Bromide and iodide selectivity in membrane capacitive deionisation, and its potential application to reduce the formation of disinfection by-products in water treatment

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ABSTRACT

The formation of toxic disinfection by-products during water disinfection due to the presence of bromide and iodide is a major concern. Current treatment technologies such as membrane, adsorption and electrochemical processes have been known to have limitations such as high energy demand and excessive chemical use. In this study, the selectivity between bromide and iodide, and their removal in membrane capacitive deionisation (MCDI) was evaluated. The results showed that iodide was more selectively removed over bromide from several binary feed waters containing bromide and iodide under various initial concentrations and applied voltages. Even in the presence of significant background concentration of sodium chloride, definite selectivity of iodide over bromide was observed. The high partial-charge transfer coefficient of iodide compared to bromide could be a feasible explanation for high iodide selectivity since both bromide and iodide have similar ionic charge and hydrated radius. The result also shows that MCDI can be a potential alternative for the removal of bromide and iodide during water treatment.

Keywords: bromide; disinfection by-products; iodide; membrane capacitive deionization

1. Introduction

Water disinfection is important to ensure that the water is free from harmful bacteria and viruses for human use. However, the water disinfection also introduces a significant quantity of toxic disinfection by-products (DBPs) when source water contains inorganic halides such as bromide and iodide in the presence of natural organic matter (NOM) (Krasner, 2009; Yang et al., 2014). Therefore, one of the major challenges of water treatment plants is to ensure effective water disinfection while minimising the formation of toxic DBPs (Simpson and Hayes, 1998). Most of the DBPs are now considered to be an “emerging” environmental contaminants, and more than 600 types have been reported (Richardson et al., 2007; Richardson and Kimura, 2017). The discovery of many unknown DBPs indicates that our understanding of the formation of DBPs during water disinfection is still very limited.

Currently, chlorination, chloramination, ozonation and ultraviolet radiations are some of the common disinfection processes in water treatment (Krasner, 2009). All these disinfectants have different disinfection potential, but they also react differently with various DBP precursors to produce a wide range of DBPs (Richardson and Kimura, 2017). Since the DBPs are highly regulated, many water treatment plants have started to explore alternative disinfectants to comply with the regulatory requirements on DBP (Wang et al., 2015). For example, water treatment plants using chloramination were able to easily meet the regulatory requirement for regulated DBPs compared to chlorination (Goslan et al., 2009).

Both bromide and iodide salts are naturally occurring salts, and their respective concentrations depend on the geology and anthropogenic activities (Moran et al., 2002; Magazinovic et al., 2004). They are the major halide inorganic precursors for the formation of DBPs during disinfection (Kampioti and Stephanou, 2002; Hua et al., 2006;

Krasner, 2009; Liu et al., 2016). Some Australian water sources, especially in Western Australia, contain a higher concentration of natural organic matter with elevated bromide and iodide concentrations (Gruchlik et al., 2014). The dominance of brominated DBPs during disinfection of high-bromide containing water during chlorination is well documented (Winid, 2015; Tan et al., 2016). It was reported that a bromide concentration of 50-100 µg/L can lead to the formation of bromate, which is known to cause renal and thyroid cancer in mammals, and so far there is no practical solution for its removal (von Gunten, 2003; Richardson et al., 2007). Similarly, an extensive survey on water treatment plants in Canada revealed the formation of iodinated DBPs during both chlorination and chloramination (Tugulea et al., 2018). A detailed assessment of iodide related DBPs formation using chlorine dioxide disinfection in synthetic and actual water also reported to produce a varying degree of iodinated DBPs (Ye et al., 2013).

Due to the shortage of reliable freshwater source, it is common for many countries to adopt seawater reverse osmosis (SWRO) to produce freshwater. However, there are some limitations of this technology in removing bromide to an acceptable level. In Australia, for example, two-stage reverse osmosis has to be adopted to ensure bromide is reduced to an acceptable level. However, research has shown that desalinated water blended with water from regular sources had a higher potential of formation of bromide related DBPs due to the high concentration of bromide in desalinated water using reverse osmosis system (Cai et al., 2018). The concentration of iodide, on the other hand, appears to be low enough in desalinated water using reverse osmosis to reduce iodide related DBPs (Duranceau, 2010).

A common strategy adopted by water treatment plants to reduce the formation of DBPs is to remove bromide and iodide before the water is disinfected. A comprehensive review of technological options for halide removal concluded that membrane process such as reverse osmosis is the preferred method, but they are expensive to operate due to higher energy demand (Watson et al., 2012). The review also highlighted that electrochemical and adsorption processes for halide removal are not practical. Interestingly, the review suggested that optimisation of Capacitive Deionisation (CDI) or Membrane CDI (MCDI) could potentially rival membrane processes in halide removal. Especially for feed water containing low total dissolved solid (TDS), MCDI was demonstrated to be more energy efficient, where the energy consumption of MCDI was just half of reverse osmosis when the permeate from the 1st pass SWRO was treated (Choi et al., 2019b). Other previous assessment on energy consumption between MCDI and reverse osmosis also concluded that for feed water with TDS of less than 2 g/L, MCDI is more energy efficient (Zhao et al., 2013). Similarly, a pilot-scale MCDI treatment for cooling tower water demonstrated significant chemical savings, less wastewater production and higher energy efficiency (Van Limpt and van der Wal, 2014).

The CDI is an electrosorption process to remove ions from water due to the formation of the electric double layer (Pekala et al., 1998). Over the last decade, CDI research has rapidly evolved for desalination, water and wastewater treatment applications including resource recovery (Suss et al., 2015; Choi et al., 2016; Kim et al., 2017; Choi et al., 2019a). One of the major issues experienced by CDI is the occurrence of simultaneous adsorption of counterions and expulsion of co-ions in the spacer channel during adsorption and desorption phases, which reduced the desalination performance (Biesheuvel et al., 2011; Porada et al., 2013). By using ion exchange membranes in CDI, this phenomenon is greatly reduced as demonstrated in desalination of thermal power wastewater (Lee et al., 2006). Since then, MCDI has gained significant research interest. Most MCDI studies consistently reported better performance in salt removal and higher charge efficiency compared to CDI (Lee et al., 2006; Li et al., 2008; Kim and Choi, 2010;

Li and Zou, 2011; Liang et al., 2013; Liu et al., 2014; Omosebi et al., 2014; Van Limpt and van der Wal, 2014). Recently, some studies have been conducted using the so-called advanced MCDI, where ion exchange polymers were directly applied on the surface of carbon electrode instead of using a separate ion exchange membrane layer (Lee et al., 2011; Kim and Choi, 2012).

In this study, the application of MCDI for bromide-iodide selectivity and its application on removing these ions were systematically assessed using commercially available activated carbon electrodes with cation and anion exchange polymer incorporated on the surface. Although the effect of different charge and hydrated radius of ions on selectivity in CDI and MCDI have been extensively studied, this study evaluated the effect on ion selectivity between bromide and iodide which have similar hydrated radius and ionic charge (Table 1), and they are also major inorganic precursors for the formation of major toxic DBPs during water disinfection. To understand the fundamental competitive behaviour between bromide and iodide ions, several types of feed water containing single electrolyte, mixed bromide and iodide and feed water with different background total dissolved solids were prepared, and their selective removal studied under different operating conditions. Finally, for practical application of MCDI in water treatment, tap water spiked with bromide and iodide was used as actual feed to determine the removal capacity of bromide and iodide.

Table 1. Physical and chemical properties of various halides (Nightingale Jr, 1959; Watson et al., 2012)

Halide	Electronegativity (Pauling scale)	Hydrated radius (Å)
Cl^-	3.16	3.32
Br^-	2.96	3.30
I^-	2.66	3.31

2. Materials and methods

2.1. *Lab-scale MCDI and operation parameters*

The lab-scale MCDI cell composed of a pair of composite electrodes (100 mm x 100 mm) where cation and anion exchange polymers were coated on the electrodes made of activated carbon (Siontech Co., Korea). A graphite sheet was used as a current collector on which the activated carbon P-60 (Kuraray Chemical Co., Japan) was coated. A non-conductive nylon spacer (200 μm) was used to prevent electrode short-circuit. A pair of acrylic plates were used to support the entire unit. The total Brunauer-Emmett-Teller surface area and the mass of the activated carbon were 1689.5 m^2/g and 1.6 g respectively as per the manufacturer.

The feed water flowed at a constant flow rate of 40 ml/min from a peristaltic pump (GTS 100, Green Tech, Korea) from all the sides of the cell through the spacer, and the treated water was collected from the centre of the unit. A feed volume of 100 ml was used for each experiment, and the experiments were conducted under a batch process, where the effluent was constantly recycled into the feed reservoir. A constant direct current voltage was applied/regulated using a potentiostat (ZIVE SP1, WonATech Co., Korea). Prior to the experiment, the feed solution was flushed through the cell under single-pass without application of voltage till the influent and effluent conductivities were the same. After this, fresh feed solutions of 100 ml were constantly recycled under a batch-mode operation at different applied voltages. The total adsorption time was 10 minutes. After adsorption, the electrode regeneration was achieved through reverse-voltage desorption by using MQ water. Throughout the experiment, the conductivity and pH were continuously monitored and recorded using a HACH (HQ40d) multi-meter in the feed reservoir at 10-sec interval. During the adsorption phase, 2 ml sample was withdrawn after every two-minute interval from the feed reservoir to observe the changes in the ionic concentration of different ions. The operation of the MCDI is represented in Fig. 1.

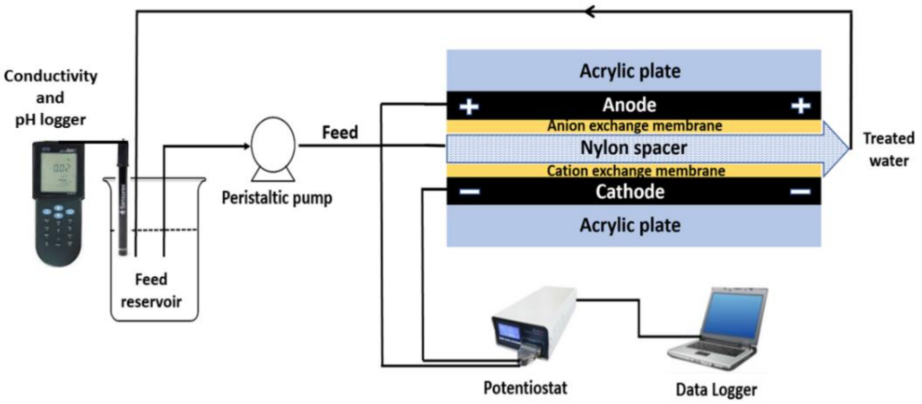

Figure 1. Process schematic of lab-scale MCDI operation.

2.2. Feed water preparation

The feed-water was prepared by dissolving an appropriate amount of analytical grade NaBr (Sigma Aldrich, Israel), NaI (Analar Nromapur, Belgium) and NaCl (AnalaR, MERCK Pty. Limited, Australia) in 18 MΩ cm resistivity Milli-Q water for the preparation of single electrolyte and mixed electrolyte feed solution. Firstly, to understand the response of individual bromide and iodide ions removal, feed water containing only bromide and iodide ions were prepared for a wide range of concentration at 0.5, 2 and 8 millimolar (mM). Secondly, to study the competitive behaviour between bromide and iodide ions, a mixed solution was prepared at a various concentration such as 0.5, 2 and 8 mM where bromide and iodide concentrations were maintained at the same molar concentration. Thirdly, to assess the ion selectivity between bromide and iodide ions under background TDS, 1 mM each of bromide and iodide were dissolved in a solution containing 1, 5 and 10 mM NaCl (AnalaR, MERCK Pty. Limited, Australia) as background TDS (Table 1). Finally, to demonstrate the applicability of MCDI in the removal of bromide and iodide from real water scenario, tap water spiked with bromide (720 µg/l) and iodide (112 µg/l) were used to simulate their actual concentration in surface water.

2.3. Sample analysis and data treatment

For the water samples with mixed ions, the concentrations were analysed using inductively coupled plasma-mass spectrometer (ICP-MS 7900, Agilent Technologies, Japan). For the feed solution containing only single electrolyte such as NaBr and NaI, the ion concentrations were calculated based on the concentration-conductivity relation as applicable in a single electrolyte solution (Porada et al., 2013). All the experiments were conducted in duplicates, and average values were reported. The standard calibration curve for bromide and iodide analysis is presented in the supplementary material as Fig. A.1. The salt adsorption capacity (SAC) was calculated using the equation:

$$\text{SAC } (\mu\text{mol/g}) = = \frac{C_0 - C}{M} * V \quad (1)$$

where C_0 and C refer to initial and final concentration (µmol/L), M is the total mass of electrodes (g), and V is the volume of treated water (L). The ion removal rate was calculated as follows:

$$\text{Removal rate } (\%) = \frac{C_0 - C}{C_0} * 100 \quad (2)$$

where C_0 and C represent initial and final concentrations (µmol/L) in the feed water and treated water, respectively.

Also, non-linear pseudo-first-order (PFO) and pseudo-second-order (PSO) rate equations

(3) and (4) respectively were used to fit the experimental data on salt adsorption under different experimental conditions (Lagergren, 1898; Blanchard et al., 1984; Tran et al., 2017):

$$q_t = q_e \left[1 - \exp(-k_1\, t)\right] \tag{3}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 {q_e}^2} \tag{4}$$

where q_t is the amount of adsorbed solute over the total mass of adsorbent (µmol/g), q_e is the maximum adsorption capacity (µmol/g), k_1 (min^{-1}) and k_2 ($g^{-1}.min^{-1}/$ µmol) are the pseudo-first-order and second-order rate constants, and t the time.

3. Results and discussion

3.1. *TDS and ion removal capacity in a single electrolyte solution*

Fig. 2 (a) and (b) show the conductivity and TDS removal rate of bromide and iodide from different initial feed concentration in a single electrolyte solution. The conductivity removal for bromide solution reduced from about 95% to just about 65% when the feed concentration increased from 0.5 mM to 8 mM. Under the same condition, the conductivity removal reduced from 95% to 86% for iodide solution. The bromide and iodide removal rate is expected to follow a similar trend in the single electrolyte solution. The adsorption capacities of bromide and iodide ions were further quantified in Fig. 2 (c) which supports that iodide was more favourably removed from the feed solution than bromide. At the initial feed concentration of 0.5 mM and 2 mM, there was not a significant difference in their adsorption capacities. For example, the adsorption capacities for both bromide and iodide were about 30 μmol/g and 120 μmol/g respectively. However, the iodide adsorption peaked at 430 μmol/g against 325 μmol/g for bromide when the feed solution concentration was raised to 8 mM. This increase in adsorption capacity of ions due to the increase in feed water TDS is a result of improved diffuse double-layer capacity (Mossad and Zou, 2012). The study by Ying et al. (2002) found the adsorption capacities of bromide and iodide between 59-108 μmol/g and 63-154 μmol/g respectively at a feed concentration of 1 mM and 2.4 mM respectively at 1.2 V using nanostructured carbon aerogel electrodes in a conventional CDI process. Similarly, the works by Gabelich et al. (2002) achieved bromide removal between 130-180 μmol/g at an applied voltage of 1.4 V with an initial bromide concentration of 5 mM.

Regarding the fitting of the experimental data to the two rate equations, it can be observed that both the kinetic rate equations and the experimental data fit well with a regression coefficient of greater than 0.99 in all cases for both the models (Table A.1). However, the pseudo-second-order model predicted much higher maximum adsorption capacities for both bromide and iodide compared to the experimental data. Since the MCDI adsorption was limited to only 10 minutes, some discrepancies can be expected because the electrodes were not completely saturated with ions within this period.

The charge efficiency (ratio between the total salt removed over total charge in CDI/MCDI operation) is an important parameter to evaluate the performance of the CDI/MCDI unit, and higher charge efficiency normally results in lower energy consumption (Zhao et al., 2012; Suss et al., 2015). The charge efficiencies for bromide and iodide at different initial concentration varied slightly between 0.70-0.90 and 0.68-0.92 respectively, with a much higher charge efficiency observed at an initial feed concentration of 8 mM for both bromide and iodide (Fig. 2 (d)). Ideally, in MCDI, due to the incorporation of the ion-exchange membrane, the charge efficiency can be close to unity (Porada et al., 2013). Further, the monitoring of the pH (Fig. A.2) showed that for the applied voltages and TDS, the fluctuation in pH is negligible. Hence a stable operation of the unit can be expected without noticeable faradaic reactions occurring at the electrodes.

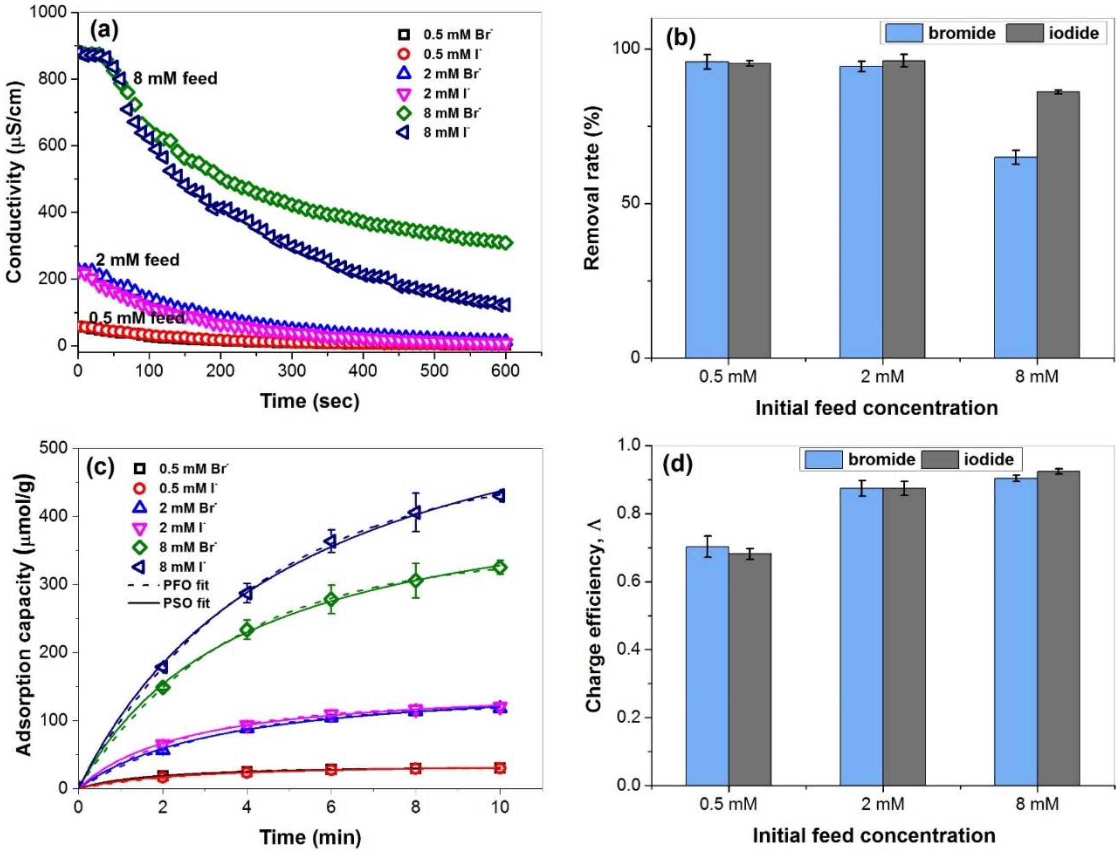

Figure 2. (a) Conductivity profiles (b) bromide and iodide removal rates (c) salt adsorption capacities under the different initial concentration of 0.5, 2, 8 mM single solute solution (d) charge efficiency. The applied voltage was 1.2 V, and the flow rate was 40 ml/min with a total adsorption time of 10 minutes. PFO and PSO are pseudo-first-order and pseudo-second-order model fitting respectively, and the symbols represent experimental data.

3.2. TDS and ion adsorption capacity in mixed bromide and iodide solution

Fig. 3 (a) shows the change in the conductivity profile of the various mixed solutions of 0.5, 2 and 8 mM with bromide and iodide mixed in the same molar concentration. The conductivity removal was between 92-98%, 68-95% and 26-49% for the three different applied voltages for different feed water condition respectively.

Regarding the selectivity of bromide and iodide ions at the initial concentration of 0.5 mM mixed solution in Fig 3 (b), there is no obvious selectivity difference in adsorption capacity between bromide and iodide, which was about 30 µmol/g for different voltages, which indicates that almost all of bromide and iodide were removed. This is not unusual because the concentrations of these ions were low, therefore, even at 0.6 V, the removal of bromide and iodide were high. However, when the initial concentrations were increased to 2 mM and 8 mM, the effect of ion selectivity between bromide and iodide became more pronounced. For example, bromide adsorption capacity under 2 mM solution was between 75-103 µmol/g against 105-115 µmol/g for iodide at a voltage of 0.6 V and 0.9 V, and the adsorption capacity at 1.2 V was 123 µmol/g for both bromide and iodide. However, when the feed solution was increased to 8 mM, the bromide adsorption capacity was significantly lower between 39-157 µmol/g compared to the adsorption capacity of iodide at 216-344 µmol/g. The increased adsorption capacity with an increase in voltage is mainly due to the formation of the thick electrical double layer as well as strong coulombic interactions between the ions and the electrode surface (Li et al., 2010).

Since bromide and iodide have the same charge and have a similar hydrated radius, their removal would be expected to be similar when they are present in the same molar concentrations. However, there is a significant difference in the electronegativity of bromide and iodide (Table 1). Since the electronegativity of iodide is lower than that of bromide, it exhibits a greater partial-charge transfer coefficient than bromide, and thus iodide is more actively adsorbed compared to bromide (Ying et al., 2002; Xu et al., 2008). Our findings, however, contradict the result of the previous study on the effect of electronegativity in the CDI process wherein it was found that the anions with higher electronegativity were more selectively removed (Sun et al., 2017). However, a closer look at their experimental methodology revealed that the concentration of different anions was fixed on mass-based instead of molar concentration. As a result, the difference in adsorption capacity could be due to a significant difference in molar concentrations of each anion, therefore, drawing a biased conclusion on the influence of electronegativity on anion adsorption.

Both pseudo-first-order and pseudo-second-order rate equations were able to fit the experimental data (Table A.2, A.3, A.4). Especially with feed TDS of 8 mM, bromide adsorption at lower voltages at 0.6 V and 0.9 V showed lower regression coefficient for both rate equations between 0.77-0.81 whereas for iodide it was greater than 0.99. This is likely due to adsorption and desorption of bromide ions taking place during the adsorption phase as evident in Fig. 3(d) probably due to the displacement of bromide ions by iodide ions from the electrode surface.

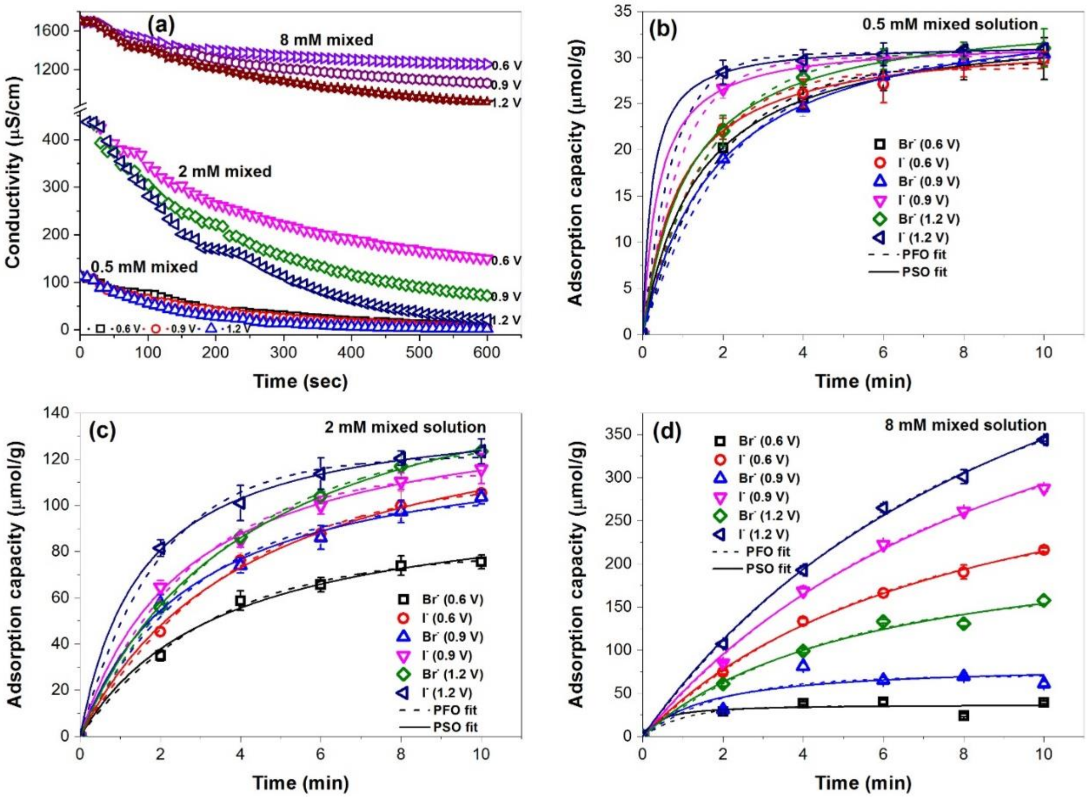

Figure 3. Bromide and iodide removal from mixed solution with same molar concentration (a) Conductivity profile (b) salt adsorption capacities of bromide and iodide under 0.5 mM mixed solution (c) salt adsorption capacities at 2 mM mixed solution (d) salt adsorption capacities at 8 mM mixed solution. The applied voltage was 1.2 V, and the flow rate was 40 ml/min with a total adsorption time of 10 minutes.

The corresponding removal rate of bromide and iodide in the mixed solution is presented in Fig. 4. At lower initial TDS of feed water at 0.5 mM, both bromide and iodide removal was between 95 - 99%. However, when the initial feed TDS was increased to 2 mM, the bromide removal rate dropped between 60 - 98% and at 8 mM solution, it further reduced to 8 - 31%. In contrast, iodide removal was between 43 - 98% for both 2 mM and 8 mM mixed solution. A definite selectivity of iodide over bromide ions in MCDI is evident as the initial concentration is increased. For example at 8 mM mixed solution, iodide removal was almost six times that of bromide at 0.6 V, almost five times at 0.9 V and more than two times at 1.2 V.

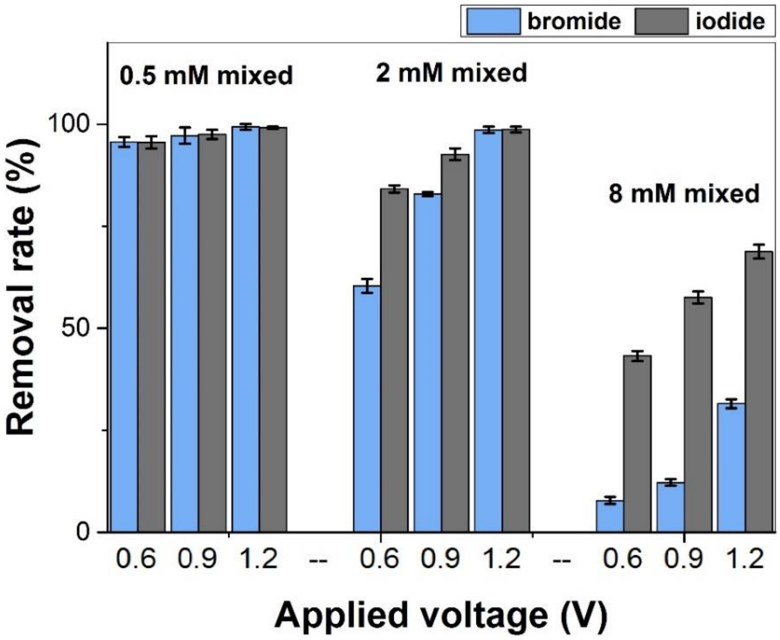

Figure 4. Removal rate of bromide and iodide in a mixed solution at various concentration and voltages. The flow rate was 40 ml/min with 10-minute adsorption.

3.3. TDS and ion selectivity under a background TDS of NaCl

The effect of background TDS on the adsorption of specific ions in CDI/MCDI and other adsorption have been well document in selectivity studies (Tang et al., 2015; Choi et al., 2016). Fig. 5 (a) shows the effect of voltage and feed water TDS on the overall removal of dissolved ions from the water. For the feed water with background TDS of 1 mM, the conductivity reduction was 89-92% at an applied potential between 0.6 and 1.2 V. At a higher feed water TDS of 5 mM and 10 mM, the conductivity reduction was between 47-78% and 30-54% respectively for the applied voltages.

Fig. 5 (b, c, d) illustrates the effect of background TDS on bromide and iodide removal. At a background TDS of 1 mM NaCl, the bromide adsorption capacities varied between 32.8 and 52.3 µmol/g, and iodide adsorption capacities between 57.4 and 59.6 µmol/g. At a higher background TDS of 5 mM and 10 mM NaCl, the bromide adsorption capacities reduced between 43.2 and 57.2 µmol/g and 32.8 and 52.3 µmol/g, respectively. Interestingly, however, the iodide adsorption capacities slightly increased between 60.4 and 61.1 µmol/g under the background TDS of 5 mM and 10 mM which was close to the adsorption capacities observed under the 1 mM background TDS within the applied voltages. Further results on the removal rate in Fig. 6 (a) showed that iodide removal rate between 92 and 98% irrespective of the applied voltage and TDS level whereas for bromide, its removal was significantly reduced with an increase in background TDS between 52-83% at 10 mM TDS solution. From these results, it is obvious that iodide shows better selectivity over bromide during CDI treatment. A similar result was reported by Xu et al. (2008) where 66% of iodide was removed from feed water containing a mixture of 0.39 mM, I and 86 mM, NaCl background, which shows the higher adsorption behaviour of iodide. Both the reaction kinetics model fit the experimental data well (Table A.5, A.6, A.7 in supplementary information).

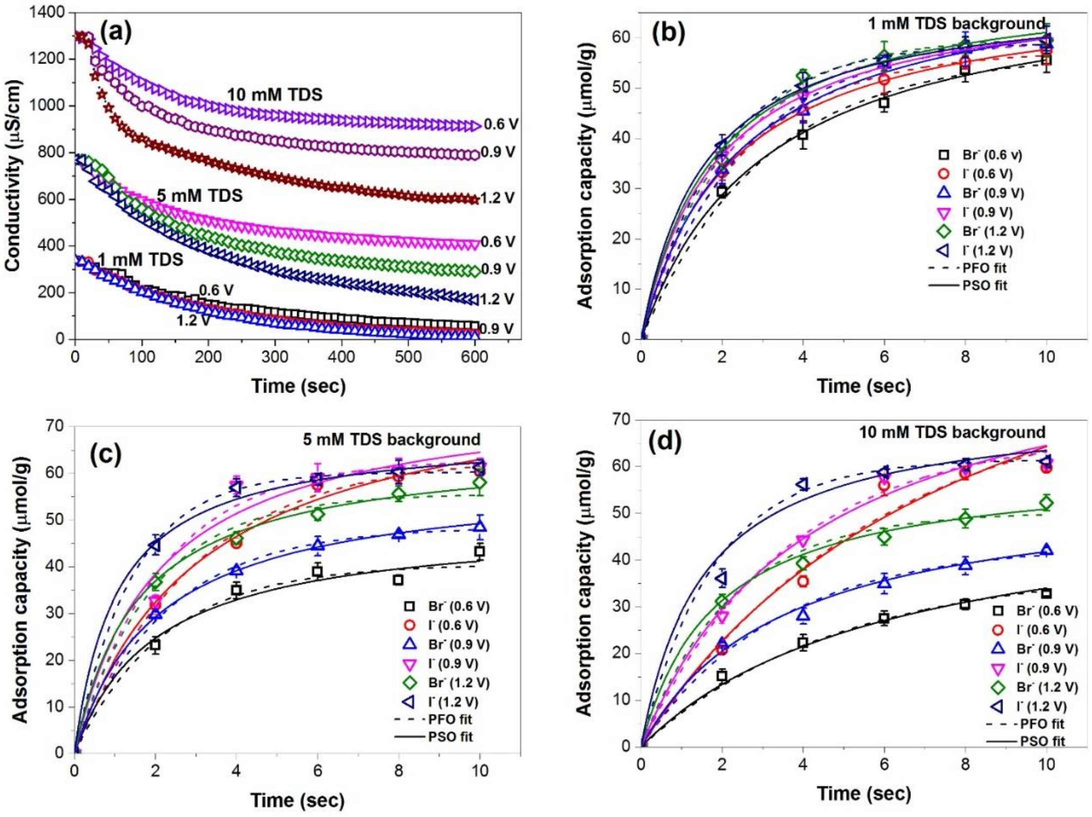

Figure 5. Effect of TDS on the bromide and iodide selectivity in different NaCl background concentration with a fixed bromide and iodide of 1 mM each (a) Conductivity profile (b) adsorption capacity at 1 mM NaCl background (c) adsorption capacity at 5 mM NaCl background (d) adsorption capacity at 10 mM NaCl background. The flow rate was 40 ml/min with a total adsorption time of 10 minutes.

Fig. 6 (a) compares the bromide and iodide removal from a mixed solution containing 1 mM each of these ions specifically at an applied voltage of 0.6 V to further assess the effect of electronegativity on electrosorption of ions from a mixed solution (Table A.8). There is less preferential adsorption of chloride compared to bromide and iodide, a result consistent with that obtained by Ying et al. (2002) using carbon aerogel. For example, the chloride adsorption capacity was about 44.1 µmol/g whereas bromide and iodide adsorption capacities under the same condition were 55.5 µmol/g and 57.4 µmol/g respectively. This further supports the influence of electronegativity (Table 1) on the adsorption capacity, where anions with lower electronegativity values are more preferentially removed when present under same molar concentrations, charge and similar hydrated radius. The dependence of electrosorption capacities based on charge, hydrated radius and concentration have been well evaluated (Mossad and Zou, 2012; Chen et al., 2015).

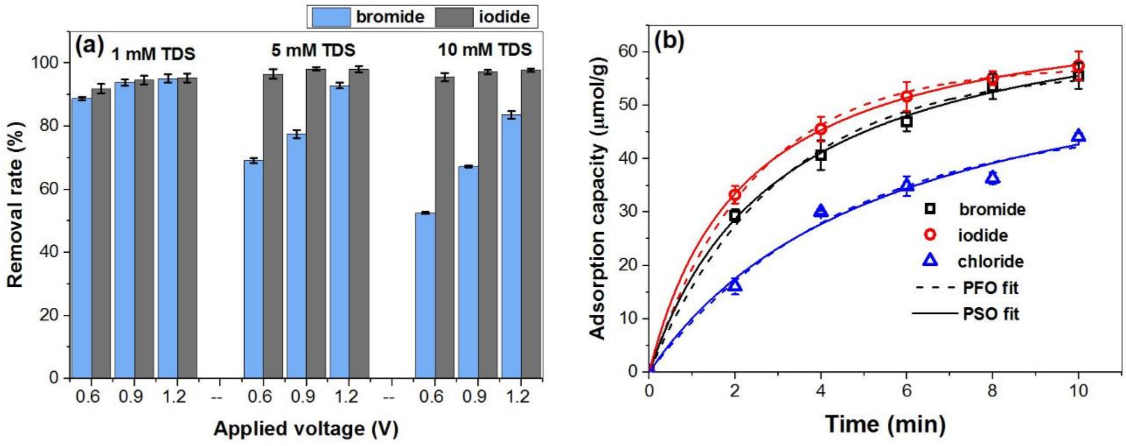

Figure 6. (a) Bromide and iodide removal rate under different voltages and background TDS (b) comparison of bromide, iodide and chloride adsorption capacity at 0.6 V with 1 mM each. PFO and PSO are pseudo-first-order and pseudo-second-order model fitting respectively, and the symbols represent experimental data.

3.4. Bromide and iodide removal in a real water treatment

To assess the practical application of the MCDI, tap water containing bromide and iodide concentration adjusted to a representative concentration of typical water system in Australia (Table 2) and the experimental results are presented in Figure 7. The overall TDS removal of the real water by was 82% while the bromide and iodide removal rates were 91.2% and 54.01% respectively with the final bromide concentration of about 63 µg/L and iodide concentration of 51.5 µg/l in the treated water. The iodide removal in the real water was much lower than that of bromide, which is mainly due to the low initial concentration of iodide compared to bromide. Although several factors such as ionic charge, hydrated radius and initial concentration of the target ions play an important role in determining the ions selectivity in capacitive deionisation (Chen et al., 2015), the higher removal of bromide compared to iodide is probably due to the significant difference in their initial concentration where molar concentration of bromide is almost 10 times that of iodide, therefore, more bromide ions were preferentially adsorbed. For comparison, the bromide concentration in the product water of a two-stage RO such as the Perth desalination plant is about 100 µg/L, and this study indicates that MCDI can provide good bromide removal.

Table 2. Basic parameters of the real water.

Parameters	**Conductivity (µS/cm)**	**TOC (mg/L)**	**Bromide (µg/L)**	**Iodide (µg/L)**	**pH**
Values	214.5	2.96	719	112	7.1

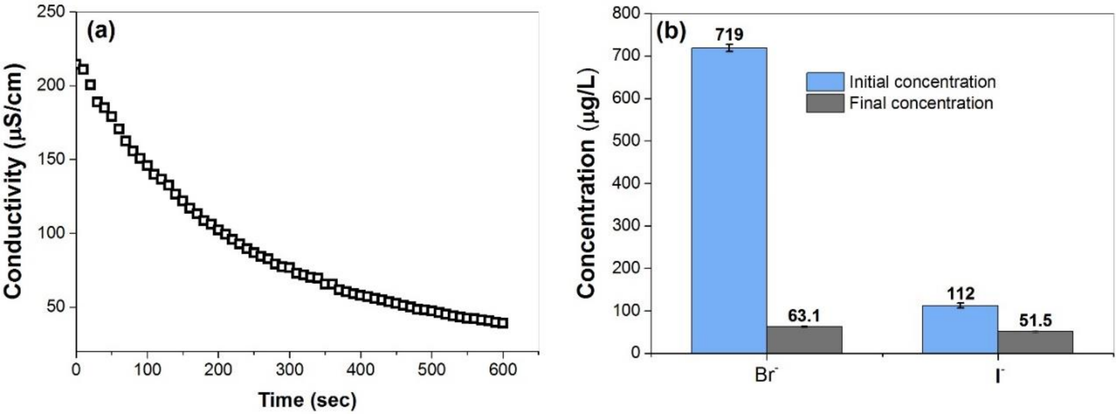

Figure 7. Bromide and iodide removal in real water (a) Conductivity profile (b) bromide and iodide concentration in the treated water. The applied voltage was 1.2 V, flow rate 40 ml/min and the feed volume was 100 ml.

4. Conclusions

In this study, the competitive nature of bromide and iodide in MCDI was systematically assessed under a single electrolyte solution, mixed solution and under the influence of background NaCl TDS. It was observed that iodide has a much higher individual adsorption capacity compared to bromide. In a mixed solution of bromide and iodide in same molar concentration, iodide was more preferentially removed than bromide. This observation was more prominent from the adsorption capacities under low voltage and a higher concentration of feed solution, where more iodide was preferentially removed. It was also demonstrated that under the influence of background TDS, bromide removal was severely impeded compared to iodide. The fitting of the reaction kinetics revealed that both pseudo-first-order and pseudo second order were able to fit the experimental data quite well however the pseudo-second-order kinetics over-estimated the theoretical maximum adsorption capacities for both bromide and iodide. Finally, this study clearly demonstrates the feasibility of MCDI for effective removal of both bromide and iodide from the water even though they are present in relatively smaller quantities compared to other anions. It is expected that application of MCDI for targeted bromide and iodide removal will result in a significant reduction in the formation of toxic disinfection by-products.

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