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Effect of capacitive deionization on disinfection by-product precursors

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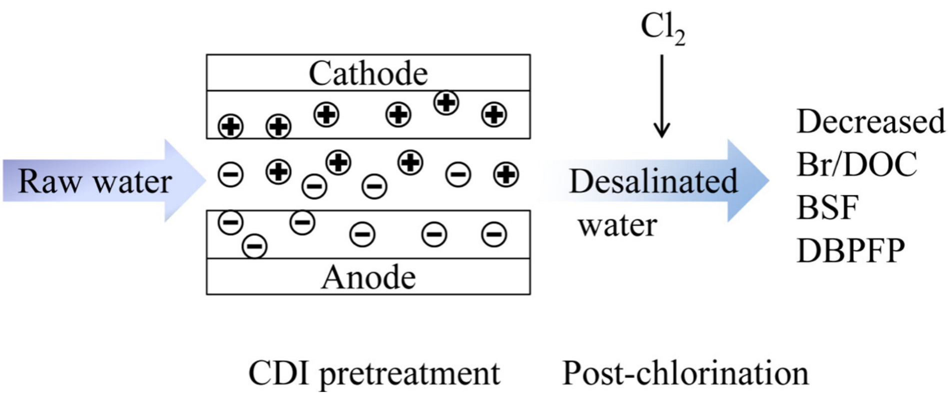
HIGHLIGHTS

- Capacitive deionization (CDI) preferentially removed bromide over humic acid.
- DBP formation potential and bromine substitution factors were reduced.
- Mechanisms for DBP precursor removal by CDI treatment were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Formation of brominated disinfection by-products (DBPs) from bromide and natural organic matter upon chlorination imposes health risks to drinking water users. In this study, capacitive deionization (CDI) was evaluated as a potential process for DBP precursor removal. Synthetic humic acid and bromide containing saline water was used as model water prior to CDI treatment. Batch experiments were conducted at cell voltages of 0.6-, 0.9-, and 1.2 V to study the influence of CDI on the ratio of bromide and dissolved organic carbon, bromine substitution factor, and DBP formation potential (FP). Results showed beneficial aspects of CDI on reducing the levels of these parameters. A maximum DBPFP removal from 1510 to 1160 μg/L was observed at the cell voltage of 0.6 V. For the removed DBPFP, electro-adsorption played a greater role than physical adsorption. However, it is also noted that there could be electrochemical oxidations that led to reduction of humic content and formation of new dichloroacetic acid precursors at high cell voltages. Because of the potential of CDI on reducing health risks from the formation of less brominated DBPs upon subsequent chlorination, it can be considered as a potential technology for DBP control in drinking water treatment.

1. Introduction

Disinfection as an essential water treatment practice for elimination of waterborne diseases brings in a variety of disinfection by-

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products (DBPs) in the finished water (Xie, 2004). Many DBPs have been found to have definitive adverse health impact even at low concentrations. For instance, trihalomethanes (THMs) and haloacetic acids (HAAs) are two typical classes of DBPs that have been regulated in many countries for decades. Since their formation is attributable to the reactions between the disinfectant (such as chlorine) and DBP precursors (such as natural organic matter (NOM) and bromide), processes targeting on the removal of these precursors are among the options for effective DBP control (Watson et al., 2012; Jiang et al., 2016).

Capacitive deionization (CDI) has been reported as a promising water desalination technology (Suss et al., 2015). It is based on an electro-adsorption concept that operates at a low cell voltage (0.6–1.2 V) using a pair of juxtaposed, highly porous electrodes. Due to the applied electric field, ions are removed from the water and temporarily stored in the electrical double layers (EDL) that form inside the porous electrodes. CDI is recently studied as a low-cost and easy-to-operate process for the removal of a variety of cations and anions such as heavy metals (Huang et al., 2016), bromide (Xu et al., 2008), and even the weakly charged organic matter (Wang et al., 2015). Comparing to conventional processes such as coagulation and ozonation that preferentially remove large DBP precursors with aromatic structures while having limited efficiency in eliminating small precursors (Chang et al., 2001; Chiang et al., 2002; Zhao et al., 2009), CDI appears to affect DBP precursors in a different mechanism. Xu et al. (2008) reported that the ion selectivity by CDI treatment of brackish produced water followed an order of I > Br > Ca > alkalinity > Mg > Na > Cl and there was a bromide removal efficiency of 50% in their CDI study. It is well known that bromide, as an important inorganic DBP precursor in water may react with chlorine to form hypobromous acid (HOBr), which may then react with NOM and generate brominated DBPs (Zhang et al., 2008; Zhang et al., 2014) that are more toxic than their chlorinated analogues (Pals et al., 2013; Yang and Zhang, 2013; Liu and Zhang, 2014). The removal of bromide therefore may be accompanied with reductions on the formation of brominated DBPs during subsequent chlorination. Simultaneous with bromide removal, NOM — the main organic DBP precursor in water may compete with the inorganic ions for adsorption sites on the surface of the CDI electrode and impair its desalination efficiency (Gabelich et al., 2002; Mossad and Zou, 2013; Wang et al., 2015). As a result of the potential of CDI for competitively removing organic matter and bromide from water, it is critical to evaluate the effectiveness of CDI on DBP control, since the desalinated water is anticipated to be exposed to subsequent disinfection prior to human use.

In this study, humic acid (HA) as a major fraction of NOM was spiked into synthetic bromide-containing saline water to simulate inland water prior to CDI treatment. The primary objective of this study was to clarify the effects of CDI on DBP precursors during the competitive removal of HA and bromide. Water samples prior to and after CDI treatment were quantified for DBP precursors using a DBP formation potential (FP) test with chlorine, and the analyzed species of DBPFP included: four THMs (chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (BF)), six HAAs (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), and dibromoacetic acid (DBAA)), four haloacetonitriles (HANs: dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN)), two haloketones (HKs: 1,1-dichloro-2-propanone (DCP) and 1,1,1-trichloro-2-propanone (TCP)), and chloral hydrate (CH). Since THMs and HAAs are the most predominant and commonly regulated DBP groups, the research into the precursors for these groups is of particular interest. This is the first study reporting the potential of CDI for DBP precursor removal.

2. Materials and methods

2.1. Chemicals

Technical grade HA was purchased from Sinopharm Chemical Reagent (Shanghai, China). Analytical grade sodium bromide (NaBr) and sodium chloride (NaCl) were purchased from Xilong Chemical Industry (Guangdong, China). Sodium hypochlorite (NaClO, reagent grade, 5%) was obtained from Sigma-Aldrich (St. Louis, MO, USA). All DBP standards were obtained from Supelco (Bellefonte, PA, USA).

2.2. Laboratory CDI experiments

A bench-scale CDI assembly was set up with one pair of pristine activated carbon cloth (ACC, FM10, Chemviron, UK) as electrodes. The ACC (0.5 g, 0.35 cm × 0.35 cm) was pre-washed with 0.01 N HCl solution and then ultra-pure water to remove any residual organics and ions. Fig. 1 shows the schematic diagram of the CDI configuration and reactor setup. The system included a CDI cell, a potentiostat as external power supply, and a magnetic stirring plate with a stirrer for sample mixing. In the CDI cell, titanium wires were attached to the ACC as current collectors. Rubber slice separators were placed between the two juxtaposed ACC to result in a channel width of 2 mm. The entire stack of all layers was bound together with a cable tie and was placed in a beaker containing 75 mL synthetic raw saline water with conductivity of 1675 μS/cm. Model water with elevated concentrations of bromide (1.78 mg/L) and HA (10 mg/L as dissolved organic carbon (DOC)) was used to simulate natural water under the influence of tributary inflows, dissolution of geological sources, and anthropogenic activities (Selcuk, 2010; Watson et al., 2012; Jiang et al., 2016). The water quality parameters of the synthetic raw water are summarized in Table 1.

Prior to each run, the cell was pre-rinsed in the raw water for 4 h to establish an equilibrium state of physical adsorption of HA and inorganic ions. A cell voltage (V_{cell}) of 0.6-, 0.9-, and 1.2 V was then applied to the CDI cell to initiate the electro-adsorption, respectively. The CDI treatment lasted 1 h prior to the sample collection. Between each run, the CDI cell was also washed with 0.01 N HCl solution and then ultra-pure water to eliminate the influence of organics and salts carryover from the previous run. To explore the effect of physical adsorption only, a control run was also performed on an open circuit ($V_{cell} = 0$ V) for 1 h.

2.3. Sample dilution and the FP test

A 5× dilution was performed on all samples after collection. These diluted samples were then sent for DOC, UV_{254}, bromide, and DBPFP analyses. DOC was analyzed by a total organic carbon (TOC) analyzer (TOC-V CPH, Shimadzu, Japan) after passing each sample through a 0.45 μm membrane. UV_{254} was measured using a spectrophotometer (UV-1800, Shanghai Aoxi, China) equipped with a 1 cm path length

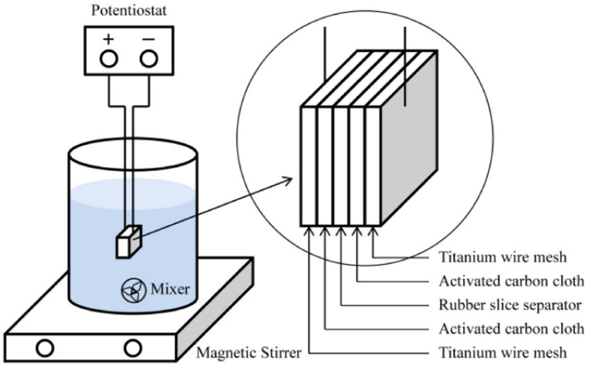

Fig. 1. Schematic diagram of CDI configuration and reactor setup.