



# 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). The lowest removal efficiency over 6 h electrolysis was for trichloromethane (chloroform; 47%) but removal efficiencies 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, 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 chloroform (63%), bromodichloromethane (96%) and dichloroacetonitrile (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.

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## 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 micro-filtration (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

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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 $\beta$ -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; Zeng et al., 2016). 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 (Farré 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; Zeng et al., 2016).

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; Zeng et al., 2016), removal of halogenated DBPs, particularly haloacetonitriles, haloketones and chlorinated and brominated trihalomethanes, can be <30% (Farré et al., 2012; Zeng et al., 2016), 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<sup>–</sup>, Br<sup>–</sup> and I<sup>–</sup> 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 (chloropicrin), 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  $\mu$ 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 nmol 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 (Fig. S1). A 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

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