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Analysis of trihalomethane precursor removal from sub-tropical reservoir waters by a magnetic ion exchange resin using a combined method of chloride concentration variation and surrogate organic molecules

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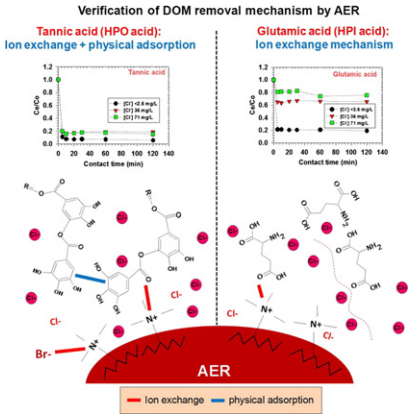
HIGHLIGHTS

- Hydrophobic acid was 75% of DOM in the reservoir waters in tropical islands.
- Hydrophilic acid had the highest specific THMFP among three DOM fractions.
- Surrogate DOM and a high chloride dose were used to find the DOM removal mechanisms.
- Hydrophobic acid was removed by multiple mechanisms and was unaffected by chloride.
- Hydrophilic acid was removed by ion exchange; thus, it was affected by chloride.

GRAPHICAL ABSTRACT



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ABSTRACT

In small reservoirs in tropical islands in Japan, the disinfection by-product formation potential is high due to elevated concentrations of dissolved organic matter (DOM) and bromide. We employed a combined method of variation of chloride concentrations and the use of DOM surrogates to investigate removal mechanisms of bromide and different fractions of DOM by chloride-based magnetic ion exchange (MIEX®) resin. The DOM in reservoir waters was fractionated by resins based on their hydrophobicity, and characterized by size-exclusion chromatography and fluorescence excitation-emission matrix spectrophotometry. The hydrophobic acid (HPO acid) fraction was found to be the largest contributor of the trihalomethane (THM) precursors, while hydrophilic acid (HPI acid) was the most reactive precursors of all the four THM species. Bromide and DOM with a molecular weight (MW) greater than 1 kDa, representing HPO acid (MW 1–3 kDa) and HPI acid (MW 1–2 kDa), were effectively removed by MIEX® resin; however, DOM with a MW lower than 1 kDa, representing HPI non-acid, was only moderately removed. The removal of THM precursors by MIEX® resin was interfered by high chloride concentrations, which was similar to the removal of glutamic acid (HPI acid surrogate) and bromide. However, elevated chloride concentrations had only a minor effect on tannic acid (HPO acid surrogate) removal, indicating that HPO acid fraction was removed by a combination of ion exchange and physical adsorption on MIEX® resin.

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Our study demonstrated that the combined use of DOM surrogates and elevated chloride concentrations is an effective method to estimate the removal mechanisms of various DOM fractions by MIEX® resin.

1. Introduction

Dissolved organic matter (DOM) is present in all drinking water sources and is a complex mixture of heterogeneous compounds derived from the decomposition of plant and animal tissue, including humic compounds, amino acids, proteins and carbohydrates. (Thurman, 1985; Norwood et al., 1987; Sellner and Nealley, 1997; Wang et al., 2009). Characteristics and concentrations of DOM in natural waters vary depending on climate, geology, topography, and other environmental factors (Fabris et al., 2008; Sharp et al., 2005). Generally, most of the compounds comprising DOM have anionic character as a result of the structure-bound carboxylic and phenolic groups such as humic and fulvic acids (Kim and Yu, 2005), while the rest of the DOM consist of neutral compounds, such as polysaccharides and proteins (Leenheer and Croué, 2003). However, DOM in natural waters is often characterized by isolation of DOM fractions, such as hydrophobic (HPO), hydrophilic (HPI), and molecular weights (MW), and/or their functionalities.

DOM and bromide are considered as the precursors of disinfection by-products (DBPs), such as trihalomethanes (THMs), produced in the chlorination process (Richardson et al., 1999; Hsu and Singer, 2010). In Japan, drinking water sources in sub-tropical islands contains high DOM concentration of 2.5–7.8 mg-C/L, while high bromide and chloride concentrations were found in the range of 0.20–0.59 mg/L and 87–205 mg/L, respectively (Tochimoto et al., 2010). Although coagulation–flocculation and adsorption by activated carbon have been extensively applied in treatment processes, the treated water still contains high concentrations of THM precursors, particularly bromide because these processes could not effectively remove bromide (Kristiana et al., 2011; Xu et al., 2013). Thus, additional processes, such as anion exchange resin (AER) processes, are required to minimize the THM precursors (Hsu and Singer, 2010). Typically, the AER process using magnetic ion exchange (MIEX®) resin has been employed as pretreatment (Drikas et al., 2011) of a coagulation–flocculation process in water treatment plants for the removal of DOM and bromide to reduce DBP formation (Gan et al., 2013; Phetrak et al., 2014). In a water treatment plant in Ogasawara Islands, located in the sub-tropical region in Japan, the MIEX® process was installed after coagulation–flocculation and sedimentation processes to prolong the operational life time of MIEX® resin. However, the second water treatment plant is now being designed employing the MIEX® process as a pretreatment for the coagulation–flocculation process.

Hsu and Singer (2010) found that chloride concentration is an important factor in inhibiting bromide removal by AER. Ion exchange was reported to be the main mechanism of charged DOM removal by AER in absence of chloride or at low chloride concentration (Boyer and Singer, 2008; Bond et al., 2010). A high NaCl concentration, i.e. 0.8 mol/L, influenced tannic acid adsorption by surfactant-modified zeolites, which was estimated to be caused by a combination of electrostatic attraction and the other interactions such as hydrogen bonding and organic partitioning (Lin et al., 2011). Nonetheless, these studies had not elaborated the influence of various chloride concentrations on the removal of DOM fractions by MIEX® resin.

To investigate physical adsorption of DOM by AERs, DOM removal by ion exchange can be minimized by decreasing the pH to a value where the negative charge on the DOM is negligible. Croué et al. (1999) observed adsorption of different DOM fractions (HPO and HPI) present in natural water by AERs at different pH (pH 4–10) and found that the effectiveness of DOM removal by AERs can be strongly influenced by pH. At basic pH (pH 10), where the negative charge of the DOM is strong, ion exchange mechanism was predominant, whereas physical adsorption was dominant for DOM removal in acidic condition (pH 4). However, varying pH may not be appropriate to identify the DOM removal mechanisms by AERs possibly due to the transformation of DOM structures (Oćwieja et al., 2015). Therefore, varying chloride concentration could be potentially an effective approach to investigate DOM removal mechanism by AER because it does not alter the structure of adsorbent and/or adsorbate (Lin et al., 2011). However, to the best of our knowledge, there is only limited number of studies that had reported the interaction between DOM fractions and AER or between bromide and AER by varying chloride concentrations in aqueous solution.

Therefore, this study aimed to elucidate the removal mechanisms of DOM fractions by chloride-based MIEX® resin using a combination of DOM surrogate compounds representing each DOM fraction in natural water and variation of chloride concentration. The competitive effect of chloride on bromide removal by MIEX® resin was also investigated. Furthermore, the effect of DOM characteristics on THM formation was investigated by the resin fractionation method (DAX-8 and XAD-4). Simultaneous removal of DOM and bromide by MIEX® resin for THM formation potential (THMFP) reduction was also investigated in this study.

2. Materials and methods

2.1. Sampling site and water collection

Water sampling was conducted in the sub-tropical islands of Ogasawara, Japan in September 2012. Water samples were collected from three reservoirs in Chichijima Island (E142°11′ N27°05′, land area 23.8 km^2), namely CH1, CH2 and CH3. Another sample (HA) was obtained from a reservoir in Hahajima Island (E142°10′ N26°38′, land area 20.2 km^2) (Fig. 1). The water samples were packed in an icebox and transferred to the laboratory at the University of Tokyo. The samples were then pre-filtered through 0.45 μm hydrophilic PTFE membrane filters (Millipore, JHWP09025), hereafter referred to as raw waters, and stored in the dark at 4 °C until use.

2.2. DOM fractionation by resins (DAX-8 and XAD-4)

DOM in the raw water was fractionated using a two-column array of Supelite DAX-8 and Amberlite XAD-4 (SUPELCO, Supelco Park, Bellefonte, PA, USA), which separated DOM into three fractions, i.e., HPO acid (DAX-8 adsorbable), HPI acid (XAD-4 adsorbable), and HPI non-acid (neither DAX-8 nor XAD-4 adsorbable). Briefly, 750 mL of raw water was acidified with 10 N HCl to pH 2. The acidified water was passed through column arrays of DAX-8 and XAD-4 to fractionate the DOM, following the same procedure employed by Lohwacharin et al. (2010). The HPI non-acid fraction was collected in the effluent from both DAX-8 and XAD-4 columns. The HPO acid and HPI acid fractions were removed from the DAX-8 and XAD-4 columns by rinsing with 0.1 N NaOH, respectively. After fractionation, each DOM fraction was adjusted to neutral pH.

2.3. Batch adsorption experiment

Batch adsorption experiments were conducted using a commercially available strong base AER in a bottle-point method to investigate DOM and bromide removal from raw waters and synthetic waters. The MIEX® resin is a polyacrylic macroporous resin with magnetized iron