbon repeatedly loaded with H\textsubscript{2}O\textsubscript{2} experiment was conducted with different high initial H\textsubscript{2}O\textsubscript{2} concentrations to explore the relationship between activated GAC concentration and cumulative H\textsubscript{2}O\textsubscript{2} quenched by per gram GAC.

Each type of GAC was exposed to 1000mg/L, 2000mg/L and 3000mg/L H\textsubscript{2}O\textsubscript{2} solutions respectively. In this test, the reaction between GAC and H\textsubscript{2}O\textsubscript{2} was assumed to follow second-order kinetics model:

$$ \frac{d[H_2O_2]}{dt} = -k[H_2O_2][GAC] \quad (B-16) $$

k was determined by measuring the initial reaction rate after 15 minutes' reaction. The k values from different high concentrations were found to be different.

Carbon pre-loaded with high concentrations of H\textsubscript{2}O\textsubscript{2} were then removed from H\textsubscript{2}O\textsubscript{2} solution and put in Milli-Q water for 14 days rest. After the rest, there was no H\textsubscript{2}O\textsubscript{2} washing out from carbon. In addition, the GAC performance for quenching H\textsubscript{2}O\textsubscript{2} is not recovered when exposed to new high concentration of H\textsubscript{2}O\textsubscript{2} solution.

**B.2.2 H\textsubscript{2}O\textsubscript{2} Decomposition Kinetics Pre-test**

In order to find an accurate reaction rate constant “k” for GAC capacity experiment, kinetics tests for high concentrations of H\textsubscript{2}O\textsubscript{2} decay were conducted. From test results, it is time consuming to finish one kinetics test when initial H\textsubscript{2}O\textsubscript{2} concentration is relatively high. In full-scale operation, GAC is always at an excess level compared to the concentration of H\textsubscript{2}O\textsubscript{2}. If the concentration of one reactant is much larger than the other one, the concentration of the excess reactant could be regarded as constant and then pseudo first-order kinetics model can be applied. Experiments with several low concentrations of H\textsubscript{2}O\textsubscript{2} and a fixed GAC dose were conducted. In
this set of kinetics test, 5mg/L, 10mg/L and 15mg/L were selected and the GAC dose is set to be 0.25 gram. Results are shown in Figure B.16. One-way ANOVA was conducted to compare the difference of $k$ values among three low concentrations. The ANOVA result shows a P-value of 0.422 to indicate the difference among three concentrations is not statistically significant with 95% confidence. Thus, pseudo-first order kinetics reaction law is chosen for the expression of $H_2O_2$ decomposition kinetics tests in the presence of GAC. 5mg/L $H_2O_2$ and 0.25 gram GAC dose are selected for future kinetics tests.

![Figure B.16: Kinetics Test Results for Different Low Concentrations of $H_2O_2$](image)

5mg/L: $y = 0.0017x$, $R^2 = 0.99374$
10mg/L: $y = 0.0019x$, $R^2 = 0.99816$
15mg/L: $y = 0.0017x$, $R^2 = 0.99795$
C: QA/QC
QUALITY CONTROL TEST FOR FREEZE-DRYING METHOD

In order to evaluate the impact of freeze-drying method, both virgin GAC and aged GAC were tests using samples with and without freeze-drying. k values from H$_2$O$_2$ kinetics tests are shown in Table C.1 and Table C.2.

Table C.1: Comparison between Freeze-dried and Non-freeze Dried Virgin GAC

<table>
<thead>
<tr>
<th>GAC</th>
<th>freeze dried 1</th>
<th>freeze dried 2</th>
<th>STD</th>
<th>non-freeze dried 1</th>
<th>non-freeze dried 2</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>0.0023</td>
<td>0.0029</td>
<td>0.000424</td>
<td>0.0027</td>
<td>0.0029</td>
<td>0.000141</td>
</tr>
<tr>
<td>F300</td>
<td>0.0017</td>
<td>0.0018</td>
<td>0.000071</td>
<td>0.0021</td>
<td>0.0021</td>
<td>0.000000</td>
</tr>
<tr>
<td>GAC300</td>
<td>0.0041</td>
<td>0.0042</td>
<td>0.000071</td>
<td>0.0041</td>
<td>0.0045</td>
<td>0.000283</td>
</tr>
<tr>
<td>ADCAT</td>
<td>0.0032</td>
<td>0.0028</td>
<td>0.000283</td>
<td>0.0036</td>
<td>0.0030</td>
<td>0.000424</td>
</tr>
<tr>
<td>HD3000</td>
<td>0.0031</td>
<td>0.0027</td>
<td>0.000283</td>
<td>0.0024</td>
<td>0.0025</td>
<td>0.000071</td>
</tr>
<tr>
<td>TN5</td>
<td>0.0019</td>
<td>0.0021</td>
<td>0.000141</td>
<td>0.00209</td>
<td>0.00210</td>
<td>0.000007</td>
</tr>
</tbody>
</table>

*STD = standard deviation

Table C.2: Comparison between Freeze-dried and Non-freeze Dried Aged GAC

<table>
<thead>
<tr>
<th>GAC</th>
<th>freeze dried 1</th>
<th>freeze dried 2</th>
<th>STD</th>
<th>non-freeze dried 1</th>
<th>non-freeze dried 2</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>0.0009</td>
<td>0.001</td>
<td>0.000071</td>
<td>0.0012</td>
<td>0.0013</td>
<td>0.000071</td>
</tr>
<tr>
<td>F300</td>
<td>0.0008</td>
<td>0.0006</td>
<td>0.000141</td>
<td>0.001</td>
<td>0.0009</td>
<td>0.000071</td>
</tr>
<tr>
<td>GAC300</td>
<td>0.0017</td>
<td>0.0018</td>
<td>0.000071</td>
<td>0.0017</td>
<td>0.0019</td>
<td>0.000141</td>
</tr>
<tr>
<td>ADCAT</td>
<td>0.00151</td>
<td>0.00148</td>
<td>0.000021</td>
<td>0.0015</td>
<td>0.0017</td>
<td>0.000141</td>
</tr>
<tr>
<td>HD3000</td>
<td>0.001</td>
<td>0.0009</td>
<td>0.000071</td>
<td>0.00112</td>
<td>0.00113</td>
<td>0.000007</td>
</tr>
<tr>
<td>TN5</td>
<td>0.000631</td>
<td>0.000616</td>
<td>0.000011</td>
<td>0.0010</td>
<td>0.0009</td>
<td>0.000071</td>
</tr>
</tbody>
</table>

Student t-test (two samples assuming equal variances) was conducted to calculate the P value in order to determine the significance of freeze-drying impact on the k value. 50% significance level is also selected for a non-conservative analysis since the sample size is relatively small, and the potential impact is not clear in previous studies. Results shown in Table C.3 and Table C.4 indicate that freeze-drying method shows significant impact on most of the samples tested. For further experiments, the impact should be taken into consideration.
<table>
<thead>
<tr>
<th>Carbon type</th>
<th>P-value (Two-tail)</th>
<th>95% significance (Yes/No)</th>
<th>50% significance (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>0.5918</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>ADCAT</td>
<td>0.4929</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>F300</td>
<td>0.0198</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>GAC300</td>
<td>0.5425</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>HD3000</td>
<td>0.0198</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>TN5</td>
<td>0.4227</td>
<td>N</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table C.3: Student t-test Result for Virgin GAC

<table>
<thead>
<tr>
<th>Carbon type</th>
<th>P-value (Two-tail)</th>
<th>95% significance (Yes/No)</th>
<th>50% significance (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>0.05131</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>ADCAT</td>
<td>0.4227</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>F300</td>
<td>0.1548</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>GAC300</td>
<td>0.6985</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>HD3000</td>
<td>0.0955</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>TN5</td>
<td>0.0198</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table C.4: Student t-test Result for Aged GAC
D: SUPPLEMENTARY DATA
D.1 $\text{H}_2\text{O}_2$ Decomposition Kinetics Test using GAC from Pilot-scale Columns

Samples from pilot-scale columns after 25 000 bed volumes and 45 000 bed volumes were collected for $\text{H}_2\text{O}_2$ decomposition kinetics tests. Results for six types of GAC aged with NOM, and six aged with NOM+$\text{H}_2\text{O}_2$ are shown in Figure D.1 to Figure D.4, respectively.

Figure D.1: Kinetics Test Results using GAC aged with NOM from Pilot-scale Column (25 000 bed volumes)

Figure D.2: Kinetics Test Results using GAC aged with NOM+$\text{H}_2\text{O}_2$ from Pilot-scale Column (25 000 bed volumes)
Figure D.3: Kinetics Test Results using GAC aged with NOM from Pilot-scale Column (45 000 bed volumes)

Figure D.4: Kinetics Test Results using GAC aged with NOM+H₂O₂ from Pilot-scale Column (45 000 bed volumes)
D.2 CSTR-IN-SERIES MODEL DEVELOPMENT FOR ALL TYPES OF GAC

D.2.1 Selection of Parameters for k Expression

According to the results in Chapter 3 and Chapter 4, H$_2$O$_2$ decomposition kinetics rate constant k can be correlated to bed volumes of water treated and H$_2$O$_2$ exposure during ageing process by a multiple linear regression model:

$$k = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1 X_2 + \varepsilon_0$$  \hspace{1cm} (D-1)

where, k is the reaction rate constant, L/(mg·min);
X$_1$ is the bed volumes of water treated;
X$_2$ is the concentration of H$_2$O$_2$ exposure during ageing process, mg/L;
X$_1$X$_2$ is the interaction of two factors (i.e. bed volumes of water treated and H$_2$O$_2$ exposure)
\(\varepsilon_0\) is the standard error of the regression.

k values from H$_2$O$_2$ decomposition tests using pilot-scale GAC samples appear to decrease rapidly at the beginning and then tend to be stabilized. To model this trend, the $X_1$, $X_2$ and $X_1X_2$ in equation D-1 are transformed to be $e^{-\frac{X_1}{10000}}$, $e^{-X_2}$ and $e^{-\frac{X_1}{10000}X_2}$, respectively. Then multiple regression fitting was run in Excel. Results of fitting are shown in Table D.1. With the highest $R^2$, regression with all three items is chosen for all types of GAC.

<table>
<thead>
<tr>
<th>Parameters in the regression</th>
<th>Centaur</th>
<th>ADCAT</th>
<th>F300</th>
<th>GAC300</th>
<th>HD3000</th>
<th>TN5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e^{-\frac{X_1}{10000}}$, $e^{-X_2}$ and $e^{-\frac{X_1}{10000}X_2}$</td>
<td>0.8592</td>
<td>0.8033</td>
<td>0.8148</td>
<td>0.9786</td>
<td>0.8585</td>
<td>0.2718</td>
</tr>
<tr>
<td>$e^{-\frac{X_1}{10000}}$, $e^{-X_2}$</td>
<td>0.8587</td>
<td>0.8033</td>
<td>0.8048</td>
<td>0.9780</td>
<td>0.8255</td>
<td>0.1964</td>
</tr>
<tr>
<td>$e^{-X_2}$ and $e^{-\frac{X_1}{10000}X_2}$</td>
<td>0.4246</td>
<td>0.4198</td>
<td>0.3435</td>
<td>0.5334</td>
<td>0.39551</td>
<td>0.6494</td>
</tr>
<tr>
<td>$e^{-\frac{X_1}{10000}}$ and $e^{-\frac{X_1}{10000}X_2}$</td>
<td>0.8590</td>
<td>0.8033</td>
<td>0.7836</td>
<td>0.9762</td>
<td>0.92231</td>
<td>0.7192</td>
</tr>
</tbody>
</table>
D.2.2 Model for Each GAC

The coefficients for selected multiple regression models were computed in Microsoft Excel. The equations to interpret k value with correlation to bed volumes and H$_2$O$_2$ exposure for each type of GAC are shown in Equation D-2 to D-7.

For Centaur:

$$k = 0.0014833 + 0.001101e^{-\frac{X_1}{10000}} + 1.790 \times 10^{-5}e^{-X_2} - 0.00005285e^{-\frac{X_1}{10000}-X_2}
+ 0.0002090 \tag{D-2}$$

For ADCAT:

$$k = 0.0023637 + 0.000931e^{-\frac{X_1}{10000}} - 2.287 \times 10^{-6}e^{-X_2} + 8.1444 \times 10^{-6}e^{-\frac{X_1}{10000}-X_2}
+ 0.0002222 \tag{D-3}$$

For F300:

$$k = 0.0011693 + 0.002357e^{-\frac{X_1}{10000}} + 0.0001617e^{-X_2} - 0.0001827e^{-\frac{X_1}{10000}-X_2}
+ 0.0001849 \tag{D-4}$$

For GAC300:

$$k = 0.001887 + 0.003451e^{-\frac{X_1}{10000}} - 0.0001213e^{-X_2} - 0.0001283e^{-\frac{X_1}{10000}-X_2} + 0.0001721 \tag{D-5}$$

For HD3000:

$$k = 0.001764 + 0.0006515e^{-\frac{X_1}{10000}} - 0.0003773e^{-X_2}0.000366e^{-\frac{X_1}{10000}-X_2} + 0.0001786 \tag{D-6}$$

For TN5:

$$k = 0.001824 + 0.0003251e^{-\frac{X_1}{10000}} - 0.0002881e^{-X_2} + 0.0002511e^{-\frac{X_1}{10000}-X_2}
+ 0.0004207 \tag{D-7}$$

The k values from the prediction are proportionally adjusted, i.e., increased volumetrically by multiplying by the ratio of GAC percentage in a column and GAC in a batch reactor. And then substitute into the CSTR-in-series model:

$$[H_2O_2]_n = \frac{[H_2O_2]_0}{(1+k\cdot EBCT\cdot \frac{\epsilon}{H})^n}$$

where, [H$_2$O$_2$]$_0$ is the initial influent H$_2$O$_2$ concentration, mg/L; k is the pseudo first-order reaction rate constant, L/(mg·min);
EBCT is the empty bed contact time of the full-scale GAC bed (4.12 min for this study according to the GAC contactor at the Lorne Park Water Treatment Facility);

ε is the porosity of the GAC (0.62 is chosen as per Clements and Haarhoff, 2004);

H is the total length of the GAC column, 128cm in this study;

h is the height of one CSTR, 5cm is chosen in this study.
D.3 PILOT-SCALE INSTALLATION AT THE LORNE PARK WATER TREATMENT FACILITY

Figure D.5: Pilot-scale Installation at the Lorne Park Water Treatment Facility
(A: Full pilot-scale set-up, with 22 columns; B: sampling ports, four ports on each column)
Figure D.6: Schematic Diagram of a Pilot-scale Column

(22 columns with the same configuration)

Table D.2: Running Conditions for Each Column

<table>
<thead>
<tr>
<th>GAC type</th>
<th>Ageing conditions</th>
<th>Ageing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centaur</td>
<td>Aged with NOM to 25 000, 45 000 and 100 000 bed volumes, respectively (in duplicate); 6 columns in total</td>
<td>Aged with NOM+ 4 mg/L H₂O₂ to 25 000, 45 000 and 100 000 bed volumes, respectively (in duplicate); 6 columns in total</td>
</tr>
<tr>
<td>ADCAT</td>
<td>Aged with NOM to 100 000 bed volumes (25 000 bed volumes and 45 000 bed volumes had 1 run breakthrough test respectively); 5 columns in total</td>
<td>Aged with NOM+ 4mg/L H₂O₂ to 100 000 bed volumes (25 000 bed volumes and 45 000 bed volumes had 1 run breakthrough test respectively); 5 columns in total</td>
</tr>
<tr>
<td>F300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HD3000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>