BROMIDE REMOVAL FROM DRINKING WATER SOURCES IMPAIRED BY ENERGY WASTEWATER DISCHARGE USING ELECTRICALLY CONDUCTIVE MEMBRANE

by

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ABSTRACT

SAMONTY DAS. Bromide Removal from Drinking Water Sources Impaired by Energy Wastewater Discharge Using Electrically Conductive Membrane
(Under the direction of Dr. MEI SUN)

Bromide accelerates the formation of carcinogenic disinfection by-products (DBPs) during drinking water disinfection when it reacts with dissolved organic matter and disinfectants. The objective of this study is to develop an effective process to lower the DBP formation by removing bromide from drinking water sources. An innovative bromide removal technology has been evaluated using electrically conductive membranes (ECM). ECM made of carbon nanotubes works as the anode to oxidize bromide to bromine, while stainless steel serves as the cathode. The optimal voltage and flow rate for this process in a bench-scale flow-through system to achieve the best bromide removal were determined to be 2.59V and 1 ml/min, respectively. Common ions present in drinking water sources influence bromide removal through competition for the electrode surface and electrode fouling. To confirm the effects of these ions, several common anions (sulfate, chloride, nitrate, and bicarbonate) were spiked individually at concentrations of 0.1, 2, and 5 meq/L to solutions containing bromide at 8.76 μeq/L. The bromide removal efficiency without anions was 70%. Chloride ion showed the strongest impact on bromide removal and lowered the bromide removal efficiency down to 16% with a 5 meq/L chloride concentration. On the other hand, nitrate and sulfate ions showed less impact than other ions and resulted in 27% and 25% bromide removal efficiency, respectively with 5 meq/L ion concentration. The effect of natural organic matter (humic acid) on bromide removal was also evaluated. The dissolved organic carbon (DOC) concentrations of 2mg/L, 5mg/L, and 15 mg/L reduced the bromide removal efficiency to 63%, 38%, and 25%, respectively. In addition, DBP formation potential before and after the ECM treatment was examined to check if the ECM reduced DBP formation potential. The DBP formation potential of water samples containing both bromide and DOC were predominantly influenced by the DOC levels rather than the bromide levels. Hence, the ECM treatment did not significantly change the formation potential of the two regulated groups of DBPs, trihalomethanes (THM) and haloacetic acids (HAAs), or total DBPs measured as total organic halogens (TOX). However, the ECM treatment did inhibit the formation of more toxic brominated DBPs, reflected by lower bromide incorporation factors (BIF) in THMs and HAAs after the ECM treatment.

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The Desalination and Water Purification Research and Development Program, Bureau of Reclamation, sponsored this research. James Homiller at UNC Charlotte, Kartikeya Kekre and Ying Yao at Temple University performed initial laboratory work for this research.

DEDICATION

I dedicate my thesis work to my family, my parents, my husband, and my son, Rishaan Paul.

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LIST OF ABBREVIATIONS

BIF	Bromide incorporation factor
CNT	Carbon nanotube
DBP	Disinfection byproduct
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
ECM	Electrically conductive membranes
FGD	Flue-gas desulfurization
HAA	Haloacetic acid
THM	Trihalomethane
TOBr	Total organic bromide
TOCl	Total organic chloride
TOX	Total organic halogen

CHAPTER 1: INTRODUCTION

1.1 Bromide

Bromide (Br^-) is a reduced form of bromine, which is a member of the halogen group with fluorine, chlorine, and iodine in the periodic table. Bromide salts can be found in the earth's crust, seawater, underwater brines, and fossil fuels (Kolker et al., 2006). In recent years, the concentration of bromide has become a major concern due to its ejection from coal mines (Cravotta & Brady, 2015; McAuley & Kozar, 2006) including effluent from the coal combustion residue (Ruhl et al., 2012), cooling tower (*EPRI Product,* n.d.), and wet flue gas desulfurization (FGD) of coal-fired power plant (McTigue et al., 2014; States et al., 2013). As bromide is low in toxicity, currently it is not regulated by water quality standards or discharge limits. The median bromide concentration in US surface water is 35 μg/L (Amy et al., 1994); the median and mean bromide concentration in US drinking water source reported in the Fourth Unregulated Contaminant Monitoring Rule (UCMR4) is 36.7 and 131 μg/L, respectively.

1.2 Disinfection byproducts (DBPs)

During water treatment, disinfectant chlorine reacts with dissolved organic matter (DOM) as well as bromide present in water, and chlorinated and brominated disinfection byproducts (DBPs) form. Two representative DBP groups, trihalomethanes (THMs) and haloacetic acids (HAAs), are regulated in drinking water by the US Environmental Protection Agency (US EPA). However, compliance with the DBP standards has been a challenge for many utilities across the US (Rubin, 2013). The presence of bromide in drinking water is one reason why utilities are facing difficulties to meet the THM standard (McTigue et al., 2014). Bromide can accelerate THM formation rates and increase the molar THM yield (Krasner et al., 1994). Also, bromide promotes the formation of brominated DBPs over chlorinated DBPs (Bond et al., 2014; Fiske, 2011; Handke, 2008; States et al., 2013, Symons et al., 1993). Since the atomic weight of bromine is more than twice that of chlorine, a shift towards brominated THM species increases the mass concentration of total THMs at a given molar yield. Besides, brominated DBPs are more strongly associated with adverse health effects than their chlorinated analogs (Echigo et al., 2004; Richardson, 2003; World Health Organization, 2000; Yang et al., 2014). Human exposure to DBPs has been associated with several types of cancer (e.g., bladder, colon, and rectum) and adverse pregnancy outcomes (Hrudey, 2009); Richardson et al., 2007). Therefore, bromide removal is not only important for DBP regulation compliance but also essential for controlling the formation of unregulated brominated DBPs from a risk management standpoint.

In North Carolina (NC), the water treatment plant taking source water from the Dan River struggled to meet the THM standard when a wet FGD scrubber was set up at the coal fired power plant back in 2008 and its wastewater was discharged to the Dan River. In the city of Eden, NC, brominated THM constituted less than 20% of the total THMs in 2006 before the FGD installment (Edwards, 2012). Then, in 2011, the concentration of bromide in Dan River exceeded 400 µg/L and more than 95% THM became brominated. The shift in THM formation is combined with the higher THM yield and formation rate, causing a challenge for the city of Eden for THM compliance, despite the low level of DOM in the raw water. Besides, the wastewater discharge from shale gas extraction has been identified as a bromide source downstream (States et al., 2013; Wilson and Van Briesen, 2013). For instance, the concentration of bromide was 50- 250 µg/L in the drinking water in Pittsburgh, PA. This high concentration of bromide along with high THM shifts towards brominated THM in drinking water (States et al., 2013). These results indicate that when drinking water is impaired by industry waste discharge, bromide removal process needs to be incorporated in the water treatment process to reduce the public health risk associated with carcinogenic DBPs.

Bromate and chlorate are toxic byproducts that may form during electrooxidation of chloride and bromide if the applied potential is too high as well as during aggressive chemical oxidation. Bromate is regulated by EPA at 10 µg/L in drinking water; chlorate is currently not regulated.

1.3 Existing bromide removal techniques

In conventional drinking water treatment process, bromide removal is difficult because bromide is very soluble in water. The removal technology of bromide from drinking water has been divided into four broad categories: Electro-oxidation, adsorption, membrane technology, and ion exchange. Usually, electro-oxidation and ion exchange can remove bromide from water with the highest removal efficiency. Bromide removal with ion exchange resin is economic because the resin can be regenerated to restore the resin capacity. But the regeneration of ion exchange resin lowers the removal efficiency of bromide. Besides, electro-oxidation may increase the formation of brominated DBPs. A summary on all bromide removal processes is discussed in detailed in chapter 2 (Literature review). A new bromide removal process can be introduced in the conventional treatment process to lower the formation of DBPs using electrically conductive membrane (ECM) (Ronen et al., 2016). In this process, bromide will be removed by an electro-oxidation process where ECM will be used as anode. The main goal of this research is to develop a new bromide removal technology using ECMs.

1.4 Water treatment using electrically conductive membrane (ECM)

ECMs are innovative electrode materials with potential applications in drinking water and wastewater treatment. ECMs are made by depositing conductive nanomaterials on porous supports. The ultrafiltration membranes with relatively small pore sizes (i.e., molecular weight cut off at 1-50 thousand Da) are commonly used as such supports. Examples of the deposited nanomaterials examined in previous studies include carbon nanotubes (CNTs) (de Lannoy et al., 2013; de Lannoy et al., 2012; Dudchenko et al., 2014; Gao et al., 2015; Vecitis et al., 2011) and graphene nanoparticles (Hegab and Zou, 2015; Li et al., 2014). The CNTs are chemically cross-linked after deposition, and are physically firm while having the ability to get external electrical charges. Furthermore, a conductive polymer (polyaniline) can be electrochemically deposited on the CNT surface to prevent the oxidation of the CNT-based ECMs at anodic potentials (Duan et al., 2016). The ECMs typically have a thin CNT conductive layer (about 2 μm thick) and a low electrical resistance (200-1000 Ω/m^2). Thus, ECMs can be charged with electrical potentials and applied as an alternative to existing membrane modules in water and wastewater treatment (Ronen et al., 2016). Unlike other electrodes limited by the diffusion, transport through ECMs is dynamic and controlled by the flux through the membrane, thus diffusion restriction is eliminated. In addition, ECMs have fabrication costs less than $\$3/m^2$ (de Lannoy et al., 2012; Dudchenko et al., 2014; Ronen et al., 2015), making them affordable in water treatment. Based on previous cyclic voltammetry experiments, the energy demand of ECM operation is as low as 0.01 kWh/m^2 at 5 V (Dudchenko et al., 2014). Although the energy demand may vary according to experimental conditions, it is still expected to be insignificant compared to other treatment options (Zhu et al., 2009).

ECMs have been applied for multiple applications, including (1) mitigating organic, inorganic, and biological fouling on membranes; and (2) combining the filtration process with direct electrooxidation or electro-Fenton reactions to remove contaminants from water. For example, Duan et al. (2016) used ECMs made by pressure deposition with CNTs and electrodeposited with polyaniline to oxidize a model organic compound (methylene blue). In the flow-through experiments, methylene blue removal reached 84.1% in a single pass through the membrane (3 V, 1 μm thick membrane, <0.2 second membrane residence time). In addition, ECM fouling experiments conducted with bovine serum albumin demonstrated the possibility for *in situ* oxidative cleaning, with membrane flux restored to its initial value under an applied potential of 3V (Duan et al., 2016). Vecitis et al. (2011) vacuum-filtered multiwalled CNTs onto a 5 μm PTFE membrane to simultaneously adsorb and inactivate viral and bacterial pathogens, and found that when the ECM anode was poised at potentials of 2 and 3 V for 30 seconds, no culturable bacteria were detected in the effluent. Bacterial and viral inactivation was attributed to direct oxidation of the pathogens in contact with the ECM anode, and indirect oxidation of pathogens via anodic production of oxidants (chlorine radicals, hydroxyl radicals).

1.5 Results of previous tests

The initial tasks of the overall project began in 2018 and is summarized here as background. Kartikeya Kekre and Ying Yao at Temple University performed initial laboratory work for this research. They have determined the impact of voltage, contact time, as well as Potentiometric analysis of ECMs for anodic bromide oxidation.

1.5.1 Potentiometric analysis of ECMs for anodic bromide oxidation

Theoretically, bromide oxidation starts at an anodic potential of 1.09 V vs. standard hydrogen electrode (0.87 V vs. the standard Ag/AgCl reference electrode) at standard conditions. In practice, a higher potential is needed to overcome overpotentials and initiate the reaction. To determine the minimum required anodic electrical potential to oxidize bromide by ECMs, bromide electrooxidation was tested in both 0.1 and 0.5 N sodium bromide solutions (8 and 40 g/L of bromide). Linear voltammetry curves of the ECMs showed an increase in current starting around an applied anode potential of 0.85-1.05 V against the Ag/AgCl electrode (Figure 1). Thus, ~0.9 V vs. Ag/AgCl electrode is the minimal anodic potential needed for the system.

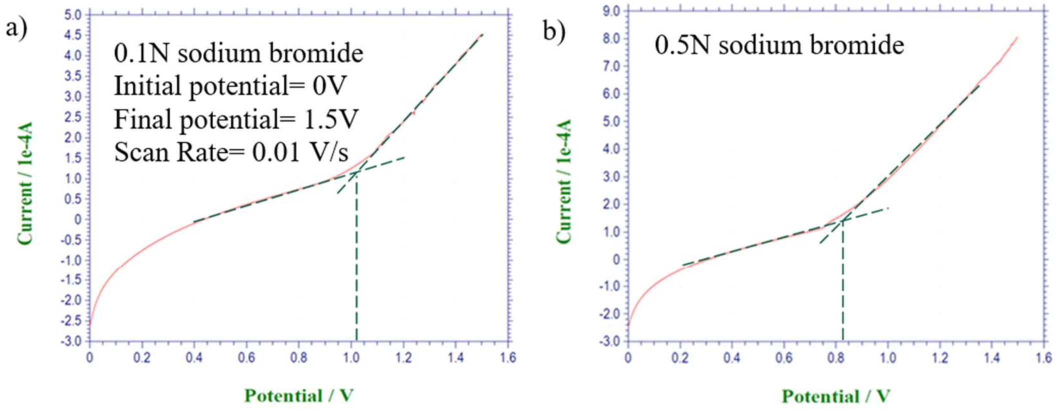


Figure 1: Linear voltammetry for a) 0.1 N and b) 0.5 N sodium bromide solutions.

The ECMs were then posed in the cyclic voltammetry mode to test their resistance to oxidation (Figure 2). When the potential range was set to 0-1.3 V or 0-1.7 V, no drop in the current was observed compared to initial cycles, suggesting the stability of ECMs at the 0-1.7 V potential range. However, with a 0-5V potential range, the current value decreased after prolonged usage. Furthermore, most of the current loss was in the 3-5 V range, while minimal loss occurred below 3V. Thus, the voltage applied to the flow reactors for bromide removal should be controlled in the <3V region.

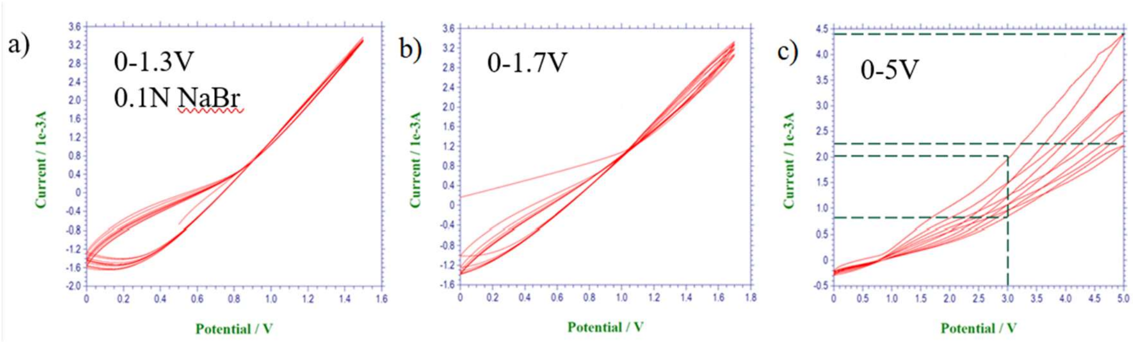


Figure 2: Cyclic voltammetry for 0.1 N sodium bromide in the potential range of a) 0-1.3V; b) 0-1.7 V; c) 0-5 V.

1.5.2 Bromide removal in control tests without power

The coated membranes (i.e., the ECMs) and uncoated polyethersulfone membranes were evaluated for bromide loss by adsorption onto the flow reactors at 10 psi. Mass balance calculations for both tests showed minor bromide losses (<5%, in the range of analytical errors) (

Table 1), indicating minor adsorptive loss.

Table 1: Bromide mass balance in control tests using uncoated and coated membranes (10 psi, 0 V, 700 µg/L bromide)

	Contact time (hour)	Feed (µg)	Concentrate (µg)	Permeate (µg)	Uncovered mass
Uncoated	1	186	92	87	3.8%
	2	157	76	75	3.7%
	3	194	94	93	3.8%
	4	197	97	94	3.0%
Coated	1	186	92	87	3.3%
	2	157	76	75	4.5%
	3	194	94	93	3.5%
	4	197	97	94	2.2%
	5	162	80	77	3.3%

As expected, no bromide cumulation in the concentrate was observed using either coated or uncoated membranes (Figure 3), since the membrane pores are too large to reject the bromide ions.

The minor differences among the feed, concentrate, and permeate concentrations could be attributed to the natural negative charges of the membrane surface when not connected to power, which repealed bromide and slightly hindered bromide transport across the membranes. Compared to the results using uncoated membranes, the bromide concentrations slightly decreased in the ECM permeate and slightly increased in the ECM concentrate. This change is attributed to the additional negative charges of the ECM surface of the carboxylic groups on the carbon nanotubes.

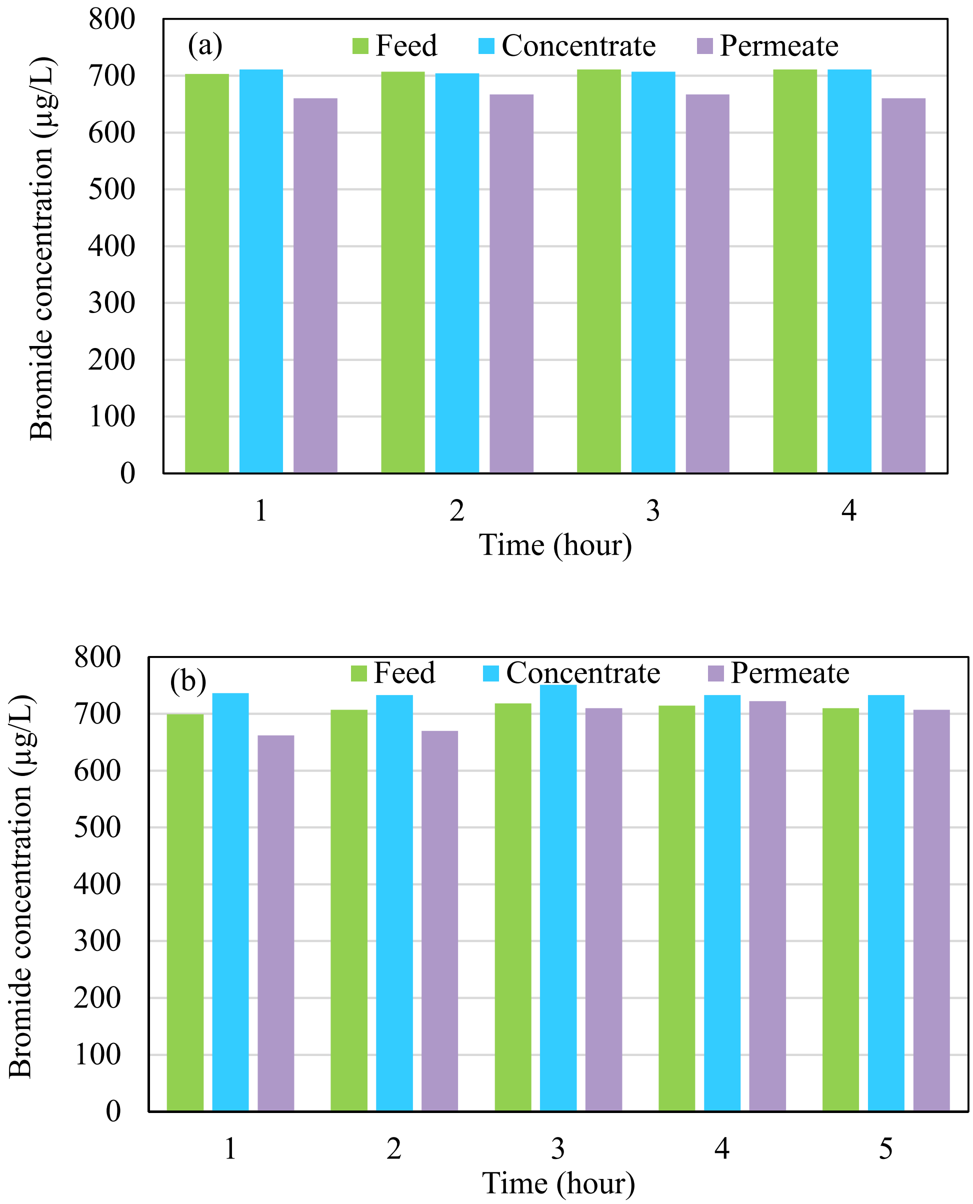


Figure 3: Bromide removal in control tests without power (10 psi, 0 V, 700 µg/L bromide): (a) with uncoated polyethersulfone membranes; (b) with coated membranes (ECMs).

1.5.3 Impact of contact time on bromide removal

The transmembrane pressure controls the contact time between bromide and the ECMs. Here, bromide removal by the ECM cells was tested at transmembrane pressures of 5 and 10 psi and a fixed voltage of 2 V. Based on the permeate flux and the thickness of the active layer (3-5 µm), the calculated liquid contact time with the ECMs in the permeant stream increased from ~0.8 seconds at 10 psi to ~3 seconds at 5 psi. In regular membrane filtration processes, contaminant concentrations decrease in the permeate and increase in the concentrate; Contrarily, bromide concentration decreased in both the concentrate and permeate in this study (Figure 4a), since bromide removal in ECM cells relies on electrochemical oxidation instead of membrane filtration. Moreover, as the concentrate stream had a longer contact time with the membrane (~10 seconds), it showed a higher bromide removal (i.e., lower concentrations) than the permeate in most cases. Such unconventional results suggest that the proposed treatment can remove bromide without producing a concentrated waste stream. As expected, at a lower transmembrane pressure (i.e., a higher contact time), higher bromide removal was achieved in both the permeate and concentrate.

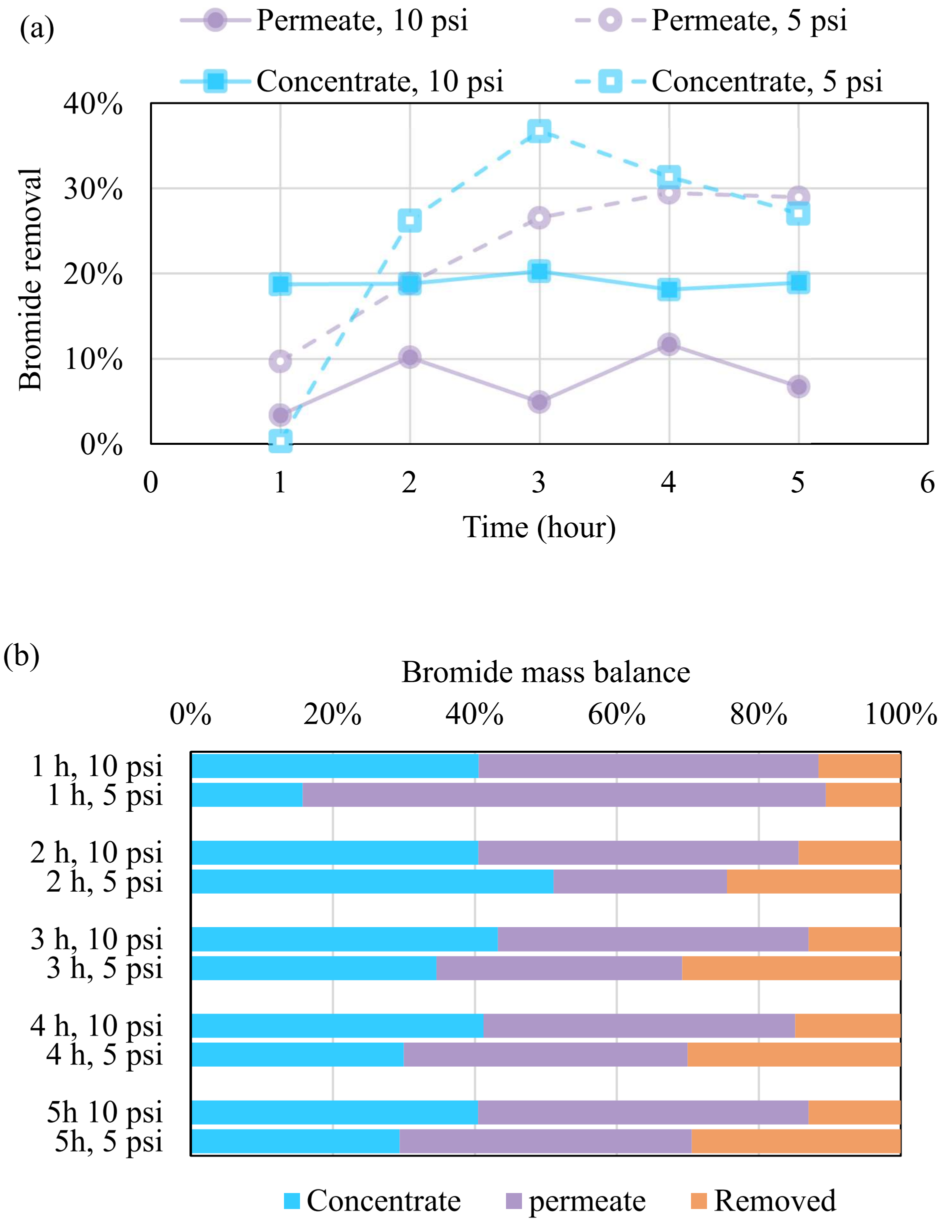


Figure 4: Bromide removal (a) and mass balance (b) by the ECM cells under different transmembrane pressures (2 V, 700 µg/L bromide)

Mass balance calculations showed that 12-15% of the initial bromide mass was removed from the treated water at 10 psi, and the removal increased to 11-31% at 5 psi (Figure 4b). Since bromide adsorption to the reactors was negligible (

Table 1), the bromide removal mechanism in the ECM cells should be electrochemical oxidation.

1.5.4 Impact of voltage on bromide removal

The overall voltage of the ECM cells drives the bromide electrooxidation reaction, thus a higher voltage is expected to enhance bromide removal. However, a voltage higher than certain thresholds would induce undesired side reactions, such as water electrolysis, DBP formation, and carbon membrane oxidation, which compete with bromide oxidation, increase energy consumption, and/or lead to toxic product formation. Thus, the impact of voltage on bromide removal was tested in the range of 2-2.9 V, at a fixed transmembrane pressure of 5 psi. Figure 5 shows bromide removal in the permeate, concentrate, and the whole system. Bromide removal in the concentrate generally increased with increasing voltage, while the trend was not very obvious in the permeate. Bromide removal was consistently higher in the concentrate than in the permeate, again suggesting bromide removal in ECM cells relies on electrochemical oxidation instead of membrane filtration. The voltage in the range of 2-2.9 V had a relatively low impact on bromide removal by the whole system. Considering the stability in removal results and the high removal in the concentrate, the optimal voltage for bromide removal was selected as 2.9 V.

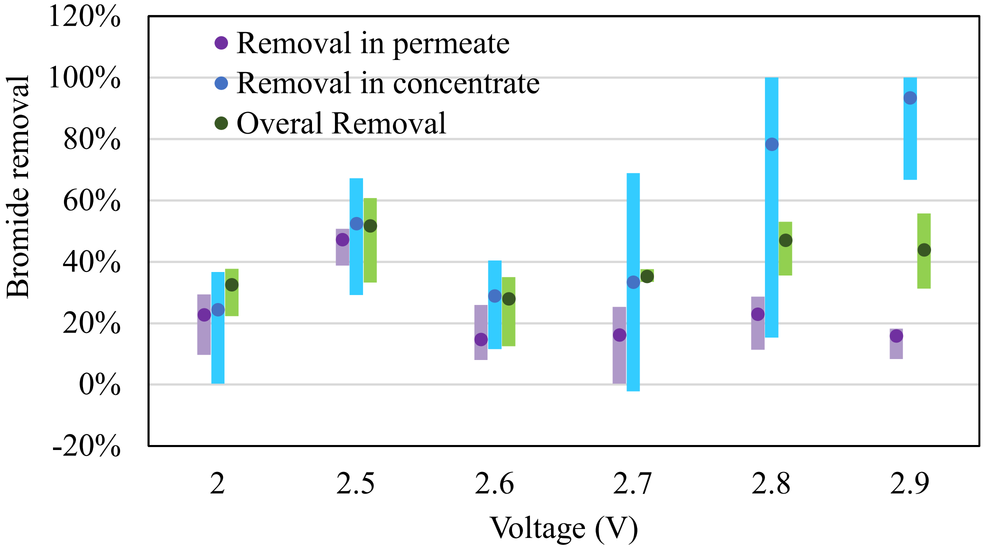


Figure 5: Bromide removal by the ECM cells under different voltage in 5 hours (5 psi, 700 µg/L bromide). The dots represent average results, and the bars represent the ranges of the results over the 5-hour treatment.

1.6 Objectives

The main objective of this research is to develop an effective and reliable process for continuous operation of bromide removal from drinking water source contaminated by wastewater discharge. In this research, a new bromide removal technology was investigated using an electrically conductive membranes (ECMs). The main goal is to establish a fundamental understanding of bromide removal as a function of ECM parameters, for example applied potential and pressure, and water matrix compositions. The hypothesis is that the application of an anodic potential on ECMs leads to fast and selective bromide removal. The treatment performance is affected by voltage, transmembrane pressure, and the presence of other chemicals in the feed water.

The impacts of applied voltage and transmembrane pressure on the bromide removal was demonstrated in the sections beforehand. This work mainly focuses on demonstrating the removal efficiency of bromide in the presence of other water constituents in drinking water, and evaluating the reduction of DBP formation potential before and after the treatment with ECM membrane.

CHAPTER 2: LITERATURE REVIEW

Bromide (Br^-) anion can be found in the drinking water because it is present in the source water. The conventional water treatment processes are not efficient for bromide removal from water (Francis et al., 2010). Now-a-days, there are several major bromide removal technologies available, for example, membrane filtration, electro-oxidation, capacitive deionization, adsorption, and ion exchange.

2.1 Membrane filtration

In membrane filtration, membrane is used as a barrier to remove contaminants from water. There are several types of membrane, for example, reverse osmosis (RO) membrane, ultrafiltration (UF) membrane, nanofiltration (NF) membrane. RO is widely used for removing bromide from water. In the RO process, water is passed through a semipermeable membrane by pressure to remove organic matter and salt (Greenlee et al., 2009). The reverse osmosis (RO) process has showed the rejection of halide sequence is Fluoride> Chloride> Bromide> Iodide (Naaktgeboren et al., 1988). That means, chloride is better removed than bromide by RO, so in the presence of chloride, extra energy is used to remove chloride instead of bromide. Mays (2004) reported that RO technology can remove 93- 99% bromide with the presence of other ions like iodide and chloride using different membrane and operating conditions. Magara et al. (1996) used RO technology with aromatic polyamide and was able to remove 99% bromide from seawater.

Nanofiltration (NF): In NF, there is non- porous diffusion like RO technology and ultrafiltration with lower pressure (Fane et al., 2011). Diawara et al. (2003) showed that the effectiveness of bromide removal is better than iodide but lower than fluoride and chloride removal. NF is used as a pre-treatment with RO technology and cost is lower than RO treatment.

The disadvantages of membrane filtration are it needs high energy to produce high pressure. This method requires pre-treatment, high cost, and have the problem with brine disposal (Yang et al., 2019).

2.2 Electro-oxidation

Electro-oxidation, also known as anodic oxidation, is the treatment process using two electrodes (anode and cathode) (Sirés et al., 2014). When voltage is applied, oxidation happens near the anode. Depending on the pH level, oxidation of bromide may form elemental bromine at a minimum potential of 1.087 V. With electro-oxidation, the concentration of bromide decreases, and the potential increases (Grgur, 2019). Sun et al. (2013) has developed a bromide removal electrolysis process using graphite electrodes that requires less energy compared to chloride oxidation and no excess reagent. The presence of high total dissolve solid (TDS) serves as strong electrolytes in the reaction, which is why the treatment requires less energy. The formation of DBPs has been recognized in the flowback water and produced water. Disinfection process during the electrochemical treatment of shale gas wastewater initiate the potential for DBPs formation (K. Z. Huang & Zhang, 2020). In the Wunsche process, the monopolar carbon electrode is used as anode and a diaphragm is used to separate the anode and cathode. In the Kossuth process, dipolar carbon electrodes are used as anode and no diaphragm is used to separate the anode and cathode (Kimbrough & Suffet, 2002). The electrolysis process can be performed using titanium rod as an anode coated with RuO_2 and TiO_2. The main product bromine is volatilized with carbon dioxide and by-products are hypobromous acid or hypobromite ion ($HOBr$ or OBr^-) and brominated

THMs. The reported bromine formation was 15% of the initial mass of bromide, which is not very significant amount (Odeh et al., 2004). The oxidation of bromide can also be done by using platinum rotating electrodes and UV adsorption can quantify the removal efficiency of bromide (Xu et al., 2014). Besides, the bromide can be removed by electrolytic volatilization using titanium as the anode (Kimbrough et al., 2013). In this experiment, the highest reduction of bromide is 55% and bromate removal rate was 86% at 98A. The oxidation of bromide has occurred by RuO_2 anode coated with titanium. The experiments were operated by controlling the reactor voltage, temperature, pH of the sample, current efficiency, and consumption of energy. It is shown that at pH 3 to 4, the main products of oxidation were bromide (90%) and tribromide ions (10%). The consumption of energy of bromide oxidation is calculated about 4.2 kWh per kg of active bromine and 1.23 kWh per kg of bromine in acidified solution (Grgur, 2019). The oxidation of bromide and reduction of DBPs has also been investigated using the graphite electrode with a potential of 3.4V or 4.5V (Tang et al., 2018). The oxidation potential was 3.4V or 4.5V. The efficiency of bromide removal was around 98.3% in 8 hours of treatment. Though formation of brominated DBPs decreased in 79%, non- brominated DBPs formation increased. The limitation of the study was that the consumption of energy increased exponentially with the production of brominated DBPs after 4 hours.

The main advantage of the electrodialysis method is that the feed water needs minimum pre-treatment, and water recovery is higher than reverse osmosis. The limitation of this process is that it does not remove the organic DBP precursors.

2.3 Capacitive deionization

Membrane capacitive deionization (MCDI) is a developing desalination technology, which can remove ions by electro-sorption. This method is a chemical-free and energy-efficient process. Dorji et al. (2018) used MCDI technology to remove bromide. A pair of porous carbon electrodes were used, and the operating parameters were voltage, flow rate, and time. The results of the experiments indicated that the efficiency of bromide removal was 98.4%- 99.9% for applied potential 0.4, 0.7, and 1V. pH had almost no effect on bromide removal (99.1% to 99.5%) for pH range 4 to 10. Operating time (1- 10 minutes) and flow rate variation also had a minor effect on bromide removal (98.2%- 99.9%). The presence of NaCl in 100 mg/L and 200 mg/L lowered the bromide removal into 97.4% and 90% respectively. Dorji et al. (2020) developed MCDI techniques to increase water recovery and decrease energy consumption. They used activated carbon electrode and maintained a flow rate at 5 ml/min. The reported results showed that bromide removal rate was around 70.3%. The continuous charging and discharging process lowered the ion removal efficiency. Recently, electrochemical desalination has been used in the bromide removal process (Cohen et al., 2018). Results indicated a 70% recovery of bromide from the solution using 1g of activated carbon. During the experiment, the amount of bromate formation was kept very low (7.8×10^{-5} M). This method requires pre-treatment, high cost, as well as the problem with brine disposal. MCDI technology can remove DBPs precursors, including bromide ion and dissolved organic matter (Liu et al., 2016). However, MCDI method is very expensive in treating bromide in drinking water.

2.4 Adsorption

Adsorption has been considered one of the cost-effective technologies with minimal operation cost and high removal efficiency of bromide from contaminated water. Silver doped carbon aerogels can be made by carbonization and physical activation of carbon dioxide (Sánchez-Polo et al., 2006). Granular activated carbon (GAC) can remove bromide efficiently from water (Zhang et al., 2015). They used GAC treatment with ultrapure water and mineral water on a pilot scale for different empty bed contact time (EBCT). For mineral water, bromide removal was around 26%- 41.9% in 2 minutes and around 51.8% to 74.9% after 5 minutes. For ultrapure water, 61.74% to 86.58% bromide was removed in 2 minutes and 62.26% to 91.17% in 5 minutes. Bromide removal was better for ultrapure water due to presence of other anions. Beside this, the reduction of bromate was 75%- 94.4% for mineral water and 87.8% to 98.8% for ultrapure water. From the results, it is clear that this method is not much efficient in removing DBPs formation potential and bromate from mineral water. Silver-impregnated activated carbon (SIAC) (e.g., 1.05% and 4.03% by weight) showed 85% to 93% bromide removal (Rajaeian et al., 2018). However, with presence of NOM (2.5 mg/L), bromide removal was decreased to 70%. With the existence of chloride (14- 40 mg/L) and TOC (3.3- 27.6 mg/L), bromide removal was lowered up to 30- 43%. The advantage of the SIAC treatment was that it has lowered the generation of brominated THMs with bromide. The adsorption capacity of silver-doped carbon aerogel is 7.32 μmol/g, 3.01 μmol/g, and 1.98 μmol/g for chloride, bromide, and iodide respectively (Sánchez-Polo et al., 2007). The existence of chloride and natural organic matter lowers the removal efficiency of bromide and iodide. For example, high chloride concentration (40 mg/L) lowered the bromide removal efficiency to 33%. Therefore, bromide removal depends on: (i) concentration of chloride ion or dissolve NOM and (ii) physical and chemical properties of the activated carbon surface. Layered double hydroxide (LDH) has a large surface area to adsorb the halide with low cost and easy regeneration techniques (Das et al., 2003; Mandal and Mayadevi, 2008; Pavan et al., 2000). The removal of bromide and iodide is higher with calcined LDH than uncalcined LDH (Lv et al., 2008). Also, the bromide and iodide adsorption increased with the increasing temperature of calcination from 200^0C to 500^0C. They reported the maximum adsorption capacity of bromide and iodide ion is 94 mg/g and 96.1 mg/g respectively.

2.5 Ion exchange resin

In ion exchange resin, the occurred chemical reaction is reversible, and dissolved ions from solution can be replaced with other ions of resin. There are several ion-exchange resins available for bromide removal, for example, magnetic ion exchange resin (MIEX), amberlite IRA 910, amberlite IRA 900, MIEX-Gold, and MIEX-DOC. MIEX resin can remove bromide and DOM (Boyer & Singer, 2006). The main advantage of resin treatment is that it can be regenerated by chloride and bicarbonate salt. Ding et al. (2012) investigated the bromide removal with MIEX resin with the dosages of 0.5- 5 mL with bromide concentration of 5, 10, and 20 mg/L. They did the experiments based on different concentrations of bromide, contact time, resin dosages, and pH. The bromide removal rate increased from 78% to 98.45% with increasing dosages of MIEX resin. Also, with the increasing of agitation speed from 50 rpm to 100 rpm and pH from 3 to 6, bromide adsorption increases. On the other hand, bromide removal decreases up to 13% with the increasing temperature of the solution. They sequenced the effect of other ions on bromide removal as follows: $SO4^{2-} > CO_3^{2-} > Cl^{-}$. Johnson & Singer (2004) experimented with a semi-batch reactor with MIEX resin doses 2, 4, 6, and 8 mL/L. They removed 64% bromide with resin dose 8 mL/L with the removal of 93% DOC from the sample water. Soyluoglu et al. (2020) used six types of resin, purolite-Br, MIEX-Br, IRA910, IRA900, MIEX-Gold, and MIEX-DOC to compare the bromide removal efficiency. The operating parameters were contact time, bed volume, pH, and regeneration have impact on bromide removal from drinking water. Purolite- Br resin is highly capable in removing bromide (up to 96%) and DBP formation potential (Br- DBPs up to 90%, and total DBPs to 85%). THM formation decreased by 60% with the treatment of purolite- Br resin. Neale & Schäfer (2009) used MIEX resin and performed continuous flow experiments and maintained hydraulic retention time 20 minutes. Results showed that bromide was removed by 20-

28%. The pre-treatment with MIEX resin could lower the coagulant demand by up to 67% and chlorine demand by 50%. So, MIEX as can be used for pre-treatment with coagulation, membrane filtration, and disinfection. Phetrak et al. (2014) did batch tests with the anion exchange resin for removal of bromide and reduction of DBP formation potential. The bromide removal rate was around 58% to 90% depending on the contact time. This paper found that resin IRA400 and IRA910 were more efficient to remove bromide (84% to 90%), while the removal rate with MIEX resin was 58% to 79% at 120 minutes. For the DBPs, polystyrene anion exchange resin is the most efficient in removing THM (85% to 92%). The limitation of MIEX resin is that it has showed the lowest bromide removal. Walker & Boyer (2011) used pure MIEX- Cl resin and MIEX- HCO_3 to compare the bromide removal. Both resins have shown the same sequence of affinity: UV-absorbing substances > DOC > sulfate > bromide. MIEX- HCO_3 could remove higher bromide (61%) than MIEX- Cl (53%). They used sodium bicarbonate for the regeneration of the resin. The limitation of MIEX-HCO_3 resin is that it could release bromide and chloride during the treatment of water. Hsu & Singer (2010) have investigated the efficiency of resin A641, IRA910, and MIEX for bromide removal. Around 64%, 62%, and 62% bromide was removed by A-641, IRA910, and MIEX resins respectively. But, A641, IRA910 could not able to remove DBPs efficiently due to the need for long contact time for NOM removal. Chubar et al. (2005) showed the adsorption technology using sol-gel ion exchange resin ($Fe_2O_3 \cdot Al_2O_3 \cdot xH_2O$) for bromide removal was significant along with fluoride, chloride, as well as bromate. In the first 10 minutes, around 50% of bromide was adsorbed. At a lower concentration, most of bromate ions were adsorbed and at higher concentration, mostly bromide ions were adsorbed to the surface of the ion exchanger.

Ion exchange resin treatment is moderately expensive, and the regeneration reduces the removal efficiency.

2.6 Aluminum coagulation

Aluminum chloride coagulant can also be used in removing bromide (F Ge et al., 2007). They investigated the bromide removal in synthetic water and raw water with different pH. The bromide removal in synthetic water increased from 93.3% to 99.2% for the coagulant dosage from 3 to 15 mg/L respectively without humic acid. With presence of humic acid and same dosages of coagulant indicated the bromide removal efficiency was in the range of 78.4% to 98.4%, which is lower. However, in raw water, the highest removal of bromide was 87% with 15 mg/L coagulant which is much lower than synthetic water. Bromide can be removed around 93.3–99.2% by coagulation with aluminium chloride ($AlCl_3 \cdot 6H_2O$) without organic matter. Bromide removal decreases with increasing pH, addition of organic matter, and other anions. With the addition of chloride ion, it decreases up to 14.6%. So, this method is not capable to remove bromide and DBPs efficiently from drinking water.

2.7 Other technology

Reverse electrodialysis (RED): RED process is the reverse of the electrodialysis process and can be used to desalinate water. Around 75% bromide can be removed with RED technology (Valero & Arbós, 2010). Van der Hoek et al. (1998) experimented with RED technology for an alternative of RO technology and got 72% bromide removal before disinfection. But the removal of DBPs is not mentioned in this process.

Recently, a batch test has been developed to chemically oxidize bromide using un-activated peroxymonosulfate (PMS) dosages in the range of 7.5 mM to 15 mM (K. Z. Huang & Zhang, 2020). The operating parameters were dosages of PMS, pH, the concentration of chloride, temperature, and the presence of organic matter. The result showed that PMS removed 86%, 94%, and 98% of bromide in 10 minutes with dosages of 7.5 mM, 10 mM, and 15 mM respectively. The effect of pH is vital in removing bromide. With the increase in the pH value, bromide removal efficiency is decreased. The removal efficiency is 99%, 98%, 72%, and 6% at pH 3, 5, 7, and 9 respectively. On the other hand, the increasing concentration of the chloride causes an increase in the bromide removal efficiency. Increasing concentration of chloride from 15 mM to 901 mM, 2140 mM, and 4169 mM increased bromide removal from 46% to 56%, 64%, and 63% respectively. Furthermore, the increase of PMS to bromide ratio from 0.5 to 0.55 and 0.60 improved bromide removal efficiency from 80% to 89% and 95% respectively. But, PMS reacts with halides and form non- radical reactive halogen species, for example HOBr, HOCl, HOI. These halogen species react with NOM and organic contaminants, and produce toxic halogenated byproducts, which makes the treatment problematic.

Table 2 summarizes all available bromide removal technologies. The electro-oxidation method using graphite as a working electrode can remove bromide efficiently. But, this method needs very high energy as well as cost, which is not optimistic for full scale water treatment. Also, it is not always capable in removing organic DBPs. The ion exchange method is cheap with respect to other technology. However, most of the resins have not showed significant DBPs removal. Besides, the regeneration of resin lowered the removal efficiency of bromide as well as other ions from water. On the other hand, the membrane filtration method needs very high energy, high pressure, and temperature. Also, this method requires pre-treatment of water which requires high cost as well as problematic with the brine disposal. Adsorption process is not suitable for removing bromate and other DBPs. So, considering all major bromide removal technologies it is clear that we need a solution of bromide removal as well as DBPs from drinking water. The ECM membrane is very cost effective and requires low energy.

Table 2: Comparison of bromide removal in different technology

Technology	Treatment method	Initial bromide concentration	Bromide removal	DBP formation reduction	References
Electro-oxidation	Titanium as the anode	0.09- 0.12 mg/L	55.00%	86.00%	(Kimbrough et al., 2013)
	Activated carbon	0.05 M	70.00%	0.16%	(Cohen et al., 2018)
	RuO_2 anode coated with titanium	0.4 M	90.00%	-	(Grgur, 2019)
	Graphite electrode	9.3 mM	98.30%	79.00%	(Tang et al., 2018)
Membrane deionization	Carbon electrode	1, 5, and 10 mg/L	99.90%		(Dorji et al., 2018)
Adsorption	Granular activated carbon	50- 105 µg/L in mineral water 30- 91 µg/L in ultrapure water	91.17% for mineral water 98.80% for ultrapure water		(Zhang et al., 2015)
	Silver-impregnated activated carbon (SIAC) 0.8 g/L	1.8 mg/L	93.00%		(Rajaeian et al., 2018)
Ion exchange resin	MIEX 8 mL/L	20, 100, and 200 µg/L	64.00%		(Johnson & Singer, 2004)
	Purolite- Br resin	100- 1000 µg/L	96.00%	90.00%	(Soyluoglu et al., 2020)

	MIEX 2 g/L	0.125 mg/L	90.00%		(Phetrak et al., 2014)
	IRA 400 2 g/L	0.125 mg/L	84.00%		(Phetrak et al., 2014)
	IRA 910 2 g/L	0.125 mg/L	90.00%		(Phetrak et al., 2014)
	MIEX- HCO_3	1000 µg/L	61.00%		(Walker & Boyer, 2011)
	MIEX- Cl	1000 µg/L	53.00%		(Walker & Boyer, 2011)
	A 641 6 mL/L	100 and 300 µg/L	64.00%		(Hsu & Singer, 2010)
	IRA 910 6 mL/L	100 and 300 µg/L	62.00%		(Hsu & Singer, 2010)
	MIEX 6 mL/L	100 and 300 µg/L	62.00%		(Hsu & Singer, 2010)
	sol-gel ion exchange resin ($Fe_2O_3 \cdot Al_2O_3 \cdot xH_2O$)	120 mg/L	50.00%		(Chubar et al., 2005)
Aluminum coagulation	Aluminum chloride coagulant	0–2.0 mg/L	99.20%		(F Ge et al., 2007)
Other technology	Reverse Osmosis	650 µg/L	99.00%		(Magara et al., 1996)
	Reverse electrodialysis	0.5–1.2 mg/L	75.00%		(Valero & Arbós, 2010)
	Reverse electrodialysis	185 µg/L	72.00%		(van der Hoek et al., 1998)
	un-activated peroxymonosulfate (PMS)	15 mM	98.00%		(K. Z. Huang & Zhang, 2020)

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Set up

A commercial membrane made with polyethersulfone was used as the supporting material for manufacturing ECMs. ECMs were prepared by pressure deposition followed by a cross-linking process (Kekre et al., 2021). In a short, carboxylic functionalized CNTs (0.1% wt.) were dispersed in deionized water with a 1:2.5 ratio of sodium dodecylbenzenesulfonate, and sonicated for 30 min. A CNT layer was then deposited on the polyethersulfone membrane by pressure deposition. Finally, the coated layer was cross-linked by polyvinyl alcohol, then cured in a 2:1 glutaraldehyde: hydrochloric acid solution at 90 °C for 60 min.

Two polyethylene flow cells with high-density was made to conduct bromide removal tests. The cell anode contained one ECM membrane anode (5 cm × 8 cm) and a titanium plate cathode (2 cm × 8 cm), with a 1 mm distance between the two electrodes. Figure 6 (a) and (b) show the top and bottom half of the reactor, respectively, and Figure 6 (c) shows the whole reactor assembled. The whole system setup is shown in Figure 7. In each reactor, a pressure gauge was used to regulate the pressure across the ECM for water filtration. A direct current power supply provided the power, and a peristaltic pump delivered water to the reactor continuously. In addition, two glass bottles filled with potassium iodide solutions was used to trap bromine produced by electrochemical oxidation and converted bromine back to bromide via Reaction 2. Note that such conversion is just for quantification in research and was not necessary for applying the proposed bromide removal in water treatment practice. Ideally, bromine generated in Reaction 1 was stripped out of the concentrate and permeate solutions by air to convert bromine in Reaction 2 in the iodide adsorption solutions.

$$2Br^- \rightarrow Br_2 + 2e^- \qquad \text{Reaction 1}$$

$$2I^- + Br_2 \rightarrow I_2 + 2Br^- \qquad \text{Reaction 2}$$

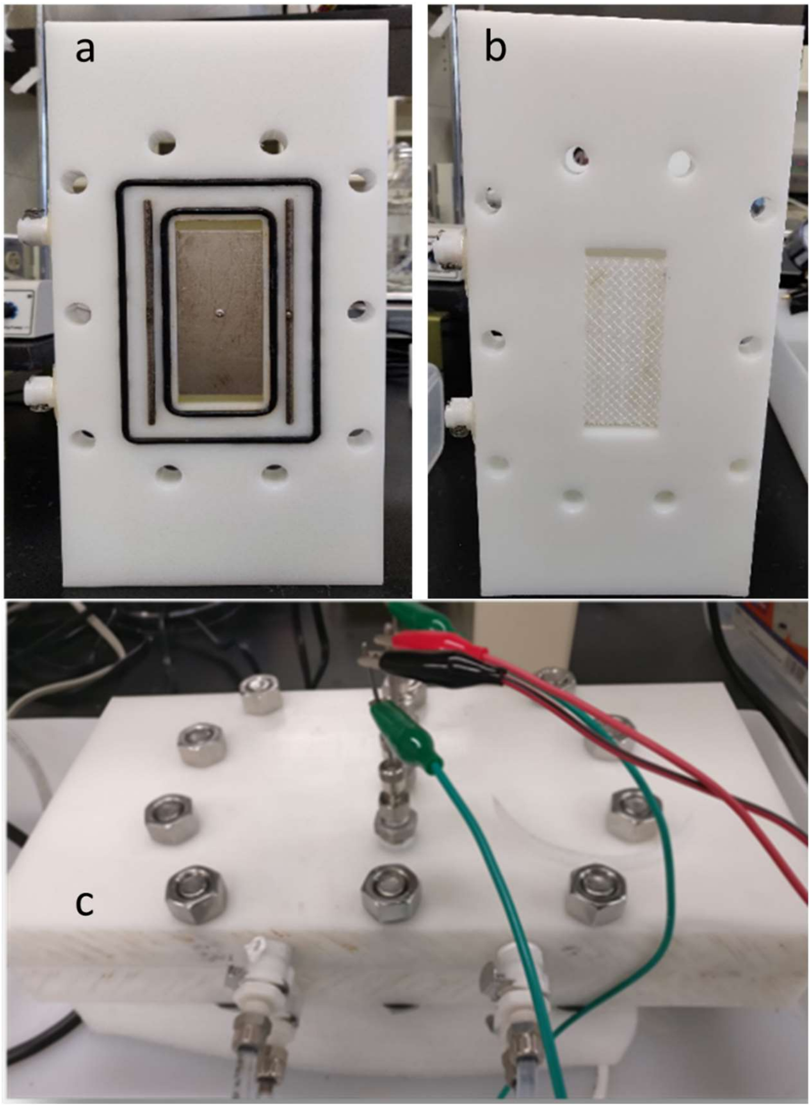


Figure 6: Flow cell setup for the experiment: (a) the top half; (b) the bottom half; (c) the whole ECM cell

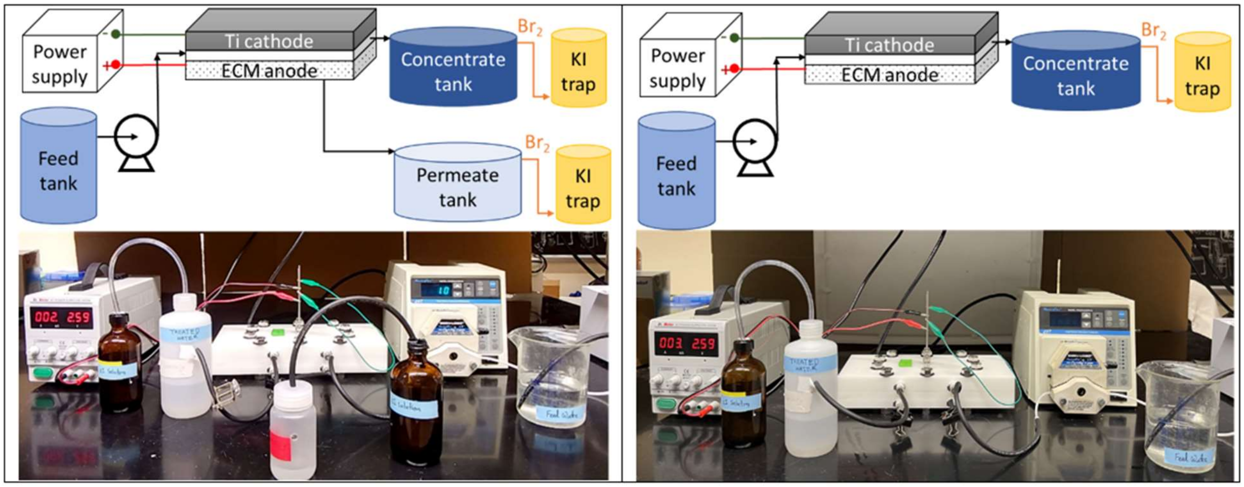


Figure 7: The schematic diagram and pictures of the experimental system setup. The left pictures show the setup with the permeate flow, and the right pictures show that without the permeate flow

3.2 Source water

The source water was used in this research is synthetic water made in the laboratory. Ultrapure water was spiked with chemicals with different concentration listed in Table 3. The median, 98th percentile, and the maximum bromide level in the US drinking water source reported in UCMR4 are 36.7, 590, and 73000 µg/L, respectively. Thus, the 700 µg/L bromide level tested in this project represents severe bromide contamination scenarios in drinking water sources.

Table 3: Water Quality Data

Chemical	**Spiked as**	**Concentration in ECM Reactor Feed**
Bromide	Potassium bromide	700 µg/L as Br^- (8.75 µN)
Chloride	Sodium chloride	3.5 - 177 mg/L as Cl^- (0.1, 2, and 5 mN)
Sulfate	Sodium sulfate	4.8 - 240 mg/L as SO_4^{2-} (0.1, 2, and 5 mN)
Nitrate	Sodium nitrate	6.2 - 310 mg/L as NO_3^- (0.1, 2, and 5 mN)
Bicarbonate	Sodium bicarbonate	6.1 - 305 mg/L as HCO_3^- (0.1, 2, and 5 mN)
DOM	Humic acid sodium salt	2 - 14 mg/L as TOC

3.4 Initial test conditions

Experiments were conducted in the ECM reactors in 700 μg/L (8.75 μN) bromide solutions. Major anions were separately spiked as their sodium salts at low, middle, and high levels typically found in drinking water sources (0.1, 2, and 5 mN, respectively). Since results at 5 and 10 psi showed that a lower transmembrane pressure enhanced bromide removal, in the anion tests, an even lower pressure of 1 psi was used to further increase the contact time for better treatment performance. Permeate water was collected and analyzed every hour, while concentrate water was collected and analyzed only at the end of the 5-hour tests. In addition to bromide removal, the formation of possible side reaction products (e.g., bromate and chlorate) was monitored.

3.5 Change in the experiment conditions

Due to the applied pressure, the volume of permeate and concentrate water were inconsistent in different experiments. So, it was impossible to get the consistent bromide removal efficiency from inconsistent flow volume for all experiments. As a consequence, the conditions of experiment were changed to no applied pressure condition (i.e., no permeate flow). All other conditions were same and the effluent samples were collected every 5 hours for analysis.

3.6 Evaluate the impact of DOM on bromide removal

Natural processes, like biomass decay and anthropogenic waste discharges, lead to the ubiquitous presence of DOM in drinking water sources. Generally, DOM is large molecules with negative charges with neutral pH conditions. So, DOM fouls membranes in water treatment by blocking the membrane pores and creating an organic layer on the membrane surface. This fouling issue is particularly severe for the positively charged ECMs. Meanwhile, since DOM is also an important DBP precursor, it is valuable to test if the ECM treatment could remove DOM while bromide is removed. This task was designed to assess the impact of DOM on bromide removal. Experiments were conducted in the ECM reactors shown in Figure 7 (right) in duplicates. Humic acid was used in the bromide solution as a surrogate of surface water DOM, at low, middle, and high levels typically found in drinking water sources (2, 5, and 14 mg/L, respectively) measured as dissolved organic carbon (DOC). Bromide concentration was 700 µg/L. Before each experiment, the reactors were conditioned in ultrapure water for 24 hours without power to open the membrane pores. Samples were collected every hour for 8 hours. Removal of both bromide and DOM was scrutinized.

3.7 Evaluate the impact of ECM treatment on DBP formation potential

This experiment was designed to assess the effect of the ECM treatment on DBP formation potential (i.e., how much DBP will form in a water sample after disinfection). The source water samples for these experiments were from previous test (section 3.6) which contain DOM. The water samples before and after ECM treatment were collected, and their DBP formation potential was measured using the uniform formation conditions (Summers et al. 1996). Concentrations of THMs, HAAs, and total organic halogen (TOX, an indicator of total DBPs) were quantified. Results before and after ECM treatment were compared to evaluate whether the ECM treatment decreased DBP formation potentials.

3.8 Chemical analysis

Anions: The concentration of bromide, bromate, and chlorate was measured following the standard method 300.1, with a Thermo Scientific Dionex ICS- 3000 ion chromatography (IC).

Bromine: The captured bromine in the iodide solution was converted to bromide and measured by IC. The remaining bromine in the reactor effluent water was not be directly quantified, but calculated by mass balance.

DOC: The concentration of DOC in water was measured following the Standard Method 415.3, with the high temperature combustion by Shimadzu TOC- LCPH/CPN analyzer.

DBP formation potential: The procedure described in literature Dotson et al. (2009) was followed to measure the DBP formation potential. In summary, water samples were transferred into bottles and buffered at pH 8 with the addition of 2 mL/L of 1 M borate buffer. After that, NaOCl solution (buffered at pH 8) was added in the water samples to maintain residual chlorine 1 ± 0.4 mg/L as Cl_2 after 24 hours incubation at 20°C under headspace-free conditions in the dark. To measure the chlorine dose for maintaining residual chlorine, the water samples were prepared with Cl_2: DOC ratios of 1.2:1, 1.8:1, and 2.5:1. When chlorination was done, the samples were dechlorinated by $Na_2S_2O_3$ and analyzed for DBP concentrations.

THMs and HAAs: The concentrations of four THM species (chloroform, bromoform, bromodichloromethane, and dibromochloromethane) was measured following Standard Method 551.1. The concentration of nine HAA species (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid, and tribromoacetic acid) was evaluated following Standard Method 552.3. All analytes were extracted using methyl-t-butyl ether (MTBE) and quantified with a Shimadzu 2014 gas chromatography with an electron capture detector.

TOX: The concentration of TOX was analyzed following a published method (Smith et al. 2010). In summary, 100 mL of acidified samples with a pH < 2, was filtered with 0.45 μm glass microfiber filters and loaded onto prepacked activated carbon cartridges. The carbon cartridges were washed with a 5 g/L nitrate solution to remove any inorganic halides, and combusted at 1000 °C using a Mitsubishi AQF-2100H furnace in the presence of oxygen and argon. Combustion products (chloride and bromide) were collected in 10 mL ultrapure water traps and analyzed for chloride and bromide, and the results were used to back-calculate the TOCl and TOBr levels in the original samples.

pH and residual chlorine: The pH levels and concentrations of residual chlorine in water samples during the disinfection steps were tested as required by the uniform formation conditions. pH was evaluated by a pH meter (Thermo Fisher Scientific). The concentration of residual chlorine was measured using a Hach DR2800 spectrophotometer with DPD reagent powder pillows following Hach Method 10069.

3.9 Equations

Bromide removal:

$$Bromide\ removal\ in\ stream\ i = \left(1 - \frac{C_{Br,i}}{C_{Br,f}}\right) \times 100\%$$

$$Bromide\ removal\ in\ the\ whole\ system = \left(1 - \frac{C_{Br,p}V_p + C_{Br,c}V_c}{C_{Br,f}V_f}\right) \times 100\%$$

Where C_{Br} is the bromide mass concentration (µg/L) and V is the volume of solution (ml). i stands for the feed (f), permeate (p), or concentrate (c) stream.

Bromide mass balance:

$$Br\ Mass\ in\ stream\ i = \sum_{j} C_{j,i} V_i$$

$$Uncovered\ Br\ mass = \left(1 - \frac{\sum_{i,j} C_{j,i} V_i}{C_{Br,f} V_f}\right) \times 100\%$$

Where i stands for the feed, permeate, concentrate, iodide trap for the permeate stream, and iodide trap for the concentrate stream. j stands for bromide or bromate. To facilitate mass balance calculation, concentrations of bromate were converted to as bromide (i.e., µg/L as Br instead of µg/L as BrO_3^-) using the following equation:

$$\frac{\mu g}{L} as\ Br = \frac{80}{128} \frac{\mu g}{L} as\ BrO_3^-$$

Where 80 and 128 are the molecular weight of Br and BrO_3^- respectively. As the bromide adsorptive loss to the reactors was proved minimal, assuming mass balance in the system, the uncovered Br is considered to be dissolved bromine in the permeate and concentrate solutions.

Bromine incorporation factor (BIF):

$$BIF = \frac{\sum y \times [RCl_x Br_y]}{\sum [RCl_x Br_y]}$$

Here $[RCl_x Br_y]$ is the molar concentration of a DBP containing x chlorine atoms and y bromine atoms in a molecule. A BIF value of 0 indicates no brominated species is formed, while a BIF value of 1, 2, or 3 suggests that the "average" DBP species formed is mono-brominated, di-brominated, or tri-brominated, respectively (Zhang et al. 2020).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Impact of major ions on bromide removal

4.1.1 Initial test

Concentrations of other anions in water may influence the bromide electrooxidation process in two ways: First, dissolved ions increase the conductivity of the solution to be treated, which would promote bromide removal. Second, the anions may compete with bromide for the active sites on the ECM surface for either electrostatic adsorption or electrochemical reactions. Since the membranes used in this study are permeable to salts, higher concentrations of ions are not expected to increase osmotic pressure or reduce flux, but may still affect the adsorption or electrochemical reactions. We evaluated the impacts of major anions on bromide removal by the ECM cells.

First, the 700 µg/L bromide solution was spiked with 0.1 mN sodium chloride. Bromide removal in both the whole system and the concentrate significantly decreased in the presence of low levels of chloride (Figure 8), suggesting that chloride was competing with bromide for the surface sites on ECMs for oxidation. However, the presence of chloride promoted bromide removal in the permeate. The reason for the difference between bromide removal with and without chloride in the concentrate and permeate could not be well explained.

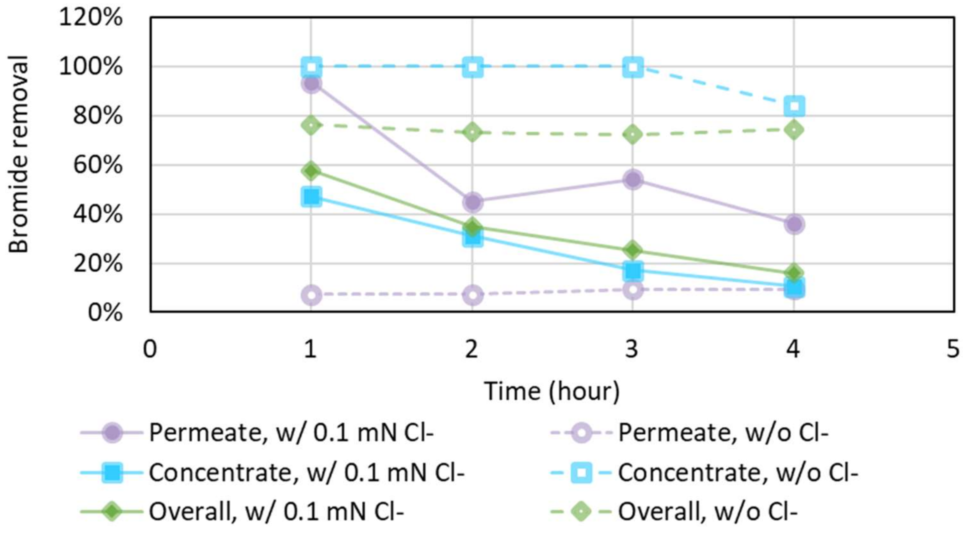


Figure 8: Bromide removal by the ECM cells with or without chloride (1 psi, 2.9 V, 700 µg/L bromide)

Bromate and chlorate are toxic byproducts that may form during electrooxidation of chloride and bromide in the ECM treatment if the applied potential is too high. Bromate is regulated by EPA at 10 µg/L in drinking water; chlorate is currently not regulated but was on the EPA Contaminant Candidate List 3, and the World Health Organization recommends a limit of 700 µg/L chlorate in drinking water. Bromate and chlorate were detected in the permeate and concentrate, both at concentrations up to 23 µg/L, suggesting that the 2.9 V voltage utilized in these tests was too high for drinking water treatment. Thus, the applied voltage was reduced to 2.6 V in the following tests.

Subsequently, sodium bromide solution (700 µg Br/L or 8.75 µN) was spiked separately with 0.1, 2, and 5 mN of chloride, sulfate, nitrate, and bicarbonate. Bromide removal in these solutions was tested at 1 psi and 2.6 V. Bromide was removed in both the permeate and concentrate, without a consistent trend on which stream had higher removal throughout all experiments. Although a control test without other anions was not conducted at this voltage and pressure, it is still clear that bromide removal decreased when another anion was present (Figure 9). Bromate and chlorate were still generated at low levels (2-10 μg/L) in the permeate and concentrate, although the bromate levels were less than the regulated 10 μg/L drinking water standard. No chlorite or perchlorate was detected when chloride was in the solution. The relatively low level of chlorate generated compared to bromide removed suggests that the chloride inhibition was mainly due to competitive electro-sorption on the ECM surface rather than competitive oxidation. The fact that sulfate, nitrate, or bicarbonate could not be further oxidized also suggests that the observed inhibition was related to adsorption instead of side reactions. Among the tested anions, chloride had the highest inhibition of bromide removal, probably because it has the hydrated radius closest to that of bromide (3.30 Å for bromide vs. 3.32 Å for chloride) (Nightingale 1959), making the two anions competing to the same set of surface adsorption sites. Meanwhile, the inhibition by sulfate (3.79 Å) and nitrate (3.35 Å) was much less pronounced, as these bigger anions may suffer more from steric effects when competing with bromide for adsorption sites.

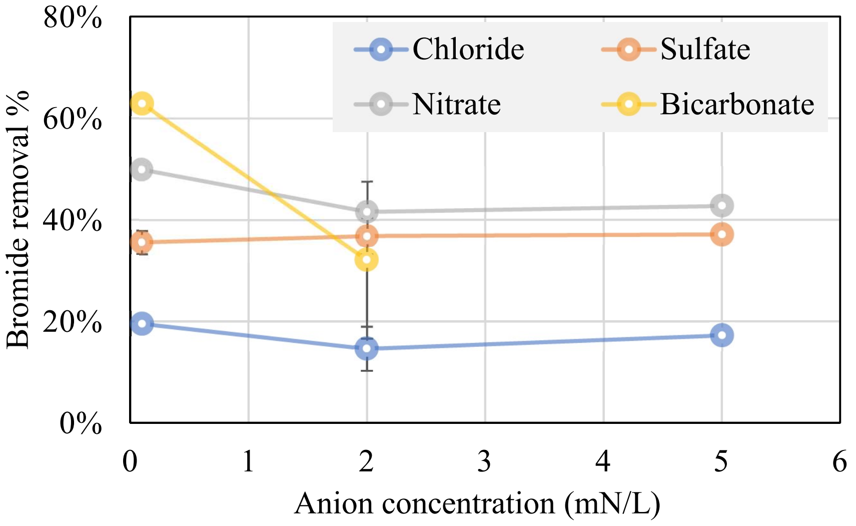


Figure 9: Bromide removal by the ECM cells after 5 hours in the presence of different anions (1 psi, 2.6 V, 700 µg/L bromide). The symbols present the average results from duplicate tests. Error bars represent one standard deviation.

Mass balance of bromide indicated that a large portion of bromide stayed in the treated concentrate stream (Figure 10, bromine in the concentrate and permeate is calculated via bromine mass balance). The volume of the concentrate stream was much larger than the permeate in most cases, thus the higher bromide masses in the concentrate do not necessarily mean higher bromide concentrations. Low bromide levels were also detected in the iodide traps, suggesting some bromine produced during electrooxidation was stripped out of the ECM cells. Nevertheless, most bromine produced stayed in the concentrate and permeate streams. Such uncaptured bromine could be stripped out by air and collected as a valuable product in field-scale water treatment applications.

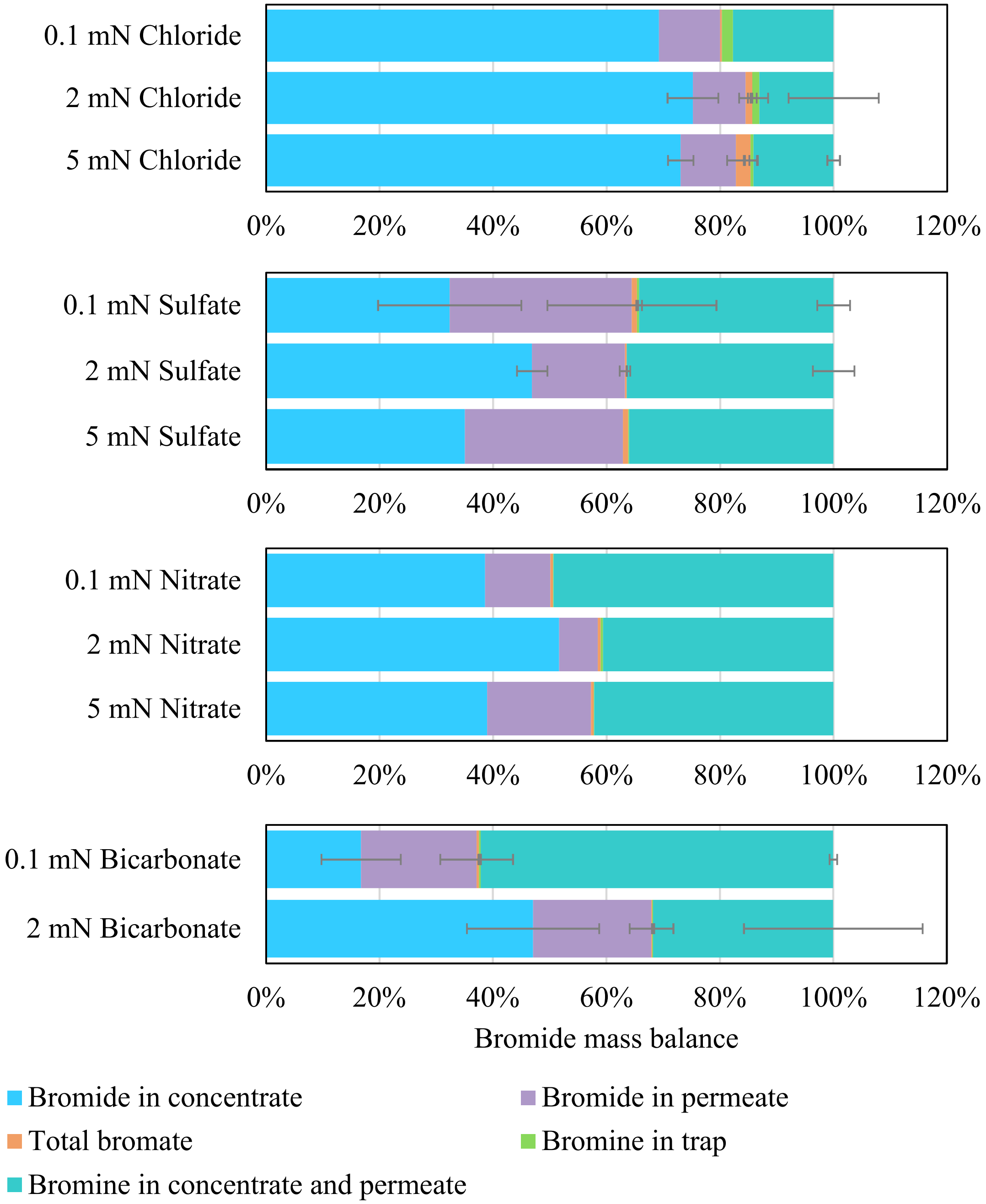


Figure 10: Bromide mass balance in the ECM cells after 5 hours in the presence of different anions (1 psi, 2.6 V, 700 µg/L bromide). The colored bars present the average results from duplicate tests. Error bars represent one standard deviation.

4.1.2 Change in the experiment conditions

During our experiments, we found that the remaining bromide concentrations in the concentrate sometimes were lower than those in the permeate. Meanwhile, the volume of concentrate was much larger than the volume of permeate. As a result, we decided to change the experiment conditions and not apply any pressure across the ECMs, so that there would be no permeate, and all effluent would be collected from the "concentrate" side of the reactors. Thus, the reactors essentially became plug-flow electrochemical treatment cells instead of membrane reactors. This change also brought additional benefits of lower energy cost without the need to apply pressure, more constant effluent flow rates during treatment, and more consistent results between duplicate tests. We repeated the anion effect tests under the new conditions and achieved similar overall bromide removal as under the old conditions (Table 4) with no bromate formation.

Table 4: Comparison of overall bromide removal under different experiment conditions (2.6 V, 700 μg/L bromide)

Anion concentration	Under new condition (no permeate)	Under old condition (with permeate)
0.1 mN chloride	35±11%	19%*
2 mN chloride	22±0%	15±4%
5 mN chloride	13±1%	17±1%
0.1 mN sulfate	49±1%	36±2%
2 mN sulfate	41±3%	37±4%
5 mN sulfate	27±7%	37%*
0.1 mN nitrate	55±1%	50%*
2 mN nitrate	35±0%	42%*
5 mN nitrate	33±3%	43%*
0.1 mN bicarbonate	59±6%	63±1%
2 mN bicarbonate	40±1%	32±15%
5 mN bicarbonate	15±3%	Not tested
* Test conducted only once so no standard deviation available		

4.2 Effect of major anions on bromide removal under new experiment conditions

Under the new condition, 68% bromide removal was achieved in 700 µg/L bromide solutions without other anions. All the tested anions inhibited bromide removal, and the inhibition was more pronounced at higher anion concentrations as expected (Figure 11 and Figure 12). Similar to the results from the old condition (i.e., with 1 psi transmembrane pressure), the impact of sulfate and nitrate were similar, both smaller than the impacts of the other two anions, while chloride reduced bromide removal the most among the four anions at all concentrations. The impact of bicarbonate was relatively small at low concentrations (0.1 and 2 mN), comparable to that of nitrate and sulfate; however, at a high concentration (5 mN), bicarbonate showed the same degree of inhibition to bromide removal as chloride. No bromate, chlorite, or chlorate formed during the experiments, and all bromine produced stayed in the reactor effluent instead of in the iodide traps.

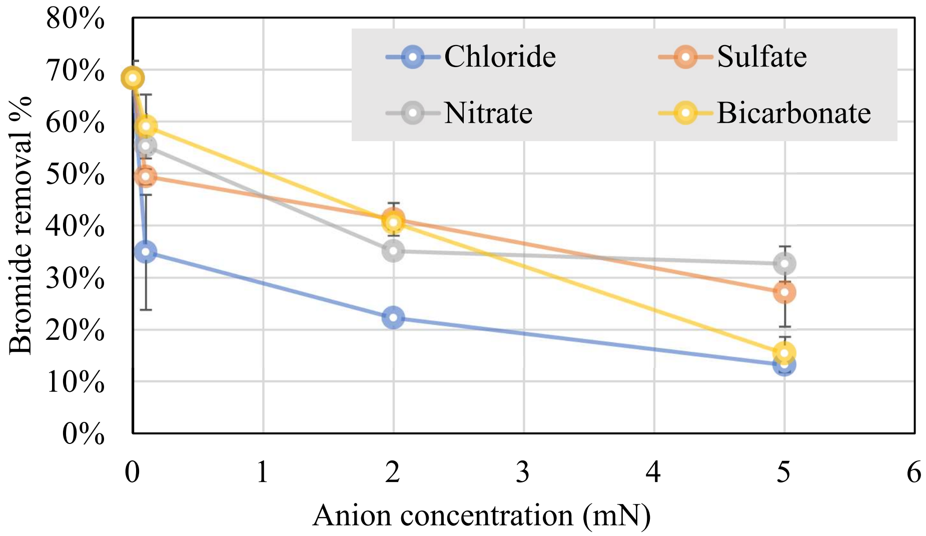


Figure 11: Bromide removal by the ECM cells after 5 hours in the presence of different anions (0 psi, 2.6 V, 700 µg/L bromide). The symbols present the average results from duplicate tests. Error bars represent one standard deviation.

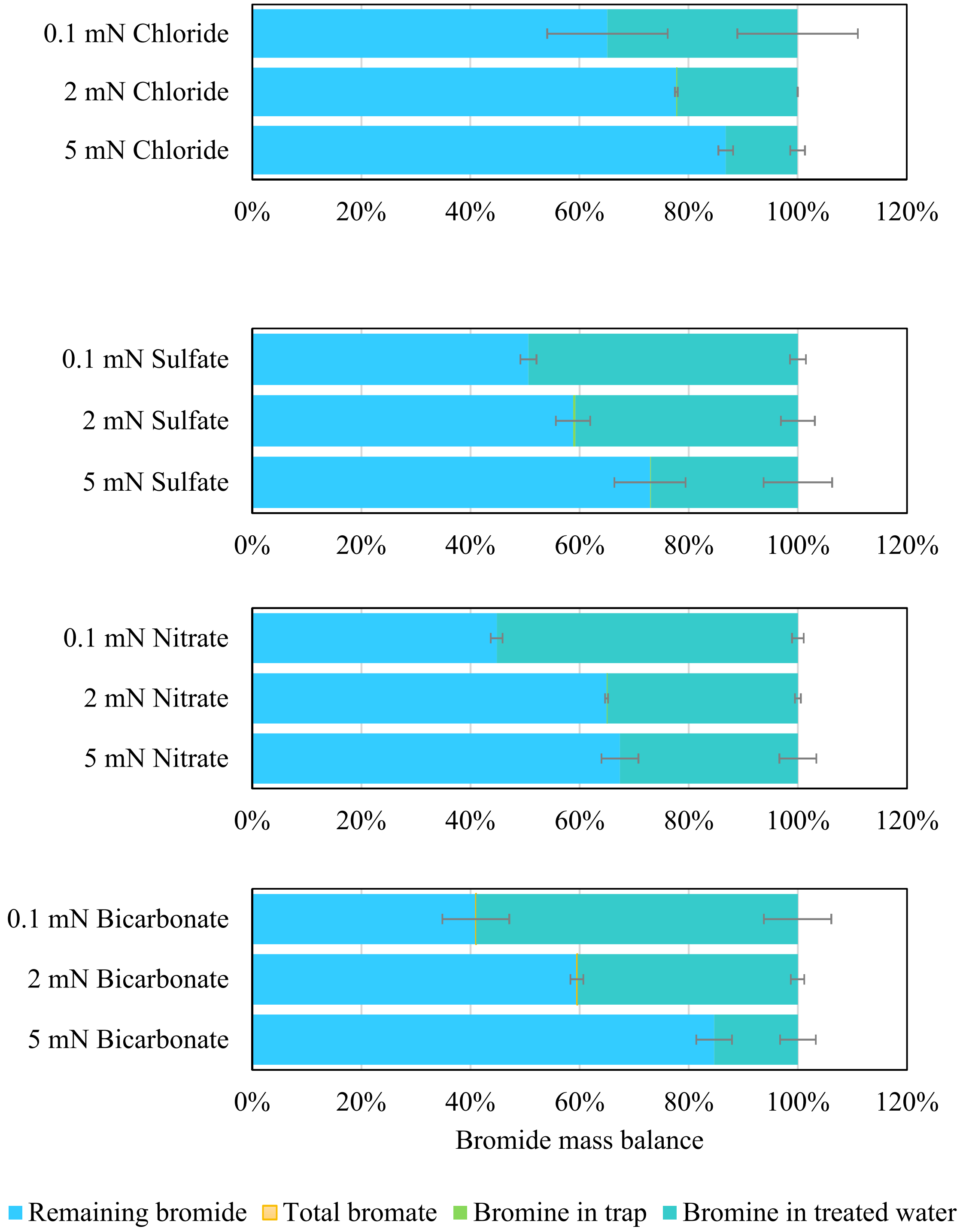


Figure 12: Bromide mass balance in the ECM cells after 4 hours in the presence of different anions (1 psi, 2.6 V, 700 µg/L bromide). The colored bars present the average results from duplicate tests. Error bars represent one standard deviation.

4.3 Impact of DOM on bromide removal efficiency

Natural processes (e.g., biomass decay) and anthropogenic waste discharges lead to the ubiquitous presence of DOM in drinking water sources. The mean DOC concentration in US drinking water source reported in UCMR4 is below the method detection limit (MRL) of 1 mg/L, while the mean value is 1.5 mg/L (concentrations <MRL are considered ½ MRL for statistical analysis). DOM contains molecules of various sizes, and a high portion of DOM is too large to pass the ECM pores. Hence, DOM may block the membrane pores and cumulate on the membrane surface. The fouling problem is even more challenging for the positively charged ECM anode since DOM is typically negatively charged under neutral pH conditions. In this task, the DOM effect on bromide oxidation and filtration was studied using humic acid as the representative DOM, and DOM concentration is quantified as DOC. Furthermore, since DOM is also a DBP precursor, its potential removal by electrooxidation was also examined in concurrence with bromide removal. Note that no transmembrane pressure was applied in the new reactor setup, thus DOM could not be removed via membrane filtration.

With increasing DOC concentrations, the bromide removal dramatically decreased from 68% with no DOC to 25% with 14 mg/L DOC (Figure 13). Meanwhile, the simultaneous DOC removal by the ECM treatment was minimal (2-11% at the three tested DOC concentrations) and relatively constant in the tested range. Therefore, the inhibition in bromide removal is likely caused by DOM blocking the active sites on the ECM surface, rather than competition for the electrooxidation capacity. This conclusion is further supported by the severe membrane fouling observed at high DOC levels. No bromate was detected in the treated water.

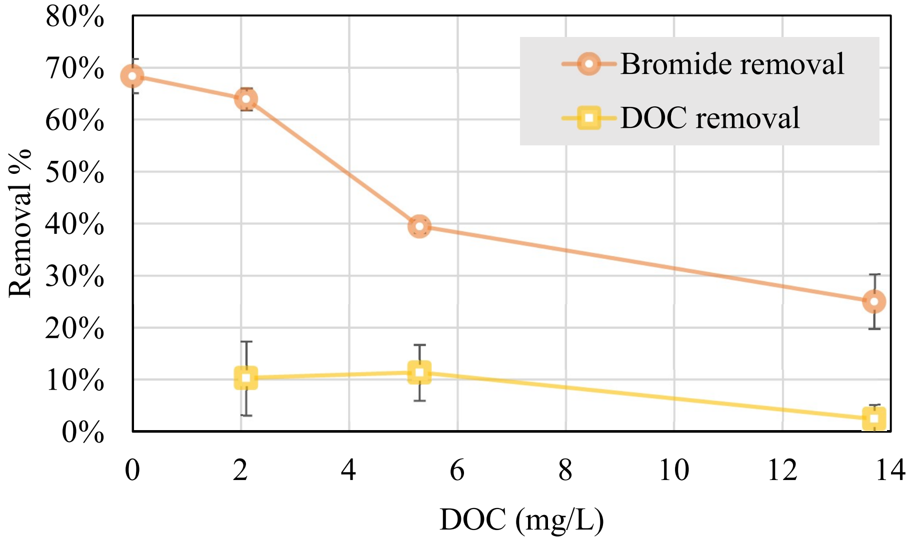


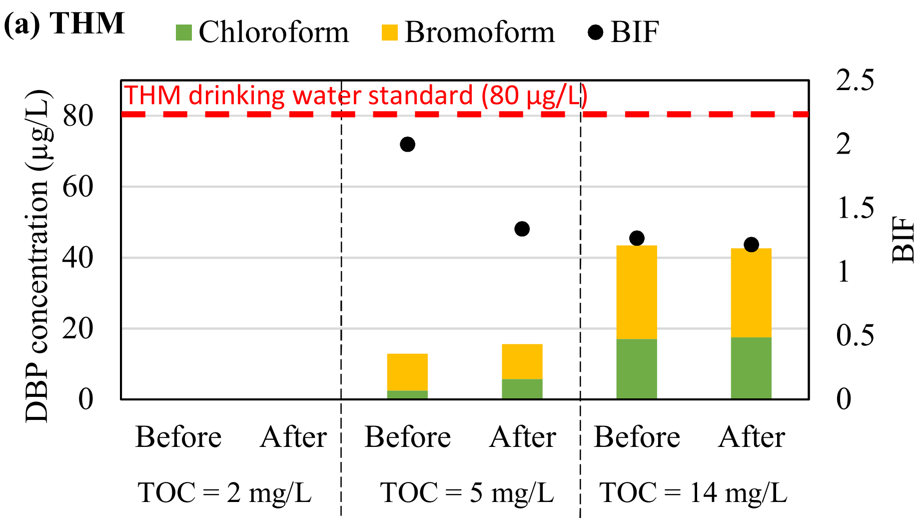
Figure 13: Bromide removal by the ECM cells after 8 hours in the presence of different DOC levels (0 psi, 2.6 V, 700 μg/L bromide). The symbols present the average results from duplicate tests. Error bars represent one standard deviation.

4.4 DBP formation before and after bromide removal

As shown in Figure 13, the applied voltage (2.6 V) was insufficient to mineralize DOM (indicated by the minimal DOC removal after treatment); however, the treatment may have partially oxidized DOM, converted it into smaller molecules, or added functional groups to the molecules. DOM after such changes may lead to different DBP formation potentials in the following disinfection step. Meanwhile, the ECM treatment is expected to reduce DBP formation by removing bromide as a DBP precursor. To decide the overall effect of the ECM treatment on DBP formation, DBP formation potentials were quantified for water samples with 700 μg/L bromide and different levels of DOC, as well as for the same samples after ECM treatment. These samples were subject to chlorination under the uniform formation conditions with a chlorine dose of Cl_2: DOC ratio at 2.5:1. After 24-hour incubation, the pH of all samples was 8±0.2, and the residual chlorine was

1.0±0.2 mg/L as Cl_2. Then the samples were quantified for speciated THMs, HAAs, as well as TOX as the surrogate for total DBPs. In general, samples with higher initial DOC levels had higher DBP formation potentials both before and after ECM treatment (Figure 14). At the low DOC level (2 mg/L), the concentrations of all THMs were below the limit of quantification (2 µg/L), and the total concentrations of the five regulated HAAs (monobromoacetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid) were well below the drinking water standard of 60 µg/L. THM concentrations increased when the DOC level increased to 5 and 13 mg/L, but their total concentrations never exceeded the drinking water standard of 80 µg/L, and only chloroform and bromoform were detected among the quantified THM species in the samples. Meanwhile, the sum concentrations of the five regulated HAA species exceeded the 60 µg/L regulatory limit when DOC was 5 and 13 mg/L; among the nine quantified HAA species, all but tribromoacetic acid were detected in at least one sample.

At all tested DOC levels, the formation potential of neither THMs nor HAAs changed significantly after the ECM treatment (i.e., when 25-64% of bromide and negligible DOC were removed). Such results suggest that the DOC level (and possibly its speciation), rather than the bromide concentration, is the determining factor for DBP formation. However, ECM treatment did reduce the bromide to DOC concentration ratios, which subsequently reduced the BIF for both THMs and HAAs (Figure 15). Since BIF indicates the portion of bromated DBPs in all DBPs, such results suggest that the ECM treatment inhibited the formation of more toxic brominated species at the same overall DBP formation potential. Such inhibition is more pronounced in the low and median DOC group (i.e., when DOC = 2 or 5 mg/L) than in the high TOC group. In the high DOC group, the BIF was low both before and after ECM treatment, because the very low bromide to DOC ratio strongly drove DBP formation towards the chlorinated species.



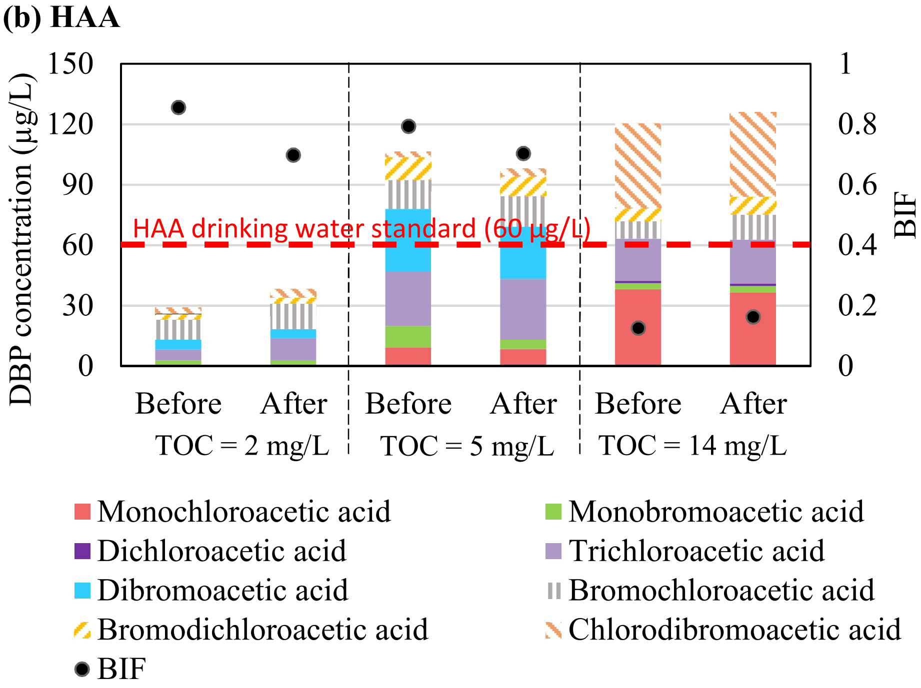


Figure 14: THM and HAA formation potentials and bromide incorporation factors (BIF) in chlorinated samples before and after ECM treatment at different initial DOC levels (0 psi, 2.6 V, 700 µg/L bromide). DBPs with concentrations lower than the limit of quantification are not included in this figure. The average results of duplicate tests were presented, and the standard deviations are not presented for figure clarity. In panel (b), solid bars represent regulated HAAs, and pattern-filled bars represent unregulated HAAs.

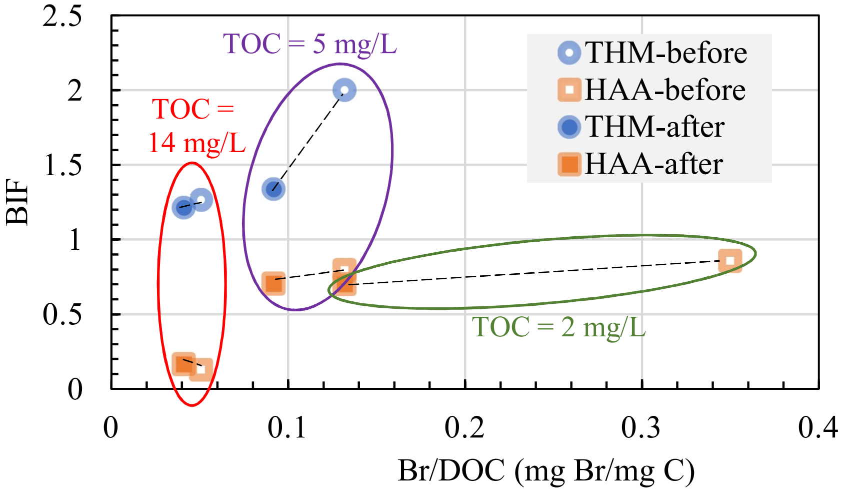
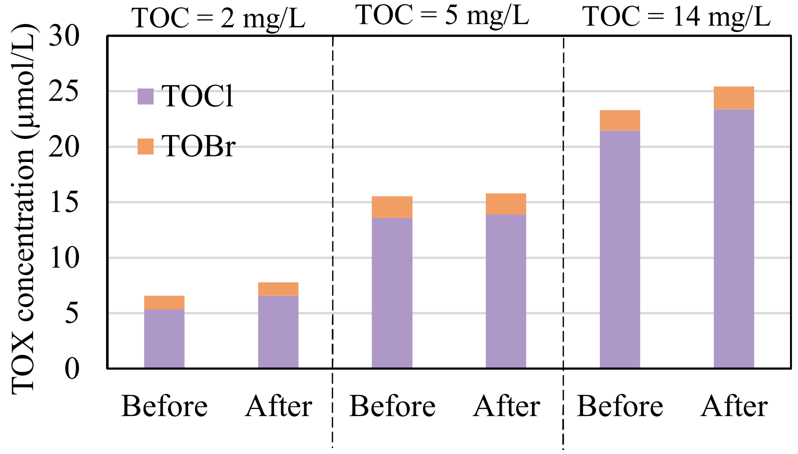


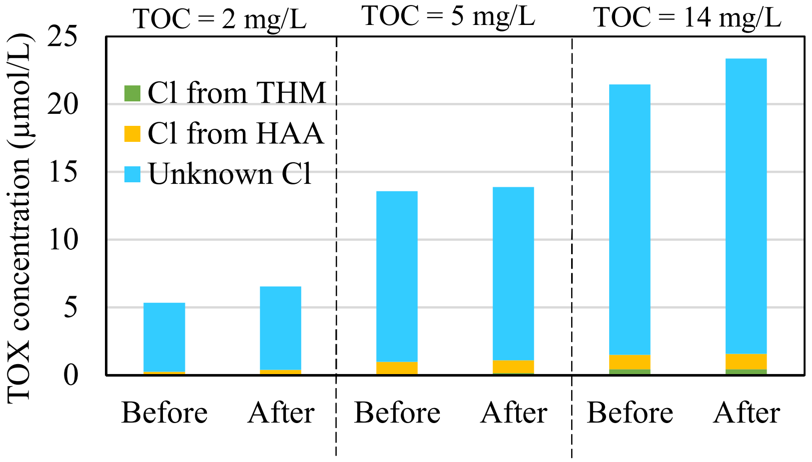
Figure 15: The relationship between the bromide/DOC concentration ratio and the bromine incorporation factor (BIF) in THMs and HAAs before and after ECM treatment. Each pair of samples before and after ECM treatment (0 psi, 2.6 V, 700 µg/L bromide) was connected with a dashed line. The BIF for THM at 2 mg/L TOC level was not included in the figure since no THM was detected in this group after disinfection.

Total organic chloride (TOCl) and total organic bromide (TOBr) were measured to represent total DBPs in the samples, including the unregulated/unidentified species. Figure 16 shows that the ECM treatment did not substantially change TOX formation potential of the samples, and in all cases, the chlorinated species overweighed the brominated species. The majority (93-96%) of TOCl was contributed by unknown species, while for TOBr, the unknown portions reduced to 59-87%, with up to 41% TOBr accounted by THMs and HAAs. Overall, the TOX results suggest that the bromide removal treatment did not change the formation potential of either the chlorinated or brominated DBPs. The results again suggest the dominant role of DOC over bromide in DBP formation.

(a) TOX



(b) TOCl



(c) TOBr

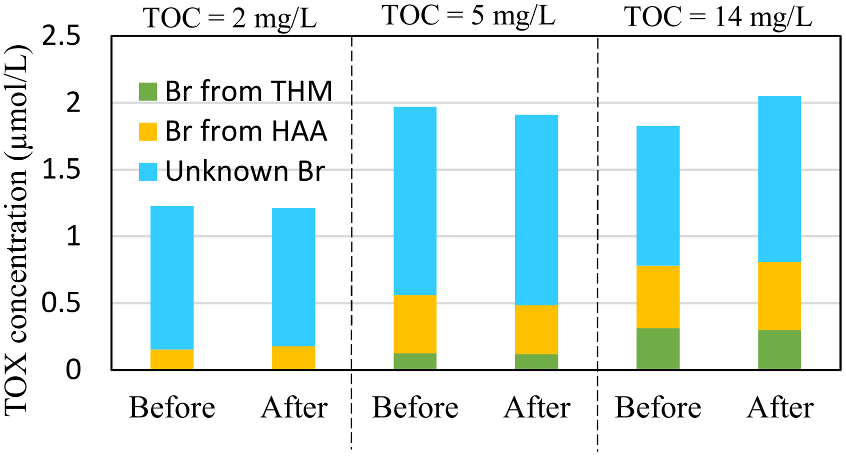


Figure 16: TOX formation in chlorinated samples before and after ECM treatment with different initial DOC levels (0 psi, 2.6 V, 700 µg/L bromide).

CHAPTER 5: CONCLUSIONS

1) The ECM cells are capable of removing bromide (around 70%) from simulated drinking water sources. The removal mechanism is electrochemical oxidation rather than membrane filtration. The impact of cell voltage on bromide removal is limited in the range of 2-2.9 V, and undesired byproducts (bromate and chlorate) form at high voltage; thus, a cell voltage of 2.6 V is considered optimal for bromide removal.
2) A lower transmembrane pressure increases the contact time between ECMs and bromide, thus promotes bromide removal. Furthermore, similar levels of bromide removal could be achieved whether or not a transmembrane pressure was applied. Hence, it is recommended to use the ECM cells as electrolysis cells instead of membrane filters.
3) Chloride, bicarbonate, sulfate, and nitrate all suppress bromide removal by the ECM cells. The inhibition is the most pronounced for chloride and less significant for sulfate and nitrate.
4) With increasing DOC concentrations, bromide removal by the ECM cells decreased significantly. The DOM inhibition is likely caused by membrane fouling instead of competition for electrooxidation capacity.
5) The THM and HAA formation potential of water samples containing both bromide and DOC was predominantly controlled by the DOC levels rather than the bromide levels. Since the ECM cells only removed bromide and had minimal removal of DOC, the ECM treatment did not significantly change the DBP formation potential of water samples. However, the ECM treatment did inhibit the formation of more toxic brominated species and mitigate bromide incorporation in THMs and HAAs.

6) Similarly, the ECM treatment had limited impacts on the TOCl and TOBr formation potential of the tested water samples containing both bromide and DOC.
7) At the cell voltages tested in this study (2-2.9 V), the current detected during treatment was in the range of single-digit mA. Therefore, the energy requirement for bromide removal is around 0.5 kWh/g in the bench scale.

CHAPTER 6: CHALLENGES AND FUTURE RECOMMENDATIONS

6.1 Challenges

The most important challenge for the future development of this ECM treatment in bromide removal from impaired drinking water sources is the limited performance achieved in this bench-scale demonstration. While bromide removal was achieved in all tested conditions, and the operational conditions were optimized for the treatment, overall, the removal was only up to 68%. The bromide removal and DBP formation reduction achieved in this project were not as high as expected because of the limited contact time between the treated water and the ECMs (0.8-10 seconds) and the relatively challenging concentrations of DBP precursors (bromide and DOM) tested.

Considering the contact time between the ECMs and bromide in this project, the removal achieved by the ECM cells is efficient compared to solid electrodes which require a significantly longer time to reach a similar removal percentage. To further increase removal efficiency, we could upgrade the reactor design in the following two approaches:

1) Instead of having the bromide solution flow through the ECM cells in a single pass module, ECM cells could be deployed in series, or the effluent could be recirculated to extend overall contact time.
2) The ECM thickness could be increased by depositing a higher mass of CNTs on the supporting membranes.

In addition, the reduction in DBP formation potential after the treatment was also limited due to the high DOC level we tested. In drinking water treatment practice, the feed water would be pretreated by coagulation/fluctuation/sedimentation/filtration to lower the DOC level. Such pretreatment is also beneficial for preventing ECM fouling.

Finally, the ECM production is still in lab-scale currently, and scaling up the production is needed for potential commercialization.

6.2 Recommended next steps

Based on the results of the bench-scale demonstration of bromide removal by the ECM treatment, further investigation is needed before commercializing such technology to address the challenges identified above. For example, new reactor configurations should be tested to achieve better bromide removal and DBP formation reduction. A detailed cost analysis is also desirable to compare with other bromide treatment methods. In addition, the treatment needs to be tested using real drinking water sources instead of simulated samples, preferably in pilot scales. All the information together will help water treatment facilities with source water impaired by bromide make the decision on whether it is cost-effective to adopt this method for their treatment practice.

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