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2 **REMOVAL OF BROMIDE FROM SURFACE WATERS USING SILVER**
3 **IMPREGNATED ACTIVATED CARBON**

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6 Chen Chen, Onur Guven Apul, Tanju Karanfil*

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9 *Department of Environmental Engineering and Earth Sciences*
10 *Clemson University*
11 *342 Computer Court*
12 *Anderson, SC 29625*
13 *United States*
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23 *Corresponding author: email: tkaranf@clemson.edu; phone: +1-864-656-1005; fax: +1-864-656-0672

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ABSTRACT

The main objectives of this study were to develop an understanding of silver impregnated activated carbon (SIAC) preparation for enhanced bromide (Br^-) removal from water, and to investigate the impact of aqueous background composition on the Br^- removal. Several SIACs were produced using various combinations of oxidation and silver impregnation procedures and powdered activated carbons (ACs). Regardless of the preparation procedure, SIACs showed significantly Br^- uptakes than the virgin ACs. The Br^- removal efficiency was affected by (i) the background water composition (e.g. Cl^- and NOM competition reduced the Br^- uptake), (ii) silver impregnation process (e.g. silver content, pre-oxidation of virgin AC; silver impregnation largely increased the Br^- removal, and the pre-oxidation of AC prior to silver impregnation was found to be important), and (iii) AC characteristics (e.g. surface area, oxygen content; SIACs with higher silver contents and larger surface areas exhibited higher degrees of Br^- removal). The Br^- removal by SIAC reduced the formation of brominated THMs. Jar test results showed that coagulation did not have an impact on Br^- removal by SIAC.

Keywords: Adsorption, Bromide, Silver Impregnated Activated Carbon, Disinfection Byproduct, Natural Organic Matter

1. INTRODUCTION

Bromide (Br^-) is ubiquitous in surface waters especially in areas impacted by anthropogenic activities such as discharge of treated or untreated wastewaters, the releases from coal-fired power plants and hydraulic fracturing operations, and sea water intrusion. [Krasner et al., 1989; Amy et. al., 1993; McCuire et. al., 2002]. Br^- is not a contaminant; however its presence in water may lead to formation of regulated disinfection byproducts (DBPs) during water treatment, such as bromate (BrO_3^-), and brominated trihalomethanes (THMs) and haloacetic acids (HAAs). Brominated DBPs are more cyto- and geno- toxic than their chlorinated analogues [Plewa et al., 2008]. Due to potential health risks of DBPs, increasingly stringent regulations have been imposed for eleven DBPs under the Stage II Disinfectants/Disinfection Byproducts Rule (D/DBPR) by the United States Environmental Protection Agency (USEPA). [U.S. Environmental Protection Agency, 2006]

Numerous materials, including metal impregnated sorbents (e.g. zeolite and alumina), activated carbons (AC), activated carbon fibers, and anion exchange resins have been evaluated for removal of Br^- from water. Other techniques, including electrochemical treatment, nanofiltration, co-precipitation with magnesium hydroxide have also been investigated [Chellam et al., 2000, Amy et al., 1999, Prados et al., 1993]. However, the low Br^- removal efficiency and the low feasibility of application limited the use of such technologies. Therefore, there is yet no well-established technology to control Br^- at drinking water treatment plants.

Previous studies showed that sorbent surfaces may be tailored to enhance the removal of Br^- and other halides from water [Hoskins et al., 2001; Cumbie et al., 2003]. Adsorbents including Ag-doped activated carbon aerogels and silver loaded porous carbon spheres have been evaluated as promising adsorbents to remove Br^- from water. The effects of operational variables, such as Cl^- and NOM concentrations on Br^- removal were also examined [Sanchez-Polo et al. 2006, 2007; Gong et al. 2013]. However, the influence of carbon surface tailoring on Br^- removal have not been extensively investigated,

and very few studies have explored the Br⁻ removal by tailored AC surface at practical adsorbent doses [Watson et al. 2016] along with the control of brominated DBPs in natural waters.

The main objectives of this study were to: (i) conduct a systematic investigation to develop an understanding of carbon surface tailoring and SIAC preparation to enhance removal of Br⁻ from natural waters; (ii) investigate the impact of background water composition (i.e., the presence of NOM and competing anions like chloride, nitrate and sulfate) on the Br⁻ uptake; and (iii) evaluate the impact of selected SIACs for THM control during water treatment.

2. MATERIALS AND METHODS

2.1. Activated Carbons

Four coal based ACs (HD3000 and 20B from Norit, Inc., F400 from Calgon Corp., WC800 from Standard Purification, Inc.) with different physicochemical properties were used to produce SIACs. In addition, two bituminous coal based commercially available SIACs with different silver contents, 1.05 % by weight SIAC, (TOG-NDS-20*50, Calgon Corporation), and 4.03 % by weight SIAC (Nusorb A 20*40, Nucon International, Inc.) were also evaluated as received from the manufacturers.

Virgin AC samples were crushed, sieved to 200-325 µm mesh size, and then washed with distilled and deionized water (DDW), dried at 90 °C. The produced powdered activated carbon (PAC) from each AC was stored in sealed containers. The selected physicochemical properties of the virgin PACs are summarized in Table 1.

2.2. Bromide Solution

The Br⁻ stock solution (1000 mg/L) was prepared by dissolving reagent grade (99.0%) sodium bromide (NaBr) salt (Sigma-Aldrich) in DDW and desired concentrations were obtained by diluting the Br⁻ stock solution with DDW.

2.3. NOM Solution and Natural Waters

The NOM isolate used in the study was collected from the influent of a drinking water treatment plant in South Carolina using a reverse osmosis and followed by resin fractionation, as described elsewhere [Song et al., 2009]. The SUVA₂₅₄ value of the NOM solution used was around 4.0 L/mg-m. Using an aquatic NOM allowed an independent assessment of the NOM effect on Br⁻ removal without the confounding effects of background anions and cations in natural waters. Experiments were also performed with natural water samples collected from Charleston, Myrtle Beach, Bushy Park Reservoir, Edisto River, Savannah River, Lake Hartwell, and Broad River. Selected water quality characteristics of the natural waters are summarized on Table 2.

2.4. Preparation of SIACs

2.4.1 Pre-oxidation of Activated Carbons

The virgin PACs (F400, HD3000, WC800 and 20B) were pre-oxidized with nitric acid solutions of varying acidic strengths (10N and 15.7N) for one hour while heating at temperatures 90 °C or 160 °C prior to silver impregnation.

High temperature oxidation with nitric acid were performed by adding 6 g of PAC sample in 150 mL concentrated nitric acid solutions (10 N or 15.7 N) and boiled (~160 °C) for one hour on a hot plate. The Erlenmeyer flask was removed from the hot plate and cooled to room temperature. The carbon samples were filtered and washed thoroughly with DDW several times. The pH of the supernatant was measured after each washing until it remained constant to make sure that the excess acid was removed. Then, PAC was dried at 90 °C and stored in a sealed container. Low temperature oxidation with nitric acid (15.7 N) was performed utilizing the same procedure at 90 °C instead of 160 °C.

2.4.2 Silver Impregnation of Pre-oxidized Activated Carbons

The silver impregnation of pre-oxidized activated carbons was performed at three silver nitrate (AgNO₃) concentrations: 0.1, 0.5 or 1.5 mol/L. One g of pre-oxidized PAC was added in an AgNO₃

solution and the carbon slurry was stirred for two days at 150 rpm at room temperature (20±3 °C). Then, the carbon samples were filtered (through 0.45µm membrane filter) and washed several times with DDW, dried by vacuum oven at 90 °C and stored in sealed glass vials.

According to stoichiometry (Reaction 1), for the removal of 300 µg/L Br⁻ in water (at 25 mg/L SIAC dose), the amount of silver required on SIAC is about 1.62 % by weight. The SIACs prepared in this study have silver contents higher than the stoichiometric requirement (Table 2).

Since several SIAC samples were produced in this study with various combination of conditions and activated carbons, the following coding system was used to label the final carbons – **ox**: oxidized with 15.7N HNO₃, **ox2**: oxidized with 10N HNO₃; **H**: high temperature (160 °C) oxidation; **L**: low temperature (90 °C) oxidation; **S01**: impregnation with 0.1 M AgNO₃ solution; **S05**: impregnation with 0.5 M AgNO₃ solution; and **S15**: impregnation with 1.5 M AgNO₃ solution. Therefore, as an example, **HD3000ox2-L-S05** is the SIAC produced using HD3000 activated carbon oxidized with 10N HNO₃ at low temperature (90 °C) and subsequent silver impregnation using 0.5 M AgNO₃ solution.

2.5. Characterization of Adsorbents

Nitrogen gas adsorption at 77 K was performed with a physisorption analyzer (Micromeritics ASAP 2010) to determine the specific surface area (SSA), pore volume and pore size distribution of the adsorbents. The Brunauer-Emmett-Teller (BET) equation was used to calculate SSAs. The total pore volume was obtained from the adsorbed volume of nitrogen near the saturation point (P/P₀ = 0.99). Pore size distribution of adsorbents was determined from the nitrogen isotherms using the Density Functional Theory (DFT) model. Oxygen contents of the carbonaceous adsorbents were measured using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation). The pH of the point of zero charge (pH_{PZC}) of adsorbents was determined according to the method described by Muller et al., [1980] and Summers [1986]. The silver contents of SIAC were determined through digestion followed by inductively

couple plasma mass spectroscopy (ICP-MS) analysis. Details about the carbon characterization methods were described elsewhere [Dastgheib et al., 2004].

2.6. Bromide Removal Experiments

AC doses of approximately 25 mg/L were used in two types of experiments conducted at room temperature (20 ± 3 °C):

(1) Constant carbon dose adsorption experiments

For selected natural water experiments, adsorption experiments were conducted in completely mixed batch reactors (CMBRs, i.e., 50 mL plastic bottles), with WC800, HD3000, 20B and F400 SIACs for 4 hours contact time to mimic the conditions at drinking water treatment plants. The initial bromide concentration (e.g., 300 µg/L) was attained with a spike from a sodium bromide stock solution.

(2) Jar tests

Natural water (Broad River) spiked with bromide was used for the coagulation test (Br^- 300 µg/L, NOM 5.4 mg TOC/L, Cl^- 14 mg/L). 4% commercial SIAC (10 and 50 mg/L, Nusorb A 20*40.) was added to water before coagulation/flocculation processes. The virgin F400 carbon with no silver was used as a control in the experiment (50 mg/L). The initial pH was 7.3 and decreased to 6.5 after alum (30 mg/L) addition. The pH remained unchanged during rapid and slow mixing. The rapid mixing was conducted at 200 rpm for one minute followed by slow mixing at 25 rpm for 20 min, and then two hours of settling time.

2.7. THM Formation Control Experiments

The SIAC dose was 25 mg/L, and the Br^- spike concentration in water was approximately 300 µg/L. SIAC adsorption experiments were conducted in 250 mL sealed plastic bottles for four hours. After adsorption, the filtered samples were contacted with HOCl to achieve >0.4 mg/L residual after one day

contact time in the presence of phosphate buffer maintaining pH about 7.8. The chlorinated samples were extracted and analyzed by GC-ECD to measure THM concentrations. WC800ox-L -S05, with 3.4% silver content and 664.5 m²/g BET surface area, was used for these experiments under three conditions: NOM+40Cl (2.5 mg/L TOC, 40 mg/L Cl⁻), Lake Hartwell (2.3 mg/L TOC, 2.6 mg/L Cl⁻), and Lake Hartwell + 40Cl (2.3 mg/L TOC, 40 mg/L Cl⁻).

The analytical methods used to measure various parameters in this study are provided on Table S1.

3. RESULTS AND DISCUSSION

3.1. Carbon Surface Tailoring with Silver for Bromide Removal

3.1.1. Step 1- Pre-oxidation

Oxidation prior to silver impregnation (i.e., pre-oxidation) creates various oxygen-containing functionalities on the carbon surface, particularly strong (e.g., carboxylic) and intermediate (e.g., lactone and lactol) acidic groups [Vinke et al., 1994]. Oxidation may also alter the physicochemical properties (e.g. SSA and oxygen content) of ACs. The severity of wet oxidation can be adjusted or controlled by a combination of oxidant concentration, and oxidation time and temperature [Wanmohd et al., 2009]. Two PACs (HD3000 and WC800) were used to investigate the effect of pre-oxidation parameters. The results i.e., oxygen content and specific surface areas (SSAs) of virgin and oxidized PACs are tabulated in Table 3.

Three major observations were made: (1) Both PACs (i.e., HD3000 and WC800) showed elevated oxygen contents and decreased SSAs after strong acid oxidation. Higher acid concentration (15.7N vs. 10N) resulted in higher oxygen content due to higher oxidation strength. (2) Larger SSA reduction was observed when more concentrated nitric acid (15.7 N) was used, as there was more wall

erosion caused by the more concentrated nitric acid and activated carbon pore blockage. (3) After pre-oxidation by 15.7 N HNO₃, higher degree of SSA deduction was observed on WC800 when compared to HD3000. This was attributed to WC800 being more microporous than HD3000. More decrease in SSA of microporous WC800 was attributed to one or a combination of reasons such as pore blockage by oxygen surface groups (produced by acidic treatment); and wall erosion or destruction of micro pore walls by liquid oxidants [Gorgulho et al., 2008; El-Sayed et al., 2001; Szymanski et al., 2004; Strelko et al., 2002]. Previous researchers have also observed decrease in surface area and pore volume when microporous AC was oxidized by HNO₃ [Wan and Amir, 2010].

In addition, HD3000, WC800 and F400 were used to investigate the effect of oxidation temperature. Both low and high temperature oxidation (i.e., 90 °C and 160 °C) were applied to the same virgin PAC. Higher oxygen content and larger decrease in SSA was observed at higher temperature oxidation (see Table 3 for ~ 270 - 500 m²/g SSA decrease for PAC pre-oxidation at 160 °C compared to 20 - 100 m²/g SSA decrease at 90 °C). The changes were attributed to the high temperature oxidation causing more wall erosion and collapse of carbon pores [Barton et al., 1997]. The severity of oxidation; thus the PAC characteristics were largely influenced by oxidation temperature.

3.1.2. Step 2 -Silver Impregnation

The ACs were impregnated by silver following the pre-oxidation step. The SSAs, oxygen contents and silver contents of produced SIACs are presented in Table 3. The SSAs, oxygen contents and silver contents range between 263 and 1748 m²/g, 1 and 20%, and 1.1 and 12.3%, respectively. A negative correlation ($R^2 = 0.80$) was obtained between silver content and SSA (Figure 1). The decrease in SSA with increasing silver content was attributed to depletion of available surface and physical blockage of pores as a result of silver attachment onto PAC surface.

3.2. Br⁻ Removal by Silver Impregnated Activated Carbon

3.2.1. The Effect of SIAC Characteristics on Br⁻ Removal

All the SIACs removed Br⁻ from DDW (~85 - 93%). The pre-oxidation in SIAC preparation had a notable effect on Br⁻ uptake. The Br⁻ removal was in the order of HD3000ox-L-S05 > HD3000ox2-L-S05 > HD3000-L-S05 following the order of their silver (i.e., 10.4, 7.8 and 2.1, respectively) and oxygen (i.e., 19.1, 18.9 and 4.3, respectively) contents. HD3000 surface oxidized with the most concentrated nitric acid solution (i.e., 15.7 N) showed ~25 µg/L more Br⁻ removal than 10N nitric acid oxidation (Figure S1).

PACs with silver impregnation showed 85 - 93% Br⁻ removal, by contrast there was negligible Br⁻ uptake by the oxidized PACs with no silver impregnation indicating that the bromide was removed by the silver on the PAC surface. Slightly more Br⁻ was removed by WC800 impregnated by higher concentration of silver salt (Figure S2), which resulted higher silver content. However, WC800 impregnated by 0.1, 0.5 and, 1.5 M AgNO₃ salt decreased the bromide concentration below 50 µg/L. This was attributed to silver contents of all three SIACs (13.7%, 14.6%, and 18.5%) being much higher than the silver content stoichiometrically required (1.62%). These results show that PAC surface was successfully impregnated with 0.1 M silver salt enabling bromide removal from water.

Four SIACs, (20Box-L-S05, F400ox-L-S05, HD3000ox-L-S05, and WC800ox-H-S05), were investigated to assess the effect of carbon characteristics on Br⁻ removal. Silver impregnation greatly enabled the removal of Br⁻ from water. The virgin PACs showed no Br⁻ removal from DDW, while the SIACs showed up to 95% of Br⁻ removal in DDW spiked with ~300 µg/L Br⁻ at a 25 mg/L carbon dose. The Br⁻ residual concentrations after SIACs adsorption are presented in Figure 2. The Br⁻ removal by SIACs from high to low is: 20Box-L-S05 > F400ox-L-S05 > HD3000ox-L-S05 and WC800ox-H-S05. The SSAs of the SIACs follow the order of 20Box-L-S05 (1681 m²/g) > F400ox-L-S05 (905 m²/g) > WC800ox-H-S05 (539 m²/g) > HD3000ox-L-S05 (525 m²/g). The silver content of the SIACs are: WC800ox-H-S05 (10.8%) > HD 3000ox-L-S05 (10.4%) > 20Box-L-S05 (3.6%) > F400ox-L-S05 (2.3%).

It was observed that the SIACs with higher SSAs showed better Br^- removal in DDW. The enhanced removal was attributed to more sorption sites on the SIAC surface. Furthermore, 20B was also a mesoporous carbon, making easier for Br^- reacting with Ag^+ on the carbon surface. The higher silver content SIACs did not necessarily result in higher bromide removal than lower silver content SIACs. Up to 10.5% silver of WC800ox-S05 SIAC had similar or even less Br^- adsorption than the 3.5% silver percent 20Box-S05 SIAC. This was attributed to better dispersion of silver on the mesoporous PAC surface with high SSAs, and given the fact that less than 2% silver on PAC was stoichiometrically sufficient to remove all the bromide from water at 25 mg/L carbon dose.

3.2.2. The Effect of Background Water Components on Br^- Removal by SIACs

Natural waters have varying concentrations of anions (e.g. Cl^- , SO_4^{2-} , NO_3^- , etc.) and NOM that may impede the Br^- removal by competing for sorption sites on the SIAC surface. Preliminary results indicated no/little competition between Br^- and NO_3^- or SO_4^{2-} . However, Cl^- is an effective competitor with Br^- , due to low silver chloride solubility ($K_{\text{sp}} \text{AgCl} = 2.8 \times 10^{-10}$) and its high concentration in natural waters. NOM is another competitor through pore blockage and/or site competition. Sanchez-Polo et al. [2006] reported that the Br^- removal capacity of Ag-coated aerogels in the presence of Cl^- was decreased by 35% indicating a competition for sorption sites. While they also observed NOM molecules in natural water block pores or compete for Ag-coated surface sites, they did not distinguish the respective effects of Cl^- and NOM since the selected natural water had both constituents. In the following sections, some of the background water components are systematically investigated one-by-one.

3.2.3 The Effect of Cl^- Competition on Br^- removal

Br^- removal experiments under Cl^- competition were conducted to investigate the effect of the Cl^- competition at its environmentally relevant concentrations, and at pH 6 to 7 which encompass the typical pH of water treatment.

As seen in Figure 3a, it is evident that as the Cl^- concentration increased, the Br^- removal by SIAC decreased. The Br^- removal was approximately 83.5% at 10 mg/L Cl^- ; 38.1% at 50 mg/L Cl^- , and 7.0% at 200 mg/L Cl^- . The large decrease of Br^- removal at increasing Cl^- dose showed the Cl^- in water was a strong competitor with Br^- . Possible explanation was that the Cl^- and Br^- compete to reach to the silver located in the carbon pores and form silver halide precipitate ($\text{AgCl}_{(s)}$ and $\text{AgBr}_{(s)}$). Although the $\text{AgCl}_{(s)}$ solubility is higher than $\text{AgBr}_{(s)}$ ($K_{\text{sp,AgCl}} = 2.8 \times 10^{-10}$, $K_{\text{sp,AgBr}} = 5.2 \times 10^{-13}$), the Cl^- had much higher concentration (~33- 670 times) than the Br^- . This indicates the importance of the Cl^- to Br^- ratio in the removal of Br^- by SIACs. The mass Cl^- to Br^- ratio typically ranges between 50 and 1000 in surface waters [Mullaney, J.R et al., 2009]. Higher Cl^- : Br^- ratios are caused by urban runoff containing halide that is used as an anti-icing agent; the lower ratios indicate presence of anthropogenic bromide sources. To further investigate, Br^- adsorption experiments by WC800ox-S05 SIAC were undertaken at two different Br^- initial concentrations (750 $\mu\text{g/L}$ and 290 $\mu\text{g/L}$) in NOM isolate and Lake Hartwell waters (Cl^- initial concentration 2.6 mg/L). The results are presented in Figure S3. For Lake Hartwell sample spiked with 40 mg/L chloride, 58% of Br^- was removed at a Cl^- : Br^- mass ratio of 55 (Figure S3a), but the Br^- removal percentage largely decreased to 39% when the Cl^- : Br^- mass ratio increased to 140 (Figure S3b).

3.2.4 The Effect of NOM Competition on Br^- Removal

NOM competition experiments were conducted to investigate the NOM effect on Br^- removal by different SIACs; results were presented in Figure 3b. The DDW was spiked with ~260 $\mu\text{g/L}$ initial Br^- and 2.5 mg/L NOM to determine the NOM effect without the interference of any other ions or substances. Five SIACs were used in the Br^- removal experiments (WC800ox-H-S01, 20Box-L-S05, F400ox-L-S05, and HD3000ox-L-S05 and WC800ox-H-S05). At 25 mg/L carbon dose, there was about 87% to 95% Br^- removal in DDW, but in the presence of 2.5 mg/L NOM isolates, the bromide removal decreased to ~70% to 84%. About 15% decrease in Br^- uptake by the same SIAC was observed in the presence of 2.5 mg/L NOM. This suggests that some NOM components compete with the Br^- for adsorption site on the SIAC

surface, and/or the larger NOM molecules could even block the carbon pores and prevent the Br⁻ from reaching into the pores, and result in less Br⁻ removal by the SIACs.

Among the five SIACs tested, NOM had the most influence on 20Box-L-S05. The 20B AC was mesoporous (diameter between 2 nm and 50 nm) with large SSA (1028 m²/g), and relatively low silver content (3.6%). Most NOM hydrodynamic diameters have been reported to be between 2 nm and 10 nm [Dastgheib et al., 2004; Baalousha et al., 2006;], which allow some NOM components to enter the mesopores and compete with the Br⁻ ions for adsorption sites in the carbon mesopores, or even block the mesopores. Therefore, NOM competition was most severe in the mesoporous 20Box-S05. In addition, the low silver content (3.6%) also decreased the chances of Br⁻ reacting with silver species on the carbon surface. WC800 and F400 SIACs had more micropores (47% and 62%, respectively) (diameter < 2 nm) allowing only Br⁻ ions to enter, and reducing the NOM competition to some extent.

As the Cl⁻ competition is another important interference for Br⁻ removal, in order to investigate the NOM effect on Br⁻ removal by SIACs in the presence of Cl⁻, experiments were performed in solutions spiked with NOM and Cl⁻. As is shown in Figure 3a, at low Cl⁻ concentration (1 mg/L), the Cl⁻ competition was not considerable. The NOM was the dominant interference on Br⁻ adsorption; about 5% Br⁻ removal decrease was observed. As the Cl⁻ concentration increased, the NOM and Cl⁻ competition worked as a combined interference on Br⁻ removal. At 10 mg/L Cl⁻, the Br⁻ removal decreased by 14% compared to at 1 mg/L Cl⁻ dose, while at 50 mg/L Cl⁻, the Br⁻ removal dropped by 20%. At very high Cl⁻ dose (200 mg/L), the Cl⁻ dominated the Br⁻ uptake competition and resulted in very low Br⁻ uptake (Br⁻ removal decreased by 77% compared to 1 mg/L Cl⁻ dose) by SIACs with or without presence of NOM.

3.3. Bromide Removal from Natural Waters

Bromide removal was also assessed in a series of natural water samples to investigate the performance of the SIACs in natural waters. The water samples sources and the quality parameters are

tabulated in Table 2. The samples were spiked with Br^- to increase its concentration to about 250 $\mu\text{g/L}$ before the adsorption experiments. The Br^- removal results were shown in Figure 4. In Lake Hartwell water, with relatively low TOC (2.3 mg/L), low SUVA_{254} value (1.8 L/mg-m) and low background ions concentrations, the Br^- removal by SIAC was 72%. Other natural water samples (Bushy Park, Edisto River, Savannah, Charleston and Broad River), with Cl^- levels ranging from 14 to 40 mg/L and TOC levels from 3.3 to 27.6 mg/L, showed Br^- removals within 30-43%. Comparing the Br^- removal efficiencies by WC 800ox-L-S05 SIAC in model solutions and natural waters with relatively comparable TOC and Br^- levels, Br^- removal percentages were, in general, similar (Figure 4). For example, in model solution of 2.5 mg/L NOM + 10 mg/L Cl^- and in Lake Hartwell water (~2.5 mg/L NOM, 3 mg/L Cl^-), the Br^- removal efficiencies were 72% and 73%, respectively. Similarly, at higher Cl^- levels, in the model solution (2.5 mg/L NOM + 40 mg/L Cl^-) and in Savannah water (3.3 mg/L NOM + 40 mg/L Cl^-), the Br^- removal efficiencies were 49% and 43%.

3.3.1 The Effect of Alum Coagulation

Activated carbon is typically added to water before or after coagulation/flocculation during water treatment [Kristiana et al., 2011]. The results of the jar test experiments mimicking the application of PACs in water treatment operation are presented in Figure 5. As anticipated, alum alone and PAC with no silver impregnation were not able to remove Br^- from water. During alum coagulation, the initial DOC concentration was 5.4 mg/L, which was reduced to ~ 3 mg/L (about 45% NOM removal) after coagulation. Higher amount of Br^- removal and lower degree of NOM competition (about 8% at 50 mg/L SIAC) was observed with increasing SIAC dose, which was attributed to higher SIAC to DOC ratio.

3.3.2. The Application of SIACs for THM Control

Br⁻ is an important DBPs precursor (e.g. brominated THM and HAA precursors). In this study, experiments were conducted to investigate the effect of removing Br⁻ with SIAC from natural waters on the THM formation

The THMs formation experiments were conducted to assess the impact of bromide removal by SIACs on the subsequent control of brominated DBPs formation. From the Br⁻ removal experiment results presented in Figure 6A, in NOM+ 40Cl, Lake Hartwell raw, and Lake Hartwell+ 40Cl waters, the Br⁻ removal percentages were ~ 52.6%, 67.4% and 39.0%, respectively. In the raw waters with no bromide spike, the overall THM formation in NOM+40Cl, Lake Hartwell raw and Lake Hartwell +40Cl were 72, 33, 32 µg/L, respectively. The major THM speciation was TCM (from 75% to 90%), as the bromide concentration was low in each water (~0 µg/L in NOM+40Cl, 20 µg/L in Lake Hartwell). Although the TOC levels of both waters were close, the higher THM formation in the NOM solution than the Lake Hartwell water was attributed to the higher SUVA of the former (4.0 L/mg-m) than the latter (1.8 L/mg-m).

When spiked with 300 µg/L Br⁻, the THM formation speciation largely shifted from TCM to DCBM, DBCM, and TBM, and the overall THM formation greatly increased. For NOM+40Cl, the overall THM formation increased from 72 µg/L to 122 µg/L (Figure 6B). About 114 µg/L of brominated THMs (93.4% of total THMs) were created after chlorination as a result of 300 µg/L Br⁻ spiking. For Lake Hartwell raw water, after 300 µg/L Br⁻ spiking, the overall THM formation increased from 33 µg/L to 76 µg/L (Figure 6C), about 69 µg/L of brominated THMs (90.7% of total THMs) were created. For Lake Hartwell +40Cl water, after Br⁻ spiking, the overall THM formation increased from 32 µg/L to 70 µg/L (Figure 6D), about 64 µg/L of brominated THMs (91.4% of total THMs) were created.

After SIACs adsorption, the Br⁻ residual concentration in NOM+40Cl, Lake Hartwell raw, Lake Hartwell +40Cl, decreased from 300 µg/L to 138 µg/L, 95.2 µg/L and 177 µg/L, respectively (Figure 6A). Accordingly, because Br⁻ was removed, the THM formation was largely decreased. After SIAC treatment,

in NOM+40Cl, the brominated THMs concentration decreased from 114 $\mu\text{g/L}$ to 55 $\mu\text{g/L}$ (Figure 6B); in Lake Hartwell raw, brominated THMs decreased from 69 $\mu\text{g/L}$ to 30 $\mu\text{g/L}$ (Figure 6C); in Lake Hartwell +40Cl, brominated THMs decreased from 64 $\mu\text{g/L}$ to 37 $\mu\text{g/L}$ (Figure 6D). The dramatic reduction of brominated THM formation was due to the Br^- removal by SIACs. Another important precursor, natural organic matter, was also measured before and after SIAC treatment, and very limited TOC reduction (below 10%) was observed. Therefore, the large Br^- removal realized by SIAC adsorption played an important role in THMs formation control, especially for the control of brominated THM formation.

4. CONCLUSIONS

Assessing the adsorption of bromide by SIACs indicate that SIACs with higher SSAs generally showed better Br^- removal in water; SIACs with pre-oxidation showed slightly better Br^- uptake than SIACs with no pre-oxidation, in addition, SIACs impregnated at higher AgNO_3 concentration showed better Br^- removal. There was a negative correlation ($R=0.80$) between silver content and SSAs of SIACs, possibly due to the carbon pore blockage during silver impregnation. Cl^- and NOM were two main competitive for Br^- , there was a decrease in Br^- removal with increasing Cl^- concentration. In addition, the Cl^- : Br^- ratio played an important role in the Br^- removal, the lower the Cl^- : Br^- ratio, the higher the Br^- removal can be achieved by the SIACs. Presence of NOM also decreased Br^- removal, which was attributed to pore blockage and NOM competition. Furthermore, the Cl^- and NOM competition work as a combined interference for Br^- removal by SIACs, higher Cl^- and NOM concentration in water can lead to low Br^- removal. Comparing the Br^- removal by different SIACs, it was observed that mesoporous SIACs are more likely to be influenced by NOM competition, as the carbon mesopore sizes approach to typical NOM size range (2 nm to 50 nm). According to the jar test results, alum and virgin activated carbon were not able to remove Br^- from water, and adding alum did not make a notable difference for the Br^- removal by SIAC. Analyzing the THM formation experiments results, it was found that Br^- spiking largely shifted the THM species from chlorinated to brominated species, and the overall THM formation was increased.

The Br⁻ removal by SIAC adsorption played an important role in the control of brominated THM formation.

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References:

- Abdel-Nasser A. El-Hendawy (2003). Influence of HNO₃ oxidation on the structure and adsorptive properties of corncob-based activated carbon. Carbon 41, 713-722.
- Amy, G., Siddiqui, M. (1999). Strategies to control bromated and bromide. AWWA Research Foundation.
- Amy, G., Siddiqui, M., Zhai, W., Debroux, J. (1993). National survey of Br⁻ in drinking waters. Proceedings in AWWA Annual Conference. Denver, CO: AWWA.
- Baalousha, M., Kammer, F.V.D., Motelica-Heino, M., Hilal, H., Le Coustumer, P. (2006) Size fractionation and characterization of natural colloids by flow-field flow fractionation coupled to multi-angle laser light scattering. Jour. Chromatography A 1104, 272-281.
- Baker F.S (1992). Kirk Othmer Encyclopedia of Chemical Technology, Vol.4. John Wiley, New York, P.1015.
- Chellam, S. (2000). Effects of nanofiltration on trihalomethane and haloacetic acid precursor removal and speciation in waters containing low concentrations of bromide ion. Environ. Sci. Technol. 34(9), 1813-1820.
- Gong, C., Zhang, Z., Qian, Q., Liu, D., Cheng, Y., Yuan, G. (2006). Removal of bromide from water adsorption on silver-loaded porous carbon spheres to prevent bromate formation. Jour. Chemical Engineering 218, 333-340.
- El-Sayed, Y., Bandosz, T.J. (2001). A Study of Acetaldehyde Adsorption on Activated Carbons. Journal of Colloid and Interface Science 242, 44-51.

405 Szymański, G.S., Grzybek T., Papp, H. (2004). Influence of nitrogen surface functionalities on
 406 the catalytic activity of activated carbon in low temperature SCR of NO_x with NH₃. Jour.
 407 Catalysis Today 90, 51-59.

408 Gorgulho, H.F., Mesquita, J.P., Gonçalves, F., Pereira, M.F.R., Figueiredo, J.L. (2008).
 409 Characterization of the surface chemistry of carbon materials by potentiometric titrations
 410 and temperature-programmed desorption. Carbon 46, 1544-1555.

411 Krasner, S.W., McGuire, M., Jacangelo, J., Patania, N., Reagan, K., Aeita, E. (1989). The
 412 occurrence of disinfection by-products in US drinking water. Jour. AWWA 81(8), 41-53.

413 Kristiana, I., Joll, C., Heitz, A. (2011). Powdered activated carbon coupled with enhanced
 414 coagulation for natural organic matter removal and disinfection by-product control:
 415 Application in a Western Australian water treatment plant. Jour. Chemosphere 83, 661-
 416 667.

417 McGuire, M., McLain, J.L., Obolensky, A. (2002). Information collection rule data analysis.
 418 AWWA Research Foundation.

419 Mullaney, J.R., Lorenz, D.L., Arntson, A.D., 2009, Chloride in groundwater and surface water in
 420 areas underlain by the glacial aquifer system, northern United States: U.S. Geological
 421 Survey Scientific Investigations Report 2009–5086, 41 p.

422 Muller, G., Radke, C.J. and Prausnitz, J.M. (1980). Adsorption of Weak Organic Electrolytes
 423 from Aqueous Solution on Activated Carbon. Effect of pH. Jour. Physical Chemistry 84,
 424 268-276.

425 Plewa, M. J., E. D. Wagner, et al. (2004). "Chemical and biological characterization of newly
 426 discovered iodoacid drinking water disinfection byproducts." Environ. Sci. Technol.
 427 38(18): 4713-4722.

428 Prados-Ramirez, M.J., Ciba, N., Bourbigot, M.M. (1993). Available techniques for reducing
 429 bromate in drinking water. Proceedings in IWSA Conference: Bromate and Water
 430 Treatment, Paris: IWSA.

431 Richardson, S. D., F. Fasano, et al. (2008). "Occurrence and mammalian cell toxicity of
 432 iodinated disinfection byproducts in drinking water." Environ. Sci. Technol., 42(22):
 433 8330- 8338.

434 Sanchez-Polo, M., Rivera-Ultrilla, J., Salhi, E., von Gunten, E. (2006). Removal of bromide and
 435 iodide anions from drinking water by silver-activated carbon aerogels. Jour. Colloid and
 436 Interface Science 300, 437-441.

437 Sanchez-Polo, M., Rivera-Ultrilla, J., Salhi, E., von Gunten, E. (2007). Ag-doped carbon
 438 aerogels for removing halide ions in water treatment. Water Research 41, 1031-1037.

439 Dastgheib, S.A., Karanfil, T., Cheng, W. (2004). Tailoring activated carbons for enhanced
440 removal of natural organic matter from natural waters. *Carbon* 42, 547-557.

441 Song, H., Orr, O., Hong, Y., Karanfil, T., 2009. Isolation and fractionation of natural organic
442 matter: evaluation of reverse osmosis performance and impact of fractionation
443 parameters. *Environmental Monitoring and Assessment* 153 (1), 307-321.

444 Strelko Jr. V., Malik, D.J., Streat, M. (2002). Characterization of the surface of oxidized carbon
445 adsorbents. *Carbon* 40, 95-104.

446 Summers, R. S. 1986. Activated Carbon Adsorption of Humic Substances: Effect of Molecule
447 size and Heterodispersity. Ph.D. dissertation, Department of Civil Engineering, Stanford
448 University, Stanford, CA.

449 U.S. Environmental Protection Agency, 2006. National Primary Drinking Water Regulations:
450 Stage 2 Disinfectants and Disinfection Byproducts Rule, 40 CFR Parts 9, 141, and 142,
451 Federal Register, Vol 71, No. 2

452 Vinke, P., van der Eijk, M., Verbree, M., Voskamp, A.F., van Bekkum, H. (1994). Modification
453 of the surfaces of a gasactivated carbon and a chemically activated carbon with nitric
454 acid, hypochlorite, and ammonia. *Carbon* 32, 675-686.

455 Wan Daod, W., Houshamnd, A.H.,. (2010). Textural characteristics, surface chemistry and
456 oxidation of activated carbon. *Journal of Natural Gas Chemistry* 19, 267-279.

457 Watson, K., Farré, M.J., Knight, N.. (2016). Comparing a silver-impregnated activated carbon
458 with an unmodified activated carbon for disinfection by-product minimisation and
459 precursor removal. *Science of the total Environment* 542, 672-684.

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Table 1. Virgin activated carbon characteristics

Carbon Name	Carbon Type	Specific Surface Area ^a	Total Pore Volume ^b	Pore Volume Distribution (cm ³ /g) ^c			Pore Volume Distribution (%)			Oxygen Content	pH _{pzc}
		(m ² /g)	(cm ³ /g)	(<2 nm)	(2<x<50 nm)	(>50 nm)	(<2 nm)	(2<x<50 nm)	(>50 nm)	(%)	(-)
20B	Bituminous Coal	1748	1.42	0.33	0.83	0.26	23.0	58.5	18.5	0.9	5.4
F400	Bituminous Coal	849	0.50	0.31	0.07	0.12	61.9	14.0	24.1	2.4	9.2
WC800	Bituminous Coal	713	0.49	0.23	0.15	0.10	47.3	31.6	21.1	4.1	10.4
HD3000	Lignite Coal	642	0.77	0.11	0.45	0.22	13.9	58.0	28.1	4.4	6.9

^a Specific surface area calculated with the Brunauer-Emmett-Teller (BET) model, ^b Total pore volume calculated from single point adsorption at P/P₀ = 0.99, ^c Pore volume in each pore size range obtained from the density functional theory (DFT) analysis.

Table 2. Selected water quality characteristics of natural waters

	Br⁻ μg/L	Cl⁻ mg/L	Cl⁻: Br⁻ ratio	SO₄²⁻ mg/L	NO₃⁻ mg/L	TOC mg/L	UV₂₅₄ m ⁻¹	SUVA₂₅₄ L/mg-m
Charleston	81	15	189	6	0.08	11.8	0.20	1.7
Myrtle Beach	100	20	195	6	0.53	27.6	1.20	4.4
Bushy Park	80	30	369	6	0.3	4.4	0.17	3.9
Edisto River	33	38	1142	8	0.51	5.0	0.26	5.2
Savanah River	198	40	205	11	1.04	3.3	0.11	3.3
Lake Hartwell	20	3	129	2	0.61	2.1	0.040	1.8
Broad River	95	14	151	6	0.35	5.4	0.16	3.0

Table 3. Activated carbon characterization before and after pre-oxidation and silver impregnation

Sample	Description	SSA _{BET} (m ² /g)	Oxygen %	silver %
WC800	Microporous activated carbon, Calgon, Corp.	644.3	4.1	-
WC800ox2	WC800 oxidized (with 10N HNO ₃ at 90 ⁰ C)	569.3	10.9	-
WC800ox-H	WC800 oxidized with 15.7N HNO ₃ at high temperature (160 ⁰ C)	367.9	18.9	-
WC800ox-L	WC800 oxidized with 15.7N HNO ₃ at low temperature (90 ⁰ C)	624.5	15.1	-
WC800-S15	WC800 impregnated by 1.5M AgNO ₃	62.1	3.9	2.5
WC800ox-H-S01	WC800 oxidized with 15.7N HNO ₃ at high temperature & impregnated with 0.1M AgNO ₃	518.6	13.7	3.4
WC800ox-H -S05	WC800 oxidized with 15.7N HNO ₃ at high temperature & impregnated with 0.5M AgNO ₃	539.1	14.6	10.8
WC800ox-H -S15	WC800 oxidized with 15.7N HNO ₃ at high temperature & impregnated with 1.5M AgNO ₃	369.7	18.5	12.3
WC800ox-L -S05	WC800 oxidized with 15.7N HNO ₃ at low temperature & impregnated with 0.5M AgNO ₃	664.5	14.5	3.4
HD3000	Mesoporous activated carbon Norit, Inc.	642.0	4.4	-
HD3000ox-L	HD3000 oxidized with 15.7N HNO ₃	611.5	16.4	-
HD3000ox2-L	HD3000 oxidized with 10N HNO ₃	626.9	13.6	-
HD3000ox-H	HD3000 high temperature oxidized with 15.7N HNO ₃	373.6	19.1	-
HD3000ox-L	HD3000 low temperature oxidized with 15.7N HNO ₃	530.1	15.9	-
HD3000-S05-L	HD3000 impregnated by 0.5M AgNO ₃	635.3	4.3	2.1
HD3000ox2-L-S05	HD3000 oxidized with 10N HNO ₃ at low temperature & impregnated with 0.5M AgNO ₃	528.4	18.9	7.8
HD3000ox-L-S05	HD3000 oxidized with 15.7N HNO ₃ at low temperature & impregnated with 0.5M AgNO ₃	524.8	19.1	10.4
HD3000ox-H-S05	HD3000 oxidized with 15.7N HNO ₃ at high temperature & impregnated with 0.5M AgNO ₃	370.8	18.9	8.4
F400	Microporous activated carbon Calgon, Corp.	978.0	2.4	-
F400ox-H	F400 oxidized with 15.7N HNO ₃ at high temperature	472.3	19.1	-
F400ox-L	F400 oxidized with 15.7N HNO ₃ at low temperature	905.3	15.6	-
F400ox-H-S05	F400 oxidized with 15.7N HNO ₃ at high temperature & impregnated with 0.5M AgNO ₃	469.8	18.7	6.9
F400ox-L-S05	F400 oxidized with 15.7N HNO ₃ at low temperature & impregnated with 0.5M AgNO ₃	904.8	15.0	2.3
20B	Mesoporous activated carbon Norit, Inc.	1748	0.93	-
20Box-L-S05	20B oxidized with 15.7N HNO ₃ & impregnated by 0.5M AgNO ₃	1681	19.6	3.6
1% commercial SIAC	1.05 wt. percent SIAC, (TOG-NDS-20*50, Calgon Corporation	918.0	N/A	1.1
4% commercial SIAC	4.03 wt. percent SIAC (Nusorb A 20*40, Nucon International, Inc.	658.0	N/A	4.0

Figure 1. Correlation between specific surface area and silver content of SIACs.

Figure 2. Br^- adsorption experiments in DDW by different SIACs (carbon dose: 25mg/L). All Br^- concentrations reported as mean $\pm$ percentage error obtained from duplicates.

Figure 3. (a) Br⁻ removal by 4% commercial SIAC in NOM (2.5 mg/L) and Cl⁻ spiked waters (carbon dose: 50 mg/L). All Br⁻ concentrations reported as mean ± percentage error obtained from duplicates, **(b)** Br⁻ removals by different SIACs in DDW and NOM (2.5 mg/L) solutions, all Br⁻ concentrations reported as mean percentage error obtained from duplicates.

Figure 4. Br⁻ removals by WC800ox-L-S05 SIAC (a) in different source waters and (b) in model solutions. All Br⁻ concentrations reported as mean± percentage error obtained from duplicates.

Figure 5. Alum coagulation (alum dose was 30 mg/L, NOM concentration was 5.4 mg/L) effect on Br^- removal by 4% commercial SIAC in jar test (F400 PAC with no silver was added as black sample). All Br^- concentrations reported as mean $\pm$ percentage error obtained from duplicates.

Figure 6. (a) Br⁻ removals by WC800ox-L -S05 (b) THM formation reduction in NOM and (c) Lake Hartwell raw water and (d) Lake Hartwell water spiked with Cl⁻ (2.5 and 2.1 mg/L TOC for NOM and Lake Hartwell waters, respectively, and SIAC dose was 25 mg/L

TOC ART

Silver Impregnation of Activated Carbon

 Powdered Activated Carbon

+
 Silver

Bromide Adsorption by Silver Impregnated Activated Carbon (SIAC)

Brominated Disinfection Byproduct Control