Graphical Abstract

Reductive Dehalogenation of Disinfection Byproducts by an Activated Carbon-Based Electrode System

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Abstract

Low molecular weight, uncharged, halogenated disinfection byproducts (DBPs) are poorly removed by the reverse osmosis and advanced oxidation process treatment units often applied for further treatment of municipal wastewater for potable reuse. Granular activated carbon (GAC) treatment effectively sorbed 22 halogenated DBPs. Conversion of the GAC to a cathode within an electrolysis cell resulted in significant degradation of the 22 halogenated DBPs by reductive electrolysis at -1 V vs. Standard Hydrogen Electrode (SHE). Removal efficiencies over 6 h electrolysis was lowest for trichloromethane (chloroform; 47%) but were >90% for 13 of the 22 DBPs. In all cases, DBP degradation was higher than in electrolysis-free controls, and degradation was verified by the production of halides as reduction products. Activated carbons and charcoal were more effective than graphite for electrolysis, with graphite featuring poor sorption for the DBPs. A subset of halogenated DBPs (e.g., haloacetonitriles, chloropicrin) were degraded upon sorption to the GAC, even without electrolysis. Using chloropicrin as a model, experiments indicated that this loss was attributable to the partial reduction of sorbed chloropicrin from reducing equivalents in the GAC. Reducing equivalents depleted by these reactions could be restored when the GAC was treated by reductive electrolysis. GAC treatment of an advanced treatment train effluent for potable reuse effectively reduced the concentrations of chloroform (TCM), bromodichloromethane and dichloroacetonitrile measured in the column influent to below the method detection limits. Treatment of the GAC by reductive electrolysis at -1 V vs. SHE over 12 h resulted in significant degradation of the TCM (63%), BDCM (96%) and DCAN (99%) accumulated on the GAC. The results suggest that DBPs in advanced treatment train effluents could be captured and degraded continuously by reductive electrolysis using a GAC-based cathode.

1. Introduction

Recent droughts, impacts of future climate change, and the high population growth in the arid southwestern U.S. have heightened interest in municipal wastewater as a secure, local supply of potable water. The advanced treatment trains frequently employed to purify municipal wastewater to potable quality encompass microfiltration (MF), reverse osmosis (RO), and advanced oxidation processes (AOPs). A physical removal process, RO treatment is able to remove a wide range of pathogens and chemical contaminants when operating properly. However, while RO treatment achieves efficient removal (i.e., high rejection) of charged compounds, the removal efficiency declines with molecular weight for uncharged compounds with molecular weights <250 (Agus and Sedlak, 2010; Linge et al., 2013; Doederer et al., 2014). AOPs typically employ the UV photolysis of hydrogen peroxide to produce hydroxyl radicals as a broad-screen chemical barrier to degrade compounds that pass through the RO membranes.

Regarding chemical contaminants, the National Research Council indicated that concentrations of disinfection byproducts (DBPs), including *N*-nitrosodimethylamine (NDMA), trihalomethanes (THMs), and haloacetonitriles (HANs), in advanced treatment train effluents were far closer to levels of potential human health concern than other compounds such as pharmaceuticals, triclosan and 17 β -estradiol (National Research Council, 2012). Because many halogenated DBPs are of low molecular weight, and uncharged, they can be poorly rejected by RO. For example, while removal efficiencies were >85% for haloacetic acids, which are charged at circumneutral pH, the removal efficiencies for THMs and HANs declined with molecular weight to nearly 60% (Agus and Sedlak, 2010; Linge et al., 2013; Doederer et al., 2014). Experience in Australia showed for an advanced treatment train that RO removed ~95% of the total halogenated organic material (TOX), including high molecular weight material, but only ~40-55% of the low

molecular weight DBPs (Farre et al., 2012). Similarly, RO removal efficiencies for NDMA can be lower than 50% (Plumlee et al., 2008; Gerrity et al., 2015; Sgroi et al., 2015; Dai et al., 2015).

While AOPs effectively reduce *N*-nitrosamine concentrations in advanced treatment trains (Plumlee et al., 2008; Gerrity et al., 2015; Sgroi et al., 2015; Dai et al., 2015), removal of halogenated DBPs, particularly haloacetonitriles, haloketones and chlorinated and brominated trihalomethanes, can be <30% (Farre et al., 2012), suggesting a need to identify technologies for halogenated DBP removal. Granular activated carbon (GAC) treatment of the AOP effluent may be effective for the sorption of halogenated DBPs, but an improved process involving dehalogenation of the sorbed DBPs would ensure prolonged usage of the GAC without breakthrough of the DBPs. Reductive dehalogenation could be achieved by converting the GAC into a cathode within an electrolysis cell. Radjenovic et al. (2012) had evaluated the reductive electrolysis of 17 regulated and emerging DBPs using a resin-impregnated graphite cathode. In deionized water solutions containing mixtures of the 17 DBPs, they observed >70% removal over 24 h of most DBPs when the water was circulated past the cathode at constant potentials of -700, -800 or -900 mV vs. Standard Hydrogen Electrode (SHE). However, removal of chloroform, chloral hydrate and 1,1-dichloropropanone were <50%. Yields of Cl⁻, Br⁻ and I⁻ were ~70%, ~75% and ~90% of theoretical for these DBP mixtures, suggesting degradation rather than loss by sorption to the graphite or volatilization. However, although the concentrations of halogenated DBPs sorbed to the cathode were not measured, the DBPs were poorly sorbed to the resin-impregnated graphite such that the DBPs remained predominantly within the aqueous phase. Accordingly, the removal attributable to electrolysis vs. other aqueous phase degradation processes (e.g., hydrolysis) could not be distinguished. Indeed, the removal at -900 mV vs. SHE increased by less than a factor of 2 (e.g., bromodichloromethane), not at all (chloropicin), or even decreased

(haloacetonitriles) relative to those observed for an open-circuit control. These results suggest that, for this graphite cathode, hydrolysis in the aqueous phase may have been an important driver for dehalogenation of the DBPs rather than reductive electrolysis.

The goal of this study was to evaluate a GAC-based cathode for the capture and reductive dehalogenation of DBPs for potential future application to polish potable reuse treatment train effluents. Specifically, we sought to evaluate reductive dehalogenation of DBPs in batch experiments under conditions wherein DBPs are predominantly sorbed to the GAC, facilitating the differentiation of electrolytic dehalogenation from aqueous phase hydrolysis. We evaluated whether reducing equivalents within the GAC could dehalogenate certain DBPs sorbed to the GAC even without electrolysis, and whether electrolysis could regenerate this population of reducing equivalents. Lastly, we evaluated the potential for removal of halogenated DBPs from an authentic RO effluent of a potable reuse train. Sorption of DBPs to the GAC in column experiments was separated experimentally from degradation of the sorbed DBPs by reductive electrolysis to distinguish these processes. However, the results are relevant to potential future application for continuous treatment of DBPs in potable reuse effluents by GAC-based cathodes.

2. Materials and Methods

2.1. Materials

Chem Service (West Chester, PA, USA) TCNM (98.5% purity), Cansyn (Toronto, Canada) dichloronitromethane (DCNM, 90-95% purity), chloronitromethane (CNM, 90-95% purity), bromodichloroacetaldehyde (BDCAL, 90-95% purity), dibromochloroacetaldehyde (DBCAL, 90-95% purity), bromochloroacetamide (BCAM, 99% purity), dibromoacetamide (DBAM, 90-95%

purity), dichloriodomethane (DCIM, 90-95% purity), chlorodiodomethane (CDIM, 90-95% purity), bromochloriodomethane (BCIM, 90-95% purity), dibromiodomethane (DBIM, 90-95% purity) and bromodiodomethane (BDIM, 90-95% purity), Sigma-Aldrich (St. Louis, MO) nitromethane (NM, > 99% purity), 1,2-dibromopropane (DBP, 97%), bromoform (TBM, 99% purity), tribromoacetaldehyde (TBAL, 97% purity), trichloroacetamide (TCAM, 99% purity) and activated charcoal, Alfa Aesar (Ward Hill, MA) dichloroacetonitrile (DCAN, 98% purity), dichloroacetamide (DCAM, 98% purity), graphite powder and sheet graphite (0.13 mm thickness, catalog number 43078), Norit (Cabot, Alpharetta, GA) Hydrodarco 3000 granular activated carbon (GAC), Calgon (Moon Township, PA) Filtrasorb 300 GAC, Fisher (Pittsburgh, PA) trichloroacetonitrile (TCAN, 98% purity), GAC, ACS grade chloroform (TCM), HPLC grade methyl tert-butyl ether (MtBE), acetonitrile and acetone and Whatman 1.2 μ m glass microfiber filters, Matrix Scientific (Columbia, SC) dibromoacetonitrile (DBAN, 95% purity), Ultra Scientific (Kingstown, RI) bromodichloromethane (BDCM, 95% purity) and dibromochloromethane (DBCM, 95% purity) were used as received. Deionized water was produced by a Millipore Elix 10/Gradient A10 water purification system. All carbon materials were rinsed with deionized water and then oven-dried overnight before use.

2.2. Batch experiments

Norit GAC (0.4 g) was placed in a 1.5 cm $\times$ 4 cm cylinder constructed from sheet graphite to serve as the working cathode. One mL of phosphate-buffered (100 mM) deionized water at pH 7.0 containing 500 nanomoles of each halogenated DBP was added to the GAC-containing cathode, a volume sufficient to just wet the cathode. After 5 min, the cathode was then transferred to the cathodic chamber of an electrolysis cell described previously (Yang et al., 2015). Briefly, the glass

cathode and anode chambers (~50 mL each) were separated by a cation exchange membrane (Ultrex CMI-7000, Membranes International, USA) and filled with deionized water buffered at pH 7 with 100 mM phosphate buffer (Figure S1). Copper wire connected a CH-600D potentiostat (CH Instruments, Austin, TX) to the top of the graphite sheet tube in the headspace (~1 mL) above the water. A Ag/AgCl (1 M KCl) reference electrode (CHI111, porous Teflon tip, CH Instruments) was placed in the cathode chamber within 0.5 cm of the working electrode. A platinum wire (CH Instruments) served as the anode. A constant potential of -1000 mV vs. SHE was applied to the cathode, while the cathodic chamber was continuously stirred with a Teflon-lined magnetic stir bar. After 6 h, the electrolysis was halted and aliquots were immediately extracted for analysis of DBPs. Although dissolved oxygen can compete with DBPs for electrons during electrolysis, dissolved oxygen concentrations were not controlled during the electrolysis, because dissolved oxygen would occur during any practical application. Aliquots of the aqueous phase (10 mL) were extracted by shaking with 3 mL of MtBE containing 100 µg/L 1,2-dibromopropane as an internal standard for 2 min. The GAC was filtered with glass fiber filters and extracted with 16 mL acetone containing 100 µg/L 1,2-dibromopropane as an internal standard. Extracts were analyzed as described below. Controls included GAC-based electrodes containing 0.2 g Norit GAC loaded with 250 nanomoles of each DBP and held in phosphate-buffered deionized water in 24 mL glass vials for 6 h without electrolysis, and phosphate-buffered deionized water spiked with 10 µM of each DBP and held for 6 h.

Additional experiments evaluated the degradation of chloropicrin (TCNM) upon sorption to carbons without electrolysis. Norit Hydrodarco 3000 GAC, Alfa Aesar graphite powder, Fisher GAC, Calgon Filtrasorb 300 GAC or Sigma Aldrich activated charcoal (0.2 g) was transferred into 24 mL glass vials filled with 10 mM phosphate buffer solution at pH 7 and capped with Teflon-

lined caps without headspace. Vials were spiked with TCNM, DCNM or CNM and mixed throughout the experiment using a New Brunswick Scientific (Edison, NJ) tissue culture roller drum. Samples were periodically sacrificed for analysis of ions or organic products. Samples for organic products were extracted immediately after sacrifice. The aqueous phase (10 mL) was extracted by shaking for 2 min with 3 mL MtBE. GAC was filtered by glass fiber filters, transferred into 16 mL vials containing 8 mL of acetone and extracted by shaking for 2 min.

2.3. Column experiments

Initial column experiments evaluated the degradation of TCNM in synthetic water passed over a GAC bed by direct contact with the GAC and by subsequent electrolysis. Phosphate-buffered (10 mM) deionized water at pH 7 was pumped by peristaltic pump at 20 mL/min from a reservoir through Puri-Flex tubing (Masterflex, Vernon Hills, IL) and then a 30 cm section of Tygon[®] (Lima, OH) tubing. At 15 cm along the Tygon section, the TCNM stock solution (25 mM in acetonitrile) was injected by a syringe pump at 0.6 mL/hour to achieve a concentration of 12.5 μ M (Figure S2). A sampling port located ~5 cm below the Tygon section permitted measurement of the influent TCNM concentration. The TCNM solution proceeded into a ~15 mL glass column containing 2.0 g of Norit GAC supported by glass wool. A valve at the effluent was closed to maintain liquid in the GAC bed whenever the peristaltic and syringe pumps were shut off.

The TCNM solution was passed over the column for 8 h, with the column influent sampled every hour, and the effluent sampled every 10 min during the first hour and every 20 min thereafter. After 8 h, the flow was halted for 16 h, and then resumed for another 8 hours with the same sampling protocol. At the end of the second 8 h, flow was halted for 20 h. The valve was then opened and 10 mL of effluent was sampled. The experiment was conducted in duplicate. Aqueous

samples (10 mL) were extracted by shaking for 2 min with 3 mL MtBE containing 100 µg/L 1,2-dibromopropane as an internal standard for analysis of TCNM, DCNM, CNM, NM, and chloroform by gas chromatography with mass spectrometry, as described below. The aqueous phase remaining after MtBE extraction was analyzed for NM, chloride and nitrite as described below.

After the last samples were collected from the column experiment, the GAC in the column was transferred to a beaker, rinsed with deionized water and then filtered with a glass fiber filter. The filtered GAC was separated into five equal aliquots (0.4 g dry weight each). Two aliquots were extracted by 16 mL acetone containing 100 µg/L 1,2-dibromopropane as an internal standard for analysis of TCNM, DCNM and CNM. One aliquot was treated by electrolysis using the electrochemical system described above. A constant potential of -1000 mV vs. SHE was applied to the cathode. After 24 h, the electrolysis was halted and the GAC was immediately extracted with acetone, as described above. Aqueous samples (10 mL) from the cathode chamber were extracted by 3 mL MtBE, as described above. The final two aliquots of GAC were transferred into the same sheet graphite cylinders as used for electrolysis and submerged in 100 mM phosphate-buffered deionized water without electrolysis to serve as controls.

Using the same apparatus, an additional column experiment was conducted using authentic effluent collected from the UV treatment system at an advanced treatment train for tertiary (nitrified) municipal wastewater incorporating MF, RO and UV treatment systems. Chloramines were applied upstream of the MF system. Basic water quality parameters for the UV effluent included pH 7.0, 1.8 mg/L as Cl₂ total chlorine residual (as chloramines), <0.05 mg/L dissolved organic carbon (DOC), 0.8 mg-N/L ammonia, 1.1 mg-N/L nitrate and 32 µS/cm conductivity. Among the halogenated DBPs evaluated for the batch experiments, only chloroform (TCM; 1.9

μg/L), bromodichloromethane (BDCM; 0.3 μg/L) and dichloroacetonitrile (DCAN; 0.5 μg/L) were quantifiable. The water was pumped over the column, containing 5 g of Norit GAC, at 20 mL/min for 8 hours. Effluent samples were collected at the beginning of the run and every hour thereafter for DBP analysis. After 8 h, the GAC was retrieved from the column and mixed. Two aliquots (0.1 g dry carbon each) were extracted with 4 mL acetone for analysis of DBPs. Another two aliquots (0.1 g dry carbon each) were held in 100 mM phosphate-buffered deionized water for 12 h as controls, while the remaining carbon (4.6 g as dry carbon) was treated by electrolysis (-1000 mV vs. SHE) for 12 h in ~200 mL of 100 mM phosphate-buffered deionized water, as described above. After electrolysis, two aliquots of this GAC (0.1 g each as dry carbon) were extracted for analysis of residual DBPs, while the remainder (4.4 g as dry carbon) was placed back into the column. Water was pumped over the column for an additional 8 h and then the GAC received the same electrolytic treatment as described above.

2.4. Analytical Methods

TCNM, DCNM, CNM and chloroform were analyzed by an Agilent (Santa Clara, CA) 6890N gas chromatograph equipped with an Agilent 5973N Mass Selective Detector in selected ion monitoring (SIM) mode. Extracts (2 μL) were injected in splitless mode (inlet temperature 90 °C) onto an Agilent HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was initially held at 35 °C for 11 min, then ramped to 270 °C at 100 °C/min and then held for 1 min (Table S1).

Nitromethane (NM) and other halogenated DBPs were analyzed by an Agilent 7890A gas chromatograph equipped with an Agilent 240 ion trap mass spectrometer. Extracts (5 μL) were injected in PTV solvent vent mode (inlet temperature held at 45 °C for 0.01 min and then ramped

to 170 °C at a rate of 600 °C/min and then held for 5 min) on an Agilent DB-1701 capillary column (60 m × 0.25 mm × 1 µm). For nitromethane (NM), the oven temperature was initially held at 40 °C, then ramped to 150 °C at 10 °C/min, then ramped to 280 °C at 100 °C/min. Under these conditions, the retention time was 9.0 min for NM, and analysis was in the electron ionization (EI) mode (Table S1). For haloacetamides, the oven temperature was initially held at 65 °C for 4 min, then ramped to 205 °C at 20 °C/min, then ramped to 250 °C at 5 °C/min, then ramped to 280 °C at 40 °C/min and held for 1 min. Analysis was in the methanol chemical ionization (CI) mode. For other halogenated DBPs, the oven temperature was initially held at 65 °C for 5 min, then ramped to 170 °C at 4 °C/min and held for 2 min, then ramped to 275 °C at 60 °C/min and held for 2 min. Analysis was in the electron impact (EI) mode (Table S1).

Methylamine was analyzed by an Agilent 1260 system Liquid Chromatography system equipped with a Triple Quad 6460 mass spectrometer in negative ion mode. Aqueous samples (20 µL) were mixed with 20 µL derivatizing agent (10 mM of 6 aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) in acetonitrile) and 60 µL of 0.6 M borate buffer solution (pH = 8.8) (Cohen et al., 1993) and then incubated in a heating block at 55 °C for 10 min. The derivatized sample (20 µL) was injected onto an Agilent Poroshell 120 EC-C18 column (3 cm × 50 mm, 2.7 µm). The eluents were acetonitrile and a 5 mM ammonium acetate aqueous solution at a total flowrate of 0.4 mL/min, as follows: 95% aqueous and 5% acetonitrile for 2 min, a linear gradient to 10% aqueous and 90% acetonitrile over 4 min and maintained for 2 min, and a linear gradient to 95% aqueous and 5% acetonitrile over 1 min, maintained for 5 minutes (Table S1).

Chloride, bromide and iodide were measured by ion chromatography using a Dionex DX-500 Ion Chromatograph equipped with an AS-11 column heated to 35 °C and a conductivity detector. The mobile phase consisted of 20 mM NaOH at 1 mL/min. Total chlorine residual was

measured colorimetrically by the DPD method (American Public Health Association, 1998). Nitrate was measured colorimetrically using a WestCo SmartChem 200 discrete analyzer. Ammonia and nitrite were measured colorimetrically using Hach methods 10023 (salicylate) and 8507 (diazotization), respectively. DOC was measured using a Shimadzu TOC-L CPH total organic carbon analyzer.

3. Results and Discussion

3.1. Electrolytic degradation of DBPs in batch reactors

Radjenovic et al. (2012) demonstrated with a resin-impregnated graphite cathode that reductive electrolysis could represent a promising treatment technology for halogenated DBPs, due to its potential to promote dehalogenation. However, the relatively low degradation efficiencies observed (~20%-95% with most in the ~60% range) over 24 hours of treatment suggested that this technology would not be feasible for treatment of a continuous flow of water. Indeed, for many of the DBPs, the degradation efficiency was the same or even lower than observed in open circuit (i.e., electrolysis-free) controls. Suspecting that the low degradation was attributable to poor sorption of the DBPs to the resin-impregnated graphite electrode, we evaluated activated carbons due to their higher sorption capacity. We conducted an initial experiment in which a mixture of 4 haloacetonitriles, 9 trihalomethanes, 4 haloacetaldehydes, 4 haloacetamides and chloropicrin (500 nanomoles each) were loaded onto 0.4 g Norit GAC. The GAC was converted into a cathode for treatment in a batch reactor by reductive electrolysis at -1,000 mV vs. SHE at pH 7 (100 mM phosphate buffer). Under these conditions, >90% removal was achieved over 6 h for 13 of the 22 DBPs (Figure 1A). Removal of the more highly chlorinated analogues of trihalomethanes, haloacetaldehydes and haloacetamides was more challenging. The lowest

removal percentage was achieved for chloroform (~47% removal). Radjenovic et al. (2012) also observed poor removal of the more chlorinated analogues of trihalomethanes and haloacetaldehydes, but they did not evaluate haloacetamides. Dehalogenation by reductive electrolysis was confirmed by measuring yields of Cl^- , Br^- and I^- at 84.2%, 100% and 96.5%, respectively, relative to the loss of parent DBPs (Figure 1B).

Generally, DBP removal by reductive electrolysis was significantly improved relative to controls in which DBPs were held for 6 h in the phosphate-buffered solution without GAC or electrolysis, and in which the GAC-based cathode exposed to DBPs was held in the phosphate-buffered solution without electrolysis. Electrolysis reduced TCM concentrations relative to the electrolysis-free GAC control. TCM was lost from the aqueous control, most likely due to volatilization; the estimated hydrolysis half-life for TCM at pH 7 is ~2,000 years due to the steric hindrance imparted by the three chlorines (Schwarzenbach et al., 2003). For several other DBPs, the residual mass was lower for the aqueous controls than for the electrolysis-free GAC controls, concurring with the results of Radjenovic et al. (2012) that hydrolysis of these DBPs in the aqueous phase does occur. Within the electrolysis-free, GAC control, the percentage of DBPs sorbed to the GAC after 6 h was ~20% for haloacetonitriles, ~35-50% for haloacetamides, chloropicrin and trichloroacetaldehyde (chloral hydrate or TCAL), and >50% for all other DBPs. Despite the relatively low percentage of haloacetonitriles sorbed to the GAC, they were all nearly completely removed during electrolysis, and unlike the findings of Radjenovic et al. (2012), greater removal was observed upon electrolysis than in the electrolysis-free control. Substantial removal of several DBPs was observed upon contact with GAC even without electrolysis, with dehalogenation confirmed via measurements of halide yields (Figure 1B). For example, similar to Radjenovic et

al. (2012), we observed nearly quantitative (i.e., complete) removal of TCNM upon exposure to carbon, with or without electrolysis.

3.2. GAC-mediated degradation of TCNM in batch reactors

The degradation of DBPs upon contact with the GAC even without electrolysis suggested a key role for carbon beyond sorption of the DBPs to provide contact with electrons from the electrolysis unit. Li et al. (2010) similarly observed partial dehalogenation of bulk halogenated organic material upon extraction of DBPs with carbon-based materials. To better characterize these reactions, we conducted additional batch reactor experiments using TCNM as an example DBP in the presence of loose GAC (i.e., not contained within sheet graphite) without electrolysis; TCNM was selected because its nearly quantitative removal (Figure 1A) facilitated characterization of this process. Rapid degradation of 100 μM TCNM in a batch reactor was observed in the presence of 8.3 g/L Norit GAC at pH 7 (Figure 2A). The reaction followed pseudo-first order kinetics, with an observed rate constant (k_{obs}) of 0.0985 min^{-1} ($\pm 0.007 \text{ min}^{-1}$ standard error of the regression) and a half-life of 7.0 min. Dichloronitromethane (DCNM) was the major organic product (Figure 2B), reaching 58 μM (87% of the TCNM degraded) at 10 min and then declining. No degradation was seen when a TCNM stock solution in acetonitrile was spiked via syringe directly onto GAC in the absence of deionized water, consistent with the requirement for protons to form DCNM according to equation 1:

Low concentrations of chloronitromethane (CNM) were measured throughout, with the maximum concentration of 0.34 μM measured after 1 min. Chloride accumulated throughout, reaching 268

μM after 30 min, suggesting nearly complete dehalogenation. The chlorine atom balance, measured according to equation 2, was ~100% throughout (Figure 2B).

$$[\text{Cl}]_{\text{total}} = 3[\text{TCNM}] + 2[\text{DCNM}] + [\text{CNM}] + [\text{Cl}^-] \quad [2]$$

Nitromethane (NM), methylamine (MA), nitrate and ammonia were not detected. Total nitrogen and carbon balances were calculated using equations 3 and 4:

$$[\text{N}]_{\text{total}} = [\text{TCNM}] + [\text{DCNM}] + [\text{CNM}] + [\text{NO}_2^-] \quad [3]$$

$$[\text{C}]_{\text{total}} = [\text{TCNM}] + [\text{DCNM}] + [\text{CNM}] \quad [4]$$

While nitrogen and carbon balances were nearly 100% over the first 10 min, during which DCNM was the primary product, they declined thereafter to ~20-30% after 30 min (Figure 2C and 2D). Although nitrite accumulated slowly in the aqueous phase, accounting for 16% of the total nitrogen after 30 min, chloroform was not detected. These results suggest that cleavage of the C-N bond was relatively unimportant.

For experiments starting with 100 μM DCNM or CNM, half-lives were 6.4 min for DCNM and 5.4 min for CNM in the presence of GAC. Chloride was detected in the aqueous phase for both experiments, accounting for 91.8% and 99.1% of the total chlorine in the CNM and DCNM removed, respectively, after 30 min. In contrast, when the experiment was started with 100 μM NM, no significant loss was observed over 30 min. When the reaction was initiated with DCNM, neither CNM nor NM was detected throughout the 30 min reaction; although CNM degradation was faster than degradation of DCNM, some CNM, and certainly NM, should have been detectable if DCNM degradation proceeds via sequential loss of chloride to form NM. Thus, TCNM degradation appears to involve dechlorination to form DCNM, followed by further dehalogenation, but not via CNM or NM. The initial production of DCNM, and lower yields of CNM also were observed in previous research when TCNM was treated with hydrogen sulfide (Zheng et al., 2006)

or zero-valent iron (Pearson et al., 2005). The nature of the dehalogenated intermediate remains unclear, yet full dehalogenation is achieved. As indicated above, the low yield of nitrite and lack of detection of chloroform suggests that C-N bond cleavage was minor. Additionally, when the carbon was subjected to reductive electrolysis, we obtained high yields of methylamine (see below), confirming that C-N bond cleavage was minor. Methylamine was also reported as the major product of TCNM reduction by zero-valent iron (Pearson et al., 2005).

3.3. Effect of carbon properties on reactivity

Previous research has indicated that redox-active functional groups in black carbons, such as phenols and quinones, can be reduced or oxidized reversibly such that black carbons can behave as capacitors, reversibly storing and releasing electrons (Klүpfel et al., 2014). Using a similar electrolysis apparatus to ours, Klүpfel et al. (2014) observed that the capacitance of the carbon did not vary over several oxidation and reduction cycles, indicating that electrolysis did not create new pools of redox-active functional groups. To evaluate whether this type of electron storage was responsible for TCNM degradation, 0.2 g aliquots of Norit GAC were pretreated by electrolysis as -1 V (reduced GAC) or +1 V (oxidized GAC) vs. SHE for 1 h. The extent of TCNM (100 μ M) removal after 10 min of reaction in 10 mM phosphate-buffered deionized water at pH 7 followed the order oxidized GAC < native GAC < reduced GAC (Figure 3A). For a control in the absence of GAC, no significant TCNM loss was observed. With DCNM and chloride as the major products, nearly 100% chlorine balance was maintained for each GAC.

To evaluate the consumption of reactivity by TCNM, 0.2 g aliquots of Norit GAC were first treated with 100 μ M of TCNM for 30 min (achieving ~95% removal of TCNM). For one set of samples, denoted as “used GAC”, the GAC was separated by filtration and transferred to another

batch of 10 mM phosphate-buffered deionized water at pH 7 containing 100 μ M TCNM. For another set of samples, the filtered GAC was treated by reductive electrolysis at -1 V vs. SHE for 1 h. This GAC, denoted as “regenerated GAC”, was transferred to another batch of 10 mM phosphate-buffered deionized water at pH 7 containing 100 μ M TCNM. TCNM degradation by “used GAC” was much slower than that of the original GAC (Figure 3B), suggesting depletion of the stockpile of reducing functional groups within the GAC. For “regenerated GAC”, TCNM decay was faster than the original GAC, suggesting an increased population of reduced redox-active functional groups on the GAC surface. The TCNM remaining after 10 min of treatment with the “Regenerated GAC” (Figure 3B) was within 10% of the TCNM measured after 10 min contact with the “Reduced GAC” (Figure 3A), as expected given that the GAC for these experiments received the same reductive electrolysis treatment. These results indicated that, although TCNM reduction depletes the capacitance of the GAC, the reactivity of GAC could be regenerated by electrolysis.

When treating authentic waters, other organic constituents in the water are anticipated to compete with DBPs for sorption to the GAC. For an initial evaluation, a surface water sample (pH 8.8, DOC = 2.5 mg/L) was spiked with 100 μ M TCNM. In the absence of Norit GAC, no loss of TCNM was observed over 30 min. When this sample was spiked with 0.2 g of Norit GAC, the TCNM concentration declined over 45 min with a half-life of 13 min (Figure 3B). Although the degradation rate was slower than for the reaction in phosphate-buffered deionized water, > 90% removal was achieved within 45 min.

Lastly, several commercial GACs and other carbon materials were compared regarding their reactivity toward TCNM (Figure 3C). With respect to TCNM degradation, Sigma-Aldrich Activated Charcoal (ACC) was the most reactive and graphite powder (GP) was the least reactive.

The three GACs, Norit lignite-based GAC (NGAC), Fisher coconut shell-based GAC (FGAC), and Calgon bituminous coal-based GAC (CGAC), exhibited intermediate reactivity, although NGAC featured the greatest conversion to chloride. TCNM degradation may be limited by mass transfer to the carbon surface, which would be expected to increase with decreasing particle diameter and increasing specific surface area. TCNM degradation might also be limited by the reactivity of the carbon with respect to electron transfer, which may relate to carbon conductivity and the prevalence of surface redox-active oxygenated functional groups (e.g., quinones) (Xu et al., 2013). Previous analysis of the same graphite powder, the least reactive material, indicated that although graphite powder has a high conductivity (9.65 S/mm) and low particle diameter (45 μm), it has a very low specific surface area (9.5 m^2/g) and <0.01% by weight oxygen content (Xu et al., 2015). The activated charcoal (ACC), the most reactive material, featured a high conductivity (73 S/mm according to the manufacturer), low particle diameter (34 μm average), and a relatively high specific surface area (600 m^2/g); although the oxygen content was not reported, it is expected to be comparable to the activated carbons. The activated carbons, which featured intermediate reactivity, exhibited high particle diameters (0.7-3.4 mm) and specific surface areas (650 m^2/g for Norit GAC, 1088 m^2/g for Fisher (Xu et al., 2013), and 1000 m^2/g for Calgon). The Fisher GAC exhibited a low conductivity (0.92 S/mm), but a high oxygen content (15.9% by weight) (Xu et al., 2013); these characteristics were not available for the other carbons, but likely were similar. The results suggest the importance of a high specific surface area, the common denominator for the GACs and ACC, although the additional features of high conductivity and low particle diameter also likely contributed to the high reactivity of ACC.

3.4. Column experiments

A column experiment evaluated TCNM removal in synthetic water. When TCNM (12.5 μ M) was passed over a column containing 2.0 g Norit GAC at 20 mL/min, the effluent TCNM concentration slowly increased over time (Figure 4A). Based on the batch experiment, we expected the TCNM sorbed to the GAC to slowly degrade. To capture this effect, the flow was halted after the first 8 h for a period of 16 h, and then re-started. The effluent TCNM concentration dropped, but then the TCNM concentration increased at a faster rate. However, even after 8 additional hours of flow (i.e., 16 h of flow overall), the TCNM concentration was only 6.9% of the influent concentration. The flow was then halted again for a period of 24 h, and then re-started, and the TCNM effluent concentration again dropped significantly (Figure 4A).

The low effluent TCNM concentration resulted from TCNM degradation rather than just sorption. DCNM concentrations in the effluent increased steadily, reaching 52% yield compared to the TCNM influent concentration. Like TCNM, DCNM concentrations dropped significantly when the flowrate was halted and then resumed. CNM concentrations remained low throughout. Chloride, and to a lesser degree, nitrite were observed in the effluent, and the concentrations of both spiked when the flowrate was temporarily halted and then resumed. The total chloride mass yield was 160% compared to the influent TCNM mass (i.e., 53% chlorine atom balance) during continuous flow operations, rising to 260% (87% chlorine atom balance) when considering the entire experiment, including the yields achieved when the flow was temporarily halted.

As discussed with respect to the batch experiments, the reactivity of GAC depends on its reductive capacity, which is consumed upon exposure to TCNM. When GAC is used for continuous treatment, the time to breakthrough is expected to decrease as the reactive capacity of the GAC is exhausted. At the end of the experiment, the GAC was extracted for analysis of TCNM,

DCNM and CNM; significant amounts of TCNM and DCNM were observed (“pre-electrolysis” in Figure 4B). We expected that periodic electrolysis of the GAC could complete the reductive dehalogenation of the sorbed halonitromethanes. Aliquots of the GAC were treated in a batch reactor by reductive electrolysis at -1.0 V vs. SHE for 24 h, achieving removal of all of the residual TCNM and DCNM on the GAC; no TCNM or DCNM were observed in the aqueous phase. The yields of chloride and methylamine (MA) were nearly quantitative, and were all in the aqueous phase (Figure 4B). Additional aliquots were exposed to water for 24 h in the absence of electrolysis as a control. While the TCNM concentration continued to decline, both TCNM and DCNM remained, the molar yield of chloride was not quantitative, and MA was not observed.

A similar column experiment was conducted to treat authentic effluent from an advanced treatment train treating tertiary municipal wastewater by MF, RO and UV treatment. The UV effluent contained 1.9 µg/L TCM, 0.3 µg/L BDCM and 0.5 µg/L DCAN. After passage of the UV effluent over a column containing 5 g of Norit GAC at 20 mL/min, the concentrations of TCM, BDCM and DCAN remained below their detection limits (0.11 µg/L, 0.04 µg/L and 0.10 µg/L, respectively) over 8 h. After 8 h, the mass of DBPs extracted from aliquots of the GAC was within 10% of the mass applied to the GAC over the 8 h of treatment (Figure 5). Electrolytic treatment at -1 V vs. SHE for 12 h removed 63% of TCM, 96% of BDCM and 99% of DCAN, compared to removal in electrolysis-free controls of 29%, 54% and 78% respectively. After electrolytic treatment, the GAC was packed back into the column and used to treat the same UV effluent for an additional 8 h. The DBP concentrations in the GAC column effluent remained below the method detection limits. After 8 h, the GAC was treated via electrolysis, and the removal percentages for the DBPs were similar to those from the first cycle for the electrolysis aliquots and the controls (Figure 5).

4. Conclusions

Because they are poorly removed by RO and AOP treatment, low molecular weight, uncharged, halogenated DBPs may be important drivers of the residual toxicity in advanced treated municipal wastewater for potable reuse. Column studies demonstrated that activated carbon effectively sorbed these compounds, and degradation of DBPs sorbed to the GAC would inhibit column breakthrough and prolong the use of the GAC. Conversion of the GAC to a cathode within an electrolysis cell resulted in significant degradation of 22 halogenated DBPs by reductive electrolysis at -1 V vs. SHE. Removal efficiencies over 6 h electrolysis was lowest for TCM (47%) but were >90% for 13 of the 22 DBPs. In all cases, DBP degradation was greater than in electrolysis-free controls, and degradation was verified by the production of halides as reduction products. Activated carbons and charcoal were more effective than graphite for electrolysis, likely due to their greater ability to sorb the DBPs. A subset of halogenated DBPs (e.g., haloacetonitriles, chloropicrin) were degraded upon sorption to the GAC, even without electrolysis. Using chloropicrin as a model, experiments indicated that this loss was attributable to the partial reduction of sorbed chloropicrin from reducing equivalents in the GAC. Reducing equivalents depleted by these reactions could be restored when the GAC was treated by reductive electrolysis. GAC treatment of an advanced treatment train effluent for potable reuse effectively reduced the concentrations of TCM, BDCM and DCAN measured in the column influent to below the method detection limits. Treatment of the GAC by reductive electrolysis at -1 V vs. SHE over 12 h resulted in significant degradation of the TCM (63%), BDCM (96%) and DCAN (99%) accumulated on the GAC.

The ability of GAC-based electrodes to efficiently sorb and sequester DBPs is a major advantage in that it decouples the water and DBP residence times. While the water can be treated over short empty bed contact times (< 1 hr), the DBPs sorbed to the carbon could be degraded over longer timescales. Although the degradation efficiency for certain DBPs was poor (e.g., chloroform), the percentage degradation could be improved by increasing the electrolysis time without impacting the residence time of the water. However, it is important to note that the reductive electrolysis preferentially targets the DBPs featuring the highest toxicity. The contribution of DBPs to the toxicity of a water is a function of both their concentrations and their toxic potencies. For example, for the advanced treated wastewater effluent, the concentrations associated with a 50% reduction in growth of Chinese hamster ovary (CHO) cells in chronic cytotoxicity assays (i.e., LC_{50} values) are 9.17×10^{-3} for chloroform, 1.15×10^{-2} M for bromodichloromethane (Plewa and Wagner, 2009), and 5.73×10^{-5} for dichloroacetonitrile (Muellner et al., 2007). To weight these DBPs by their toxic potencies, their measured concentrations can be divided by these LC_{50} values. If the cytotoxicity of these DBPs are additive, the electrolysis treatment reduced the DBP-associated cytotoxicity (calculated as the sum of these ratios) by 98%.

In our experiments, the loose GAC particles were removed from the GAC columns for separate, periodic treatment by electrolysis to distinguish the sorption and degradation processes. A more desirable configuration would be to employ GAC-based electrodes to continuously capture and degrade DBPs in advanced treatment train effluents. Work is ongoing in our laboratory to design GAC-based electrode materials suitable for this purpose. In particular, electrode materials must retain the high specific surface area needed to capture and concentrate the DBPs, but the junction resistance between GAC particles must be reduced to increase the conductivity of the

electrodes. Placement of these electrodes downstream of the RO should prolong their lifetimes, because the significant removal of organic matter by the RO should inhibit electrode fouling. Although total chlorine residuals would be quenched by GAC, certain utilities practicing Indirect Potable Reuse (IPR) are not required to maintain a residual in their effluents. For those utilities that must carry a residual, they often must boost the total chlorine residual after the advanced treatment train to counteract losses in the AOP. While placement of a GAC-based cathode between the AOP and chlorine boosting station would necessitate addition of more chlorine, it would reduce subsequent DBP formation by partial removal of DBP precursors.

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Figure 1: A) Percentage remaining of a mixture of 10 μM DBPs after 6 h in deionized water. Aqueous control = concentration after 6 h in deionized water without GAC, GAC control = concentration after 6 hours in the presence of the GAC-based electrode without electrolysis, Electrolysis = concentration after 6 h in the presence of the GAC-based electrode with electrolysis at -1000 mV vs. S.H.E. B) Production of halides under the same conditions. Theoretical yields were calculated by multiplying the concentrations of each DBP removed by electrolysis by their corresponding numbers of each halogen atom and summing over all DBPs. Error bars represent the range of experimental duplicates.

A)

B)

Figure 2

Figure 2. Degradation of 100 μM TCNM vs. time in the presence of 8.3 g/L Norit GAC in deionized water at pH 7. A) Pseudo-first order decay plot for TCNM. B) Chlorine balance. C) Nitrogen balance. D) Carbon balance. Error bars represent the range of experimental duplicates. A)

B)

c)

D)

Figure 3

Figure 3. 100 μM TCNM in the presence of 8.3 g/L of different carbon materials in deionized or surface water at pH 7. A) Comparison of chlorine balance for original, reduced and oxidized Norit GAC after 10 min treatment. Oxidized = GAC pre-treated by electrolysis at +1 V. Reduced = GAC pre-treated by electrolysis at -1 V. B) Comparison of TCNM decay using original, used and regenerated Norit GAC in deionized water or original Norit GAC in a surface water. C) Comparison of chlorine balance for different commercial carbon materials. NGAC = Norit GAC, FGAC = Fisher GAC, CAC = Calgon GAC, GP = graphite powder, ACC = Sigma Aldrich activated charcoal. Error bars represent the range of experimental duplicates.

A)

B)

C)

Figure 4: A) Effluent concentrations from the column (2 g Norit GAC) experiment fed at 20 mL/min with 12.5 μM TCNM in phosphate-buffered (10 mM) deionized water at pH 7. The run was paused after 8 h for 16 h, resumed for 8 h and paused again for 20 h. B) Electrolysis of GAC from the column experiment. Initial = Compounds extracted from the GAC retrieved from the column experiment. Control = 8.3 g/L of GAC from the column experiment in 10 mM phosphate buffer at pH 7 for 24 h without electrolysis. Electrolysis = 8.3 g/L of GAC from the column experiment in 10 mM phosphate buffer for 24 h with an applied potential of -1 V vs S.H.E. Error bars represent the range of experimental duplicates.

A)

B)

Figure 5: Mass balance of DBPs in column experiments treating authentic UV effluent from an advanced wastewater treatment plant over two cycles of 8 h flow over a column containing 5 g Norit GAC at 20 mL/min and 12 h of electrolysis of the GAC at -1 V vs. SHE in 100 mM phosphate-buffered deionized water. A) Cycle 1. B) Cycle 2. Influent = DBP mass passed over the column calculated by multiplying the influent concentration ($\mu\text{g/L}$) by the flow rate and the experimental time. Pre-electrolysis = the DBP mass extracted from the GAC after the 8 h column experiment. Post-electrolysis = the remaining amount of DBPs after electrolysis. Control = the amount of DBPs on the GAC after 12 h in 100 mM phosphate buffer without electrolysis. Error bars represent the range of experimental duplicates.

B)