Comparing a silver-impregnated activated carbon with an unmodified activated carbon for disinfection by-product minimisation and precursor removal

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HIGHLIGHTS

- Silver-impregnated activated carbon controlled brominated and chlorinated DBPs
- Unimpregnated GAC led to brominated DBP formation from poor bromide adsorption.
- Halides and organic matter were adsorbed by both activated carbons.

GRAPHICAL ABSTRACT
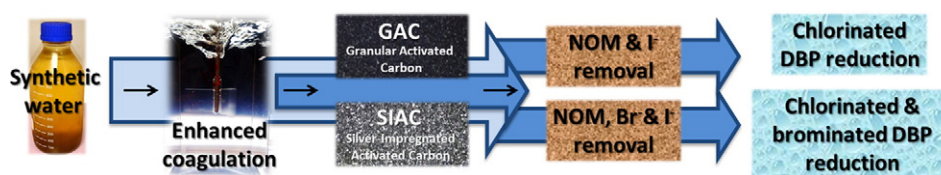
ABSTRACT

During disinfection, bromide, iodide and natural organic matter (NOM) in source waters can lead to the formation of brominated and/or iodinated disinfection by-products (DBPs), which are often more toxic than their chlorinated analogues. The objective of this study was to compare the efficiency of a silver-impregnated activated carbon (SIAC) with the equivalent unimpregnated granular activated carbon (GAC) for the removal of bromide, iodide and NOM from a matrix of synthetic waters with variable NOM, halide, and alkalinity concentrations, and to investigate the impact on DBP formation. An enhanced coagulation (EC) pre-treatment was employed prior to sample exposure to either carbon adsorbent. Excellent halide removals were observed by the SIAC treatment across the sample matrix, with iodide concentrations consistently reduced to below the method reporting limit (<2 μg/L) from as high as 25 μg/L, and $95 \pm 4\%$ removal of bromide achieved. Bromide removal by unimpregnated GAC was poor, however iodide removal was comparable to that achieved by SIAC. The combination of EC with SIAC treatment removed $77 \pm 8\%$ of the dissolved organic carbon (DOC) present, across the sample matrix, which was similar to removals by EC/GAC ($67 \pm 14\%$). Combined EC/SIAC treatment reduced both total trihalomethanes (tTHMs) and total dihaloacetonitriles (tDHANs) formation by $97 \pm 3\%$, while also achieving a greater than 74% removal of two chloropropanones and a $92 \pm 8\%$ decrease in chloral hydrate (CH), compared to untreated samples, regardless of the sample's starting water quality (bromide, alkalinity and NOM concentration). Combined EC/GAC treatment led to similar DBP removals to EC/SIAC for the fully chlorinated DBPs, however, brominated DBPs were less efficiently removed, or experienced concentration increases.

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1. Introduction

The presence of bromide and iodide in source waters can result in the formation of bromide and/or iodide containing disinfection by-products (DBPs) upon exposure to natural organic matter (NOM) and disinfectant (von Gunten, 2003). Brominated and iodinated DBPs are

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often more toxic than their chlorinated analogues (Plewa et al., 2004; Richardson, 2003; Richardson et al., 2007). Coastal drinking water sources can contain high concentrations of bromide and iodide due to seawater intrusion, which may increase the formation of brominated and iodinated DBPs, and thus alter treated water toxicity, depending on the treatment and disinfection strategy applied (Bichsel and von Gunten, 2000; von Gunten, 2003). For example, brominated trihalomethane (THM) formation is favoured by chlorination, and iodinated THM formation is favoured by chloramine disinfection (Richardson, 2003). Although bromide will generally occur at higher concentration than iodide in a salinity-impacted source water, research suggests many iodinated DBPs should be considered more toxic than their brominated analogues (Richardson, 2003). Most conventional water treatment methods, such as coagulation, are not capable of halide removal, thus, there is a need to develop practical means of applying halide removal with concurrent NOM removal prior to water disinfection, in order to minimise exposure to brominated and/or iodinated DBPs.

Activated carbons are effective adsorbent materials widely used in drinking water treatment to remove various organic pollutants because of their high, non-specific adsorption capacity (Thomas and Crittenden, 1998). The use of granular activated carbons (GAC) in organic DBP precursor removal has been widely reported (Owen, 1998). The surface of activated carbons can be modified to enhance their affinity for specific contaminants (Bhatnagar et al., 2013). Silver-impregnated activated carbons (SIAC) have extensive applications in point-of-use (POU) treatment of domestic drinking water, beverage and food industry, mineral water bottling, and laboratory POU water treatment systems (Manocha, 2003; Marsh and Rodríguez-Reinoso, 2006). They provide highly efficient NOM removal, as well as being a safe and effective method of controlling/preventing bacterial growth (Bandyopadhyaya et al., 2008). Toxicity from silver leaching can be readily controlled by a dedicated silver-impregnation process, ensuring silver leaching remains well below EPA recommended limits (secondary maximum contaminant level for silver is 0.1 mg/L) when the material is used appropriately (Cabot Norit Activated Carbon, 2010). In household POU water treatment, SIAC is typically used as a final polishing treatment on municipal water supplies which have been subject to pre-treatments including coagulation, at the water treatment plant (WTP).

Moreover, SIAC and GAC have been shown to remove iodide from aqueous solutions (Ho and Kraus, 1981; Hoskins et al., 2002; Karanfil et al., 2005; Kaufhold et al., 2007). Previous work (Hoskins et al., 2002) used X-ray diffraction to observe changes in the silver halide crystallites on the SIAC surface before and after reaction with iodide. This work demonstrated that anion exchange of chloride for iodide occurred in the silver precipitate on the carbon surface as a result of solubility differences between silver chloride and silver iodide ($K_{sp} = 10^{-10}$ and 10^{-17} for $AgCl(s)$ and $AgI(s)$, respectively). The same study (Hoskins et al., 2002) found that iodide uptake increased with decreasing pH for both SIACs and their virgin GACs, with similar iodide removal capacity between SIAC and GAC at low pH (pH = 5). They demonstrated that a combination of pH dependent adsorption onto GAC, and precipitation of silver iodide was responsible for the observed iodide removal. The adsorption onto GAC was attributed to the presence of a more positively charged GAC surface and less competition from hydroxide ions at lower pH values. Other authors (Maes et al., 2004) suggest that direct iodide adsorption onto GAC does not occur, rather, that oxygen-dependent oxidation of iodide to iodine occurs under aerobic conditions and it is this species that adsorbs to GAC, in accordance with the well-known high affinity of iodine for GAC (Juhola, 1975). Bromide adsorption by SIAC has not been previously reported, to the extent of the authors' knowledge, however, bromide removal using other silver-impregnated adsorbents has been documented (Sánchez-Polo et al., 2006, 2007). Although the silver impregnation of activated carbon has not previously been used for bromide removal from drinking waters, this technique has potential for use in this application, since both NOM and halides may concurrently be lowered using this method,

thereby mitigating brominated and iodinated DBP formation, as well as chlorinated DBP formation. However, further research is required in the areas related to; effect of competing anions, efficiency in complex water matrices, impact of varying water conditions, and the optimisation of the technique for large scale water treatment plants (Watson et al., 2012).

The objectives of this study were to: compare two combined water treatment strategies, specifically; enhanced coagulation (EC) followed by SIAC treatment, and EC followed by GAC treatment, in terms of the reduction of 1) bromide, 2) iodide, 3) NOM, 4) THMs, 5) dihaloacetonitriles (DHANs), 6) chloropropanones, and 7) chloral hydrate (CH) in finished (chlorinated) waters. A statistically designed, complex matrix of synthetic waters was used to this end, encompassing variable concentrations of NOM, alkalinity, bromide and iodide.

2. Experimental

2.1. Reagents

Chemicals were purchased from the following suppliers — Accustandard: mixed standard of trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM), 2.0 mg/mL in methanol; 1,2-dibromopropane, 5 mg/mL in methanol; and mixed standard of dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), 1,1-dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), CH, and trichloronitromethane (TCNM), 1 mg/mL in acetone. Orchid Cellmark (Canada): dichloroiodomethane (DCIM) (95%), chlorodiiodomethane (CDIM) (90–95%), bromochloroiodomethane (BCIM) (95%), dibromoiodomethane (DBIM) (95%) and bromodiiodomethane (BDIM) (90–95%). Acros organics: phosphate buffers (Na_2HPO_4 and KH_2PO_4) (99%) and ascorbic acid (ACS grade). Sigma-Aldrich: $Al_2(SO_4)_3 \cdot 18H_2O$ (98%), NaOCl (≥4%), $MgSO_4$ (≥99.5%), $CaSO_4 \cdot 2H_2O$ (98%), $NaHCO_3$ (99.7–100.3%), methyl *tert*-butyl ether (MtBE) (≥99.8%), and NaBr (≥99.0%). ThermoFisher: NaCl (99.95%). Merck: HCl (32%) and KI (99.5%). Chem-supply: NaOH (≥98%). Malcron chemicals: sodium sulfate (anhydrous) 99.7%. Suwannee river (whole) NOM isolate was purchased from the International Humic Substances Society (batch number 1R101N). Commercial DPD test kits (HACH) were used for the analysis of free chlorine (method 8021). Norit 18 × 40AG1 (0.1% Ag) SIAC and Norit GCN1840 GAC were donated by Cabot Norit, Amersfoort, The Netherlands.

2.2. Synthetic water matrix

A statistically designed matrix of 18 synthetic waters (17 plus blank) of variable water quality characteristics was utilised for all DBP formation potential and DBP precursor removal experiments, as previously published (Watson et al., 2015b). Two replicate batches of the 18 synthetic waters were made; one for EC and EC/GAC treatment, and the other for EC and EC/SIAC treatment. Each batch included 3 centrepoint replicates and a blank sample containing centrepoint concentrations of all chemical components except NOM, bromide and iodide, which were excluded. The triplicate centrepoint samples of both batches were subjected to all treatments, in order to assess experimental reproducibility throughout the various processes. The experimental matrix was developed based on a face-centred central composite design, with 3 variables each occurring at 3 levels, namely; NOM concentration (3 mg/L, 7.5 mg/L, and 12 mg/L DOC), halide precursor concentration (100 μg/L, 450 μg/L, or 800 μg/L bromide, and 4 μg/L, 18 μg/L, or 32 μg/L iodide) and mineral alkalinity (38 mg/L, 138 mg/L, or 238 mg/L as $CaCO_3$) (Table SI 1). Each synthetic water sample was made using 2 L of laboratory purified water, and halide, DOC, and alkalinity concentrations were measured both before treatment and after each treatment. Sodium chloride, calcium sulfate and magnesium