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Removal of Hydrogen Peroxide Residuals and By-Product Bromate from Advanced Oxidation Processes by Granular Activated Carbon

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Abstract: During drinking water treatment, advanced oxidation process (AOP) with O3 and H2O2 may result in by-products, residual H2O2 and BrO3−. The water containing H2O2 and BrO3− often flows into subsequent granular activated carbon (GAC) filters. A concentrated H2O2 solution can be used as GAC modification reagent at 60 °C to improve its adsorption ability. However, whether low concentrations of H2O2 residuals from AOP can modify GAC, and the impact of H2O2 residuals on BrO3− removal by the subsequent GAC filter at ambient temperature, is unknown. This study evaluated the modification of GAC surface functional groups by residual H2O2 and its effect on BrO3− removal by GAC. Results showed that both H2O2 and BrO3− were effectively removed by virgin GAC, while pre-loaded and regenerated GACs removed H2O2 but not BrO3− anymore. At the ambient temperature 150 µmol/L H2O2 residuals consumed large amounts of functional groups, which resulted in the decrease of BrO3− removal by virgin GAC in the presence of H2O2 residuals. Redox reactions between BrO3− and surface functional groups played a dominant role in BrO3− removal by GAC, and only a small amount of BrO3− was removed by GAC adsorption. The higher the pH, the less BrO3− removal and the more H2O2 removal was observed.

Keywords: bromate; granular activated carbon; hydrogen peroxide; surface functional groups; ozone

1. Introduction

The combination of an advanced oxidation process (AOP) as a pre-treatment with subsequently managed aquifer recharge (MAR) has been suggested as a comprehensive treatment system to effectively remove various organic micro-pollutants (OMPs) during drinking water production [1,2]. However, a disadvantage of applying ozone-based AOP is the formation of bromate (BrO3−) [3–5], a genotoxic carcinogen [6], when bromide (Br−) is contained in the water. WHO, USEPA, and the European Union have set drinking water regulations for the maximum allowable concentration of BrO3− at 0.078 µmol/L (10 µg/L) [7–9]. In order to reduce the formation of BrO3−, hydrogen peroxide (H2O2) may be dosed excessively during AOP [10,11]. Since H2O2 contained in the effluent of ozone-based AOP may cause undesired effects to the ecosystem of subsequent MAR systems [12], it needs to be quenched to a low concentration before flowing into the MAR systems. Therefore, a subsequent removal process may be required for both of BrO3− and H2O2 control [13].

A recent study reported that the adsorption-based physical method has been proven to be more effective for BrO3− removal than chemical methods in potable water treatment [14]. Granular activated carbon (GAC) has been used as a powerful adsorbent in water treatment and some drinking water companies use GAC filters to quench the excessive H2O2 from
AOP [15]. GAC and modified GAC also have been shown to decrease BrO$_3^-$ formation [16] or remove BrO$_3^-$ in a number of studies [17–19]. The previous studies focused on the effects of carbon type, pH, temperature, empty bed contact time, source water, natural organic matter (NOM) and other anions on BrO$_3^-$ removal through kinetic and isotherm tests [17,20]. Previous studies found that BrO$_3^-$ could be effectively removed by virgin GAC, while some studies revealed that after a certain running time, the loaded and/or regenerated GAC was no longer effective for BrO$_3^-$ removal [17,20]. For example, 100% BrO$_3^-$ removal was achieved in the first month and declined to around 5% removal after 11 months in a pilot with an empty bed contact time of 15 min [21]. The performance of GAC in most applications is influenced by its surface chemistry [22–24], so the modification of this GAC property, especially surface oxygen functional groups, has been frequently the target of a variety of GAC beneficiation treatments [25]. Oxidation as one of the most conventional modifications is mainly used to introduce carbon–oxygen surface groups in GAC [26]. Some oxidants, such as HNO$_3$, O$_3$ and H$_2$O$_2$, have been tested for GAC modification to increase the oxygen surface groups, and results indicated that the oxidation of GAC increased the content of acidic oxygen surface groups and the adsorption capacity of Hg, Cd, Cr(III), Cr(VI) and Cu(II) [26–28]. The oxidation treatment of GAC as a rule was performed mostly using O$_2$ and acid, and rarely with H$_2$O$_2$. The real situation in practice is the co-presence of BrO$_3^-$ and H$_2$O$_2$, while as far as to the authors' knowledge, it has not been known whether the presence of H$_2$O$_2$ as a modification reagent of GAC can play a positive role in BrO$_3^-$ adsorption by GAC during drinking water treatment. However, another possibility could be that the co-presence of BrO$_3^-$ and H$_2$O$_2$ may compete the active sites or oxygen-containing functional groups of GAC so that they may negatively impact each other’s removal. What is more, the H$_2$O$_2$ decomposition product oxygen was speculated to cover the active sites on the surface of GAC or block the micropores [29], so that the presence of H$_2$O$_2$ may decrease BrO$_3^-$ removal efficiency. Oppositely, the presence of H$_2$O$_2$ as a strong oxidant to modify GAC may increase the BrO$_3^-$ removal, as stated earlier. However, till now it has not yet been investigated whether the co-presence of H$_2$O$_2$ and BrO$_3^-$ can improve BrO$_3^-$ removal by GAC.

The objectives of this study were to assess whether the presence of residual H$_2$O$_2$ from AOP in the water could improve the removal of BrO$_3^-$ by GAC and to investigate the mechanism behind it.

2. Materials and Methods

2.1. GAC

Virgin, pre-loaded and regenerated GAC (Norit ROW 0.8 CAT) was used in this study. The virgin GAC was purchased from Sigma-Aldrich (St. Louis, MO, USA). The pre-loaded and regenerated GAC were collected from Dunea drinking water plant (Bergambacht, The Netherlands). The GAC pre-loaded with natural organic matter was already used for two and half years at the Dunea plant. The particle size of all GACs was 0.8–1.0 mm.

The GAC for the batch experiments was prepared by the following procedures. The GAC was ground and sieved to obtain a particle size ranging from 0.25 mm to 0.8 mm. After sieving, the GAC was washed with ultra-pure water until the water remained colorless, and finally the GAC was dried at 175 °C for 72 h to remove volatile impurities.

2.2. Water and Chemical Reagents

The water used in batch experiments was prepared using chemical reagents and deionized water from a Millipore Milli-Q system. Chemicals including sodium bromate (NaBrO$_3$), sodium hydroxide (NaOH), concentrated acid (HCl), sodium carbonate (Na$_2$CO$_3$), sodium bicarbonate (NaHCO$_3$) and hydrogen peroxide (H$_2$O$_2$) were purchased from Sigma-Aldrich. The H$_2$O$_2$ solutions were prepared from a 30% standard solution (Merck, Germany). All chemicals were of analytical grade. All solutions used in this study were prepared using water from a Millipore Milli-Q system.
2.3. Batch Experiments

In a survey of 100 drinking water utilities, BrO$_3^\text{−}$ concentrations were in the range of <0.016–0.5 µmol/L following ozonation of water containing 0.025–5.36 µmol/L Br$^\text{−}$ [30,31]. It was decided to investigate the upper value of this range in this study, so 0.5 µmol/L BrO$_3^\text{−}$ was achieved in the batch experiments. Batch experiments were conducted using glass bottles with a volume of 1 L. During all the experiments, the batch reactors were wrapped in thin foil. A 0.052 µmol/L NaBrO$_3$ solution was prepared and 3 mL was dosed into the batch reactors to obtain a concentration of 0.5 µmol/L BrO$_3^\text{−}$. The research of Lekkerkerker and Knol [32] showed that 180 µmol/L H$_2$O$_2$ dosage was enough to form sufficient hydroxyl radicals in the AOP, so the residual H$_2$O$_2$ concentration in effluent water of AOP will not exceed 180 µmol/L. Hence, 150 µmol/L H$_2$O$_2$ was dosed into the batch reactors in this study.

As is shown in Figure 1, a series of experiments were performed using 36 batch glass bottles at ambient temperature of 23–27 °C. The GAC dosage was always 5 g/L, and the H$_2$O$_2$ and BrO$_3^\text{−}$ concentrations were always 150 µmol/L and 0.5 µmol/L, respectively. All the batch reactors with H$_2$O$_2$ were covered by aluminium foils to prevent potential degradation of H$_2$O$_2$ by the light.

In experiment A as shown in Figure 1, 16 batch reactors and three different GACs (virgin GAC, regenerated GAC and pre-loaded GAC) were used to investigate the removal of bromate and H$_2$O$_2$ by GAC with different running time. This experiment involved eight treatment groups (only H$_2$O$_2$, virgin GAC + H$_2$O$_2$, regenerated GAC + H$_2$O$_2$, pre-loaded GAC + H$_2$O$_2$, only BrO$_3^\text{−}$, virgin GAC + BrO$_3^\text{−}$, regenerated GAC + BrO$_3^\text{−}$, and pre-loaded GAC + H$_2$O$_2$). The groups without GAC were references. Before the experiment started, the three GACs were collected to characterize their surface functional groups. Water samples were collected at 0, 10, 20, 60, 120 and 180 min for BrO$_3^\text{−}$ and H$_2$O$_2$ analysis.

In experiment B as shown in Figure 1, 0.5 µmol/L BrO$_3^\text{−}$ and/or 150 µmol/L H$_2$O$_2$ was dosed into batch reactors with virgin GAC to investigate whether the presence of residual H$_2$O$_2$ from AOP improved the removal of BrO$_3^\text{−}$ by GAC. This experiment involved 6 treatment groups (BrO$_3^\text{−}$, H$_2$O$_2$, BrO$_3^\text{−}$ + H$_2$O$_2$, BrO$_3^\text{−}$ + GAC, H$_2$O$_2$ + GAC, and BrO$_3^\text{−}$ + H$_2$O$_2$ + GAC). The groups without GAC were references. Water samples were collected from the reactors for the analysis of BrO$_3^\text{−}$ and H$_2$O$_2$. To identify the consumed/modified oxygen containing surface functional groups during the contact time, GAC samples were collected for the analysis of surface oxygen functional groups at the beginning and the end of the experiment.

To further assess the effect of H$_2$O$_2$ presence on BrO$_3^\text{−}$ removal in a broad pH range, batch experiment C was performed using eight batch reactors with virgin GAC, H$_2$O$_2$ and BrO$_3^\text{−}$, in different pH levels ranging from 5.5 to 10. During the whole experiment, the solutions in batch reactors were not buffered. Every 5 min, solution pH was measured, and HCl or NaOH solution was dropped into batch reactors manually to reach a stable pH level. Water samples were collected at 0, 10, 20, 60, 120, 180, 240 and 300 min for BrO$_3^\text{−}$ and H$_2$O$_2$ analysis. Additionally, GAC samples were collected to measure the initial and ending surface functional groups.
2.4. Analytical Methods

2.4.1. Functional Groups Measurement

The amount of surface acidic and basic functional groups was measured by the Boehm method [33]. Four series of GAC samples (0.5 g) were added to four flasks (100 mL). Then, 50 mL of 0.05 mol/L sodium hydrogen carbonate (NaHCO₃), sodium carbonate (Na₂CO₃) and sodium hydroxide (NaOH) were added to the flasks, respectively. The flasks were then sealed and stirred at room temperature for 24 h. The GAC samples were then filtrated and carefully washed. All filtrates were collected and subsequently diluted to 100 mL. Then, the diluent was titrated with 0.05 mol/L HCl and the surface oxygenated groups...
were determined according to the following assumptions: NaOH neutralizes carboxyl, phenolic and lactonic groups. Na$_2$CO$_3$ neutralizes carboxyl and lactonic groups. NaHCO$_3$ neutralizes carboxyl groups only. The amount of basic surface groups was determined with 0.05 mol/L HCl solution. The filtrate was collected as above, and then titrated with 0.05 mol/L NaOH solution.

2.4.2. Other Analysis and Measurements

Hydrogen peroxide test kits (L1.18789.0001, VWR Company, Radnor, PA, USA) with a detection range of 0.44–180 µmol/L were used for water-phase H$_2$O$_2$ measurements because of ease of operation, the rapid decomposition of H$_2$O$_2$ and accuracy of results. After being filtered through 0.45 µm filters, the samples were transferred to a 10/20 mm rectangular cell and measured in a photometer (Spectroquant NOVA 60).

BrO$_3^-$ was analysed using a Metrohm Schiedam ion chromatograph (SenTix® 940 IDS probe, Multi 340i, WTW, Germany) equipped with a suppressed conductivity detector, using an A Supp 16 150/4.0 column, a guard column, and a 100 µL sample loop. A 3.75 mM Na$_2$CO$_3$ and 0.375 mM NaOH solution was used as the eluent. The eluent flow rate was set at 0.7 mL/min. pH was measured with a SenTix® 940 (WTW) electrode (Xylem Inc., Weiheim, Germany), both using the WTW Multi 3420 m (Xylem Inc., Weiheim, Germany).

3. Results and Discussion

3.1. BrO$_3^-$ and H$_2$O$_2$ Removal by Three GACs with Different Usage Times

Figure 2 presents H$_2$O$_2$ and BrO$_3^-$ removal efficiencies within 180 min by virgin GAC, pre-loaded GAC and regenerated GAC, respectively. As is shown in Figure 2a, among the three kinds of GAC, virgin GAC had the best BrO$_3^-$ removal capacity (81%). No BrO$_3^-$ removal was observed in the batch reactor without GAC, indicating BrO$_3^-$ was not self-decomposed or decomposed by microbes in a short experiment period of 180 min. The pre-loaded GAC did not remove BrO$_3^-$ at all, which is in line with a previous study reporting that BrO$_3^-$ removal rate by GAC apparently decreased with increasing operation time [34], probably because the active sites or valid functional groups on the surface of GAC were exhausted due to preloading in the preceding two years with natural organic matter present in the drinking water treatment plant [35]. It seems that 3.8% BrO$_3^-$ was removed by regenerated GAC, which is in line with a previous study reporting that, compared with regenerated GAC, virgin GAC had a better removal effect on BrO$_3^-$ [36]. This result indicates that the thermal regeneration restored active sites or functional groups on the surface of GAC to some degree. In conclusion, these results indicate that GAC may become invalid for BrO$_3^-$ removal after a period of running, even after regeneration, in practice. As is shown in Figure 2b, H$_2$O$_2$ was not decomposed in the absence of GAC within 180 min, indicating that the decrease of H$_2$O$_2$ in other groups was caused by GAC instead of other factors. No obvious difference was observed between preloaded GAC and virgin GAC groups. H$_2$O$_2$ removal rate in regenerated GAC group was slightly lower than that in preloaded GAC group. GAC regeneration and recycle slightly decreased H$_2$O$_2$ removal capacity, but regenerated GAC is still able to effectively quench residual H$_2$O$_2$. Previous studies showed that GAC can be used to quench the residual H$_2$O$_2$ after drinking water treatment AOPs, and the catalytic activity of GAC has nothing to do with continuous exposure to hydrogen peroxide, but is related to the physical and chemical properties of the GAC surface [37,38].
3.2. Surface Functional Groups of Three GACs with Different Usage Times

Figure 3 presents the acidic and basic functional groups on the surface of three kinds of GAC with different usage times before the BrO$_3^-$ and H$_2$O$_2$ removal experiment. Generally, the overall concentrations of acidic and basic functional groups are observed to be in the following order: virgin GAC > regenerated GAC > pre-loaded GAC, although the concentration of basic functional groups on the surface of virgin GAC is the same as that of regenerated GAC, indicating that the virgin GAC contained rich functional groups and the regeneration can recover a portion of functional groups. Usually, regardless of the regeneration method used, the porosity, specific surface area and surface oxygen functional groups on the surface of the regenerated GAC are less than that of the virgin GAC. Mesopores formed during the regeneration are considered to promote the carbon adsorption capacity [39]. Correspondingly, BrO$_3^-$ removal ability was also recovered after GAC regeneration, but not much (Figure 2). Acid groups are classified to lactonic groups, carboxyl groups and phenolic groups. Among the three acidic functional groups, lactonic groups and phenolic groups on virgin GAC are greater than that on regenerated and pre-loaded GAC. This might also be one of the reasons why virgin GAC reached the highest removal efficiencies of BrO$_3^-$ and H$_2$O$_2$ (Figure 2).

3.3. Effect of H$_2$O$_2$ on BrO$_3^-$ Removal by Virgin GAC

To assess the interaction of BrO$_3^-$ and H$_2$O$_2$ removal by virgin GAC, Figure 4 presents the removal of BrO$_3^-$ and H$_2$O$_2$ by 5 g/L virgin GAC in the presence and the absence of the other. Figure 4a shows that the initial 0.5 µmol/L BrO$_3^-$ was removed 60–80% by GAC under the presence and absence of H$_2$O$_2$ in 180 min, respectively. It can be observed that the BrO$_3^-$ concentration decreased faster in the absence than in the presence of 150 µmol/L H$_2$O$_2$, that is the presence of 150 µmol/L H$_2$O$_2$ negatively impacted BrO$_3^-$ removal by GAC, indicating 150 µmol/L H$_2$O$_2$ may not successfully modify the surface functional groups of GAC at the ambient temperature. A previous study found that the activated carbon modified with 0.04 mol/L hydrogen peroxide at 75 °C removed 85.6% cobalt from
aqueous solution after 1h, while the activated carbon modified at a lower temperature of 25 °C removed only 74% cobalt after 1 h [40]. It further proves that the modification temperature has a great influence on the physical and chemical properties of the activated carbon surface, and the low temperature environment cannot modify GAC well. Figure 4b shows that 150 µmol/L H2O2 was decomposed fully by GAC and its decomposition in the presence and the absence of 0.5 µM BrO3− had no considerable difference during the 180 min contact time (p > 0.05), indicating an ignorable influence of 0.5 µmol/L BrO3− on H2O2 decomposition. In the reference without GAC, both BrO3− and H2O2 showed steady concentrations, indicating that no self-decomposition took place and the removal of BrO3− and H2O2 can be contributed to GAC.

Figure 4. (a) BrO3− and (b) H2O2 removal by GAC under the co-present condition.

3.4. The Mechanism of H2O2 Impact on BrO3− Removal by Virgin GAC

3.4.1. BrO3− Removal by Adsorption or Reduction?

Figure 5 presents the removal of BrO3− by virgin GAC and correspondingly the increase of reaction product Br−, in the presence and absence of H2O2. Under both situations, the BrO3− concentration gradually decreased, and correspondingly the Br− concentration gradually increased with time. The molar mass of BrO3− and Br− in the reactor tends to stabilize after a slight decrease in the first 6 min. This slight decrease could be caused by GAC adsorption. The gradual increase of Br− with the decrease of BrO3− indicates that the removal of BrO3− by virgin GAC is mainly a reduction process, which might involve redox reactions between surface functional groups and BrO3−. Obviously, the presence of 150 µmol/L H2O2 significantly inhibited the removal of BrO3− by virgin GAC. Figure 5 showed that the addition of H2O2 changed the physical and chemical properties of the GAC surface, resulting in a significant decrease in the acidic and basic oxygen-containing functional groups on the GAC surface, thereby reducing the reaction efficiency of the functional groups with BrO3−. When H2O2 and BrO3− coexist, there may be competition for GAC oxygen-containing functional groups and adsorption active sites, which is one of the reasons why BrO3− removal was inhibited by H2O2. In addition, bromine mass loss in BrO3− and Br− is observed due to the presence of H2O2, by comparing Figure 5a,b. During H2O2 decomposition, a small amount of OH− can be generated [41]. The OH− can further oxidize Br− into intermediate products, such as HOBr and BrO− [42], which could explain the bromine mass loss under the situation of H2O2 addition.
Figure 5. BrO$_3^-$, Br$^-$, and BrO$_3^-$ + Br$^-$ concentration in the absence and presence of H$_2$O$_2$. (a) with H$_2$O$_2$, (b) without H$_2$O$_2$.

3.4.2. Modification of GAC Surface Functional Groups by H$_2$O$_2$

The surface oxygen-containing functional groups of initial GAC and the modified GAC after contacting with BrO$_3^-$ and H$_2$O$_2$ are presented in Figure 6. It is observed that both H$_2$O$_2$ alone and BrO$_3^-$ alone consumed acid groups and basic groups, indicating the presence of H$_2$O$_2$ consumed oxygen-containing surface functional groups with BrO$_3^-$ instead of provided more functional groups. Therefore, the H$_2$O$_2$ concentration of 150 µmol/L could be too low to effectively modify GAC oxygen-containing surface functional groups. Among the three acid groups, both the amount of carboxyl groups and phenolic groups did not change significantly after different reactions and the main change lay in lactonic groups, indicating that H$_2$O$_2$ mainly reacted with lactonic groups. The functional group modification by H$_2$O$_2$ can be explained as follows.

Figure 6. Surface functional groups on the initial and modified GAC.

H$_2$O$_2$ has a property of electrophilic attacking, so H$_2$O$_2$ attacks the unsaturated bonds of C=C by electrophilic addition and introduces the phenolic groups [43], as shown in Equation (1). In a previous study [43], around 1.47 mol/L H$_2$O$_2$ was used to modify activated carbon at 60 °C for 2 h and the modification treatment increased the formation of carboxyl groups and carbonyl groups but decreased the formation of phenolic groups, which was explained by the fact that phenolic groups formed in Equation (1) could be further oxidized to carboxyl groups by esterification and dehydration as shown in Equations (2) and (3). A previous study [44] showed that different from the steady rise of carboxyl groups and lactonic groups, the concentration of phenolic groups first increased and then decreased with the increase of H$_2$O$_2$ concentration, which could be caused by the fact that the dehydration of phenolic groups became faster than the formation of phenolic groups with the increase of oxidation ability. Therefore, the low H$_2$O$_2$ concentration, an environmentally relevant concentration, in this study might be not enough to further...
conduct the following two steps reactions, dehydration and esterification, as shown in Equations (2) and (3), which might explain the increase of phenolic groups instead of carboxyl group. In conclusion, an environmentally relevant concentration of H$_2$O$_2$ from AOP cannot significantly increase the concentrations of carboxyl and lactonic groups due to the limited oxidation ability.

\begin{align*}
\text{AC} + H_2O_2/HO^- &\rightarrow \text{AC} + H_2O & (1) \\
\text{AC} + H_2O_2 &\rightarrow \text{AC} + HO^- & (2) \\
\text{AC} + H_2O_2/HO^- &\rightarrow \text{AC} & (3)
\end{align*}

### 3.5. Effect of pH on BrO$_3^-$ and H$_2$O$_2$ Removal

The removal of BrO$_3^-$ and H$_2$O$_2$ by virgin GAC under different pH conditions is shown in Figure 7. At pH 5.5 and 7, BrO$_3^-$ concentration decreased sharply within the first 50 min, and then remained constant. In contrast, BrO$_3^-$ concentrations slowly decreased within the whole 300 min and did not arrive at an equilibrium status at pH 8.5 and 10. Therefore, BrO$_3^-$ removal efficiency was higher at the acidic and neutral conditions than at the basic condition, which seems in conflict with a previous study [45]. This is probably because (1) BrO$_3^-$ is a strong oxidizer under low pH conditions, and its reactivity is in direct proportion to the square of the proton concentration [46]; (2) as pH decreases, the protonation of surface functional groups of activated carbon or dissociation of OH$^-$ makes the material surface electropositive, resulting in electrostatic attraction of BrO$_3^-$ [45]. As for H$_2$O$_2$, with the increase of pH, H$_2$O$_2$ decomposition was more efficient. At pH 10, almost all H$_2$O$_2$ was removed while only 64% H$_2$O$_2$ was removed at pH 5.5. The results indicate that a higher pH is favourable to H$_2$O$_2$ removal in GAC filters during drinking water treatment.

![Figure 7](image_url)

**Figure 7.** The removal of (a) BrO$_3^-$ and (b) H$_2$O$_2$ at different pH by virgin GAC.

Figure 8 presents the effect of pH on surface functional groups’ modification by H$_2$O$_2$. With the increase of pH, the surface acid groups decreased from 1 mmol/g to 0.7 mmol/g.
in the pH range of 5.5–7 and then became stable in the pH range of 7–10. In contrast, the basic group greatly increased with the increase of pH from 5.5 to 10. At pH 10, even the basic groups reached 1.2 mmol/g, higher than the initial level of 0.8 mmol/g. With regard to the three acid groups, as the pH increased, the lactonic groups and phenolic groups presented a notable decrease and a slight decrease respectively, while the carboxyl groups did not show regular changes.

Figure 8. Surface functional groups of the modified oxidized GAC under different pH levels.

It is reasonable that the change trends of the acid groups and the basic groups with pH change were caused by acid-base neutralization. What is more, with the increase of pH, the basic groups were observed to increase (Figure 8), and simultaneously the H2O2 removal efficiency also increased (Figure 7), which is in line with previous studies reporting that the basic groups enhanced the H2O2 removal [35]. More specifically, the decrease of lactonic groups might be explained by the fact that the lactonic groups produced by the esterification reaction between carboxyl groups and phenolic groups decreased with the increase of pH.

4. Conclusions

Virgin GAC has the most acidic and basic surface functional groups, and correspondingly it presented the highest BrO3− removal. However, GAC hardly remove BrO3− anymore after two years running and thermal regeneration in this study. In our experiments, 5 g/L GAC decreased H2O2 from 150 µmol/L to <3 µmol/L within 80 min and the removal efficiency was not evidently impacted by GAC running time or regeneration.

The presence of 150 µmol/L H2O2 inhibited BrO3− removal by virgin GAC, which could be explained by the fact that H2O2 competed oxygen-containing functional groups with BrO3−. H2O2 removal efficiency was hardly impacted by the presence of 0.5 µmol/L BrO3−.

Redox reactions between BrO3− and surface functional groups played a dominant role in BrO3− removal by GAC, and a small amount of BrO3− was removed by GAC adsorption. BrO3− removal efficiency was higher at acidic and neutral conditions than at basic conditions. In contrast, H2O2 removal efficiency was increased with pH increase, which could be explained by the increase of alkaline surface functional groups with the increase of pH.

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