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**Author**

Watson, Kalinda, Farré, M., Knight, Nicole

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# Strategies for the removal of halides from drinking water sources, and their applicability in disinfection by-product minimisation: a critical review

K. Watson<sup>1</sup>, M. J. Farré<sup>2</sup>, N. Knight<sup>1,3\*</sup>

<sup>1</sup>School of Environment, Griffith University, Southport, Queensland, 4222, Australia

<sup>2</sup>Advanced Water Management Centre, University of Queensland, St Lucia, Queensland, 4072, Australia

<sup>3</sup>Smart Water Research Centre, Griffith University, Southport, Queensland, 4222, Australia

*\*correspondence to be directed to [n.knight@griffith.edu.au](mailto:n.knight@griffith.edu.au); Tel: (+61) 7 5552 7817; Fax: (+61)*

*7 5552 7831*

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## Abstract

The presence of bromide ( $\text{Br}^-$ ) and iodide ( $\text{I}^-$ ) in source waters leads to the formation of brominated and iodinated disinfection by-products (DBPs), which are often more toxic than their chlorinated analogues. The increasing scarcity of water resources in Australia is leading to use of impaired and alternative water supplies with high bromide and iodide levels, which may result in the production of more brominated and iodinated DBPs. This review aims to provide a summary of research into bromide and iodide removal from drinking water sources. Bromide and iodide

removal techniques have been broadly classified into three categories, namely; membrane, electrochemical and adsorptive techniques. Reverse osmosis, nanofiltration and electrodialysis membrane techniques are reviewed. The electrochemical techniques discussed are electrolysis, capacitive deionization and membrane capacitive deionization. Studies on bromide and iodide removal using adsorptive techniques including; layered double hydroxides, impregnated activated carbons, carbon aerogels, ion exchange resins, aluminium coagulation and soils are also assessed. Halide removal techniques have been compared, and areas for future research have been identified.

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### **1.0 Background**

Disinfection of drinking water supplies is one of the greatest public health accomplishments of the last century for the prevention of waterborne diseases. However, disinfection processes used in drinking water treatment (chlorination, chloramination, chlorine dioxide, ozonation, ultra-violet (UV), and UV/H<sub>2</sub>O<sub>2</sub>) can lead to the formation of potentially toxic disinfection by-products (DBPs) (Ijpelaar, 2007; Richardson et al., 2007). Since their discovery, several hundred individual DBPs compounds have been identified, many of which are halogenated (Richardson et al., 2007; von Gunten, 2003). The presence of bromide (Br<sup>-</sup>) and iodide (I<sup>-</sup>) in source waters can result in the formation of brominated and/or iodinated DBPs upon exposure to natural organic matter (NOM) and disinfectant, which are often more toxic than their chlorinated analogues (Magazinovic et al., 2004; Plewa et al., 2004; Richardson, 2003; Richardson et al., 2007; von Gunten, 2003). Both natural processes, including seawater intrusion and dissolution of geologic sources, and anthropogenic activities, such as seawater desalination, generation of mining tailings, chemical production, production of sewage and industrial effluents, may contribute to bromide concentrations in drinking water sources (Magazinovic et al., 2004; Richardson et al., 2007; Valero, 2010; von Gunten, 2003). Similarly, seawater intrusion, seawater desalination and dissolution of geologic sources contribute to iodide concentrations in drinking water sources (Agus et al., 2009; Hua et al., 2006; von Gunten, 2003), although

biological activity of microorganisms and marine algae can contribute to iodide removal from water sources through specific metabolic processes (Suzuki et al., 2012). Table 1 shows typical bromide and iodide concentration in different source waters.

Current drinking water treatment schemes are challenged to effectively remove ambient bromide and iodide before final disinfection, in order to produce acceptable levels of the suspected carcinogen bromate (Kurokawa, 1990), when using ozone or advanced oxidation processes (von Gunten, 1995), and brominated/iodinated DBPs when disinfecting with chlorine or chloramines (Bichsel and von Gunten, 2000; Hua and Reckhow, 2007; Hua et al., 2006).

It is well known that bromide and iodide present in water may react differently with different disinfectants (Kumar et al., 1986; Kumar and Margerum, 1987; Nagy, 1988; Trofe, 1980). The kinetic rate constants of bromide and iodide with chlorine and chloramine in the formation of HOBr and HOI, respectively, are shown (Table 2).

The reaction of bromide with free chlorine is five orders of magnitude faster than with chloramine (Trofe, 1980). On the other hand both disinfectants react relatively quickly with iodide ion (Kumar et al., 1986; Nagy, 1988). HOBr, formed from bromide, may then react with NOM and generate bromine-containing DBPs. In the presence of excess free chlorine, HOI is largely oxidized to iodate ( $\text{IO}_3^-$ ), the desired sink for iodide, but in the presence of chloramines it is relatively stable, as shown by the relevant rate constants (Table 3) (Bichsel and von Gunten, 1999). Therefore, in the presence of chloramines, HOI will react with certain organic precursors

producing iodine substitution and the generation of iodinated analogues of many of the chlorine- and bromine-containing DBPs.

Although some brominated DBPs are regulated in the Australian Drinking Water Guidelines (NHMRC, 2011) (in particular; bromate, bromodichloromethane, dibromochloromethane and bromoform) the highly variable nature of NOM and its reactivity with different disinfectants means that there may be many other brominated and/or iodinated DBPs species formed in any given treated water in which these halides are present. Strategies for DBP minimisation vary, but can be broadly classified into three categories; DBPs precursor removal (halides and NOM), optimising disinfection to minimise DBPs formation, and DBPs removal prior to water distribution (for example, air-stripping of volatile DBPs such as trihalomethanes (THMs)) (Wu and Wu, 2009). One advantage that DBPs precursor removal has over other DBPs minimisation strategies is that it is not specific to removing/lowering a particular suite of DBPs, it can broadly minimise all DBPs, both known and unknown, potentially creating greater trust in the quality of the water produced. All disinfection methods produce their own suite of DBPs, however, minimising the precursors available for this to occur is applicable regardless of disinfection method employed. As water regulation become increasingly stringent and salinity impacted water sources are increasingly utilised there may be a need for effective bromide and iodide removal to control the formation of emerging DBPs.

## **2.0 Techniques for halide removal from water**

The objective of bromide and iodide removal is to control the formation of brominated and/or iodinated DBPs (both organic and inorganic). Bromide and iodide removal techniques can be

broadly classified into three categories, namely; membrane, electrochemical and adsorptive techniques.

## **2.1 Membrane techniques**

Over the past 50 years, membrane technologies have become a distinguished separation technology with significant commercial applications in the water industry. With increasing water demands and diminishing water supplies due to escalating populations, environmental degradation and climate change, membrane technologies are being employed to produce high quality potable water from impaired and alternative water supplies. Membrane techniques comprising reverse osmosis (RO), nanofiltration (NF), ion exchange membranes, electrodialysis (ED) and electrodialysis reversal (EDR) are discussed in the following sections.

### **2.1.1 Reverse osmosis**

RO is a process whereby water is forced through a semi-permeable membrane under pressure to remove organic contaminants and salts, producing purified water (Figure 1). There are 2 main types of RO membranes; cellulose acetate and more recently thin film composite membranes, each with differing water flux, rejection and physiochemical characteristics (Escobar, 2010). Most commercially successful RO membranes are thin-film composites with a top ultra-thin active filtration layer that consists most commonly of cross-linked polyamide (50-200 nm) but other polymers such as piperazine and others are employed as well. This thin layer is backed by an intermediate porous polysulfone support and a grid of polyester fibres to provide the desired mechanical stability (Robert J, 1993). Some membranes also have a surface coating that yields a more hydrophilic, neutral and fouling-resistant surface (Coronell et al., 2008; Hachisuka, 2002;



Petersen, 1993; Tang et al., 2007b). The active layer of RO membranes is the main barrier against the permeation of salt and contaminants which results from a combination of equilibrium partitioning at the water/active layer interfaces, and diffusive and advective transport (Mulder, 1996; Paul, 2004; Petersen, 1993; Tang et al., 2007b; Urama, 1997; Wijmans and Baker, 1995).

The broad spectrum of solute rejection of RO membranes allows the utilisation of seawater, brackish water and reclaimed water as alternative potable water sources (Asano, 2007; Xu, 2005). A comprehensive review of the early history of RO membrane development is available (Glaser, 1998). Recent developments in drinking water treatment applications of RO have been discussed by many including Greenlee *et al.* (Greenlee et al., 2009), Fritzmann *et al.* (Fritzmann et al., 2007), Pearce *et al.* (Pearce et al., 2004), Veza (Veza, 2001), Antrim *et al.* (Antrim et al., 2005), Koutsakos and Moxey (Koutsakos and Moxey, 2007), Redondo and Lomax (Redondo and Lomax, 1997, 2001), Wolf *et al.* (Wolf et al., 2005), Vial *et al.* (Vial et al., 2003) and Laborde *et al.* (Laborde et al., 2001).

RO membranes typically have a salt rejection of 98-99%, although several recently developed membranes can achieve 99.7-99.8% salt rejection under standard conditions (Asano, 2007; Bates and Cuozzo, 2000; Colquhoun, 2010; Fritzmann et al., 2007; Hydranautics, 2007; Reverberi and Gorenflo, 2007; Reverter et al., 2001; Tang et al., 2007a; Wilf, 2004). The current body of literature indicates that RO membranes reject monovalent halide ions to differing degrees (Table 4). The rejection of ionic solutes by RO membranes has been observed to follow the Hofmeister series, that is, rejection increases with increasing hydrated radius (Table 5). Ions with high hydration energy (determined by its hydrated radius and charge density) are superiorly rejected

due to their low partition coefficient with the hydrophilic membrane (Naaktgeboren et al., 1988; Pontié et al., 2003a). The halide rejection occurs in the following sequence:  $F > Cl > Br > I$ . This is identical to the order of decreasing hydration energy and decreasing hydrated radius of the ions. A study by Magara *et al.* (Magara et al., 1996) investigating bromide removal from seawater using RO with spiral modules of aromatic polyamide, achieved over 99% bromide rejection (Table 4). Similarly, several other studies of RO have found high bromide rejection, ranging from 93-99.3%, depending on the membrane used, and operating conditions (Bartels et al., 2009; Drage et al., 2000; Khan et al., 2005; Mays, 2004). Khan *et al.* found that RO membranes display a high rejection of iodide ions (71-90%) (Khan et al., 2005). RO can reject over 89% of the total iodide from seawater (Duranceau, 2010). The viability of several RO membranes in treating oilfield-produced brackish water for water reuse and iodide recovery has been investigated (Drewes et al., 2009; Xu et al., 2008a). The aromatic polyamide membranes were ranked according to the rejection of iodide as: Koch TFC-HR (92%) > Toray TMG-10 (87%) > Koch TFC-ULP (82%) > Dow/Filmtec XLE (80%). Furthermore, Koch TFC-HR, Koch TFC-ULP and Toray TMG-10 membranes rejected between 98-100% of both chloride and bromide ions (Drewes et al., 2009). Dow/Filmtec FT-30 membranes achieved 99.55% rejection of bromide at 2 MPa and 99.50% rejection of iodide at 5 MPa (Pontié et al., 2003b).

RO is a proven technology for the removal of an extensive range of contaminants, and this was the most effective bromide and iodide removal technique of all investigated. Importantly, this technique can remove both organic and inorganic DBP precursors simultaneously making it invaluable in DBP minimisation. However, RO remains relatively expensive, requires extensive pre-treatment, has high energy consumption due to high operating pressures, and is susceptible to

scaling, as well as brine disposal difficulties. The capital and operational expenses of RO as well as the disposal of the generated concentrate currently restricts the widespread application of this technique in drinking water treatment plants.

### **2.1.2 Nanofiltration**

NF is a pressure driven membrane process, which is an intermediate between RO (non-porous diffusion) and ultrafiltration (porous-sieving) membrane processes, and exhibits features of both (Wang et al., 2008). Compared to RO, NF generally runs at somewhat lower pressures, thereby reducing energy costs. It also has less resistance to the flow of both solvents and solutes (Mohapatra et al., 2009; Sarrade et al., 1998; Water Environment Federation, 2008). Although there are many types of membranes, most applications of NF use polyamide thin-film composite membranes in a spiral wound configuration (Asano, 2007). Like RO membranes, most NF membranes are charged, thus electrostatic interactions also influence the transport and selective rejection behaviour of NF membranes (Wang et al., 2008). Consequently, depending on the molecular weight cut-off of the membrane, many NF membranes can effectively separate both NOM, small organic molecules (such as pesticides, pharmaceuticals and endocrine disrupting compounds) (Acero et al., 2010; Agenson et al., 2003; Benitez et al., 2009; Grib et al., 2000; Hong and Bruening, 2006; Jiratananon et al., 2000; Kiso et al., 2001; Lee et al., 2002; Mänttari et al., 2002) and salts from water. Salts rejected include bromide and iodide ions, although in general, polyvalent ions may be more easily retained than monovalent ions (Al-Zoubi et al., 2007; Bougen et al., 2001; Hilal et al., 2005; Qin et al., 2004; Tanninen and Nyström, 2002). Harrison *et al.* (Harrison et al., 2007) investigated the ion rejection of two commercial NF membranes (NF-90 and NE-90) in a seawater desalination application (Table 6). The NF-90

membrane achieved 94-96% bromide rejection and 84-91% iodide rejection. Similarly, NE-90 membrane accomplished 94-97% bromide rejection and nearly 90% iodide rejection. The authors found that salt rejection generally increased with pressure, until their maximum rejection threshold was reached, beyond which, rejection started to decline with increasing pressure. This is to be expected and holds for all RO and NF membranes. A maximum rejection threshold for bromide was observed at 3.4 MPa. Anion rejection was not significantly affected by water temperature under the conditions tested.

Lhassani *et al.* (Lhassani et al., 2001) investigated the selective demineralization of water by NF with particular emphasis on monovalent anions. The study achieved a maximum rejection of iodide (80%) with NF70 membrane at a pressure of 1200 kPa. Although membrane selectivity favours chloride over iodide ion, it was demonstrated that this can be reversed at pressures over 800 kPa, thus showing that operating conditions can be adjusted to selectively remove individual ions of the same valence. Pontie *et al.* (Pontié et al., 2003a) and Diawara *et al.* (Diawara et al., 2003) demonstrated that tight NF membrane NF-45 can selectively separate monovalent halides, following the Hofmeister series of halide ions:  $F > Cl > I$ . The membrane reflection coefficient and solute permeability were observed to be correlated with the hydration energy of halide ions. Tight NF-45 membrane was shown to have mass transfer properties similar to RO membranes.

NF membranes with a molecular weight cut off of 150-300 Da have been observed to reject up to 50% of bromide and bromate from low-turbidity source waters (Amy and Siddiqui, 1998). Prados-Ramirez *et al.* (Prados-Ramirez et al., 1995) saw a 63% rejection of bromide upon conducting NF on bromide-spiked river water. Pontié *et al.* (Pontié et al., 2003b) found NF-70 membranes reject approximately 94% of bromide at a pressure of 1.5 MPa. The study

demonstrated that halide ions are transferred across NF membranes by two mechanisms; convective and solubilisation-diffusion. Pontié *et al.* (Pontié et al., 2003b) also demonstrated that under low pressure, retention of halide ions follow the Hofmeister series, however under high pressure, chloride and bromide order is inverted. Drewes *et al.* (Drewes et al., 2009) investigated the salt and iodide rejection from oilfield-produced brackish water utilising three NF membranes: NF-90 (Dow/Filmtec), TFC-S (Koch) and ESNA (Hydranautics). The membranes were ranked according to the rejection of iodide, as: NF-90 (78%) > TFC-S (69%) > ESNA (55%). The NF-90 membrane rejected over 80% of both chloride and bromide (Drewes et al., 2009). In contrast, Listiarini *et al.* (Listiarini et al., 2010) and Chellam and Krasner (Chellam, 2000; Chellam and Krasner, 2001) found that NF was inefficient for bromide removal, however, the operating conditions investigated, including pressure, permeate flux, anion concentrations and water type, varied significantly from those used for successful applications of NF for bromide removal.

When compared to RO, NF has slightly lower capital costs, significantly lower operational costs due to lower operating pressures, can be operated at a higher water recovery, which means a smaller waste concentrate stream, while achieving comparable bromide and iodide removals (Harrison et al., 2007). Due to these advantages, the application of NF has increased, especially in industrial applications and drinking water treatment. This membrane technique still experiences (although to a lesser extent) the same limitations as RO. NF requires extensive pre-treatment, has medium to high energy consumption, and is susceptible to scaling and brine disposal difficulties. Again, like RO, NF has the advantage of having capacity to remove both organic (NOM) and inorganic (halide) DBP precursors simultaneously.

### **2.1.3 Electrodialysis and electrodialysis reversal**

The ED process uses a driving force of direct current (DC) to transfer ionic species through cell pairs of oppositely charged membranes, allowing their separation from the source water (Figure 2) (AWWA, 1995; Valero, 2010). The degree of salt removal is directly proportional to the current and inversely proportional to the flow rate through each cell pair (Scott, 1995). Thus, hydraulic and electrical staging are used to achieve the desired salt removal. The hydraulic and electrical staging in the membrane stack array configuration used in ED water treatment systems is determined by the source water quality and the level of water quality required (Valero, 2010). Membranes are composed of a polymer matrix with charged groups attached, with pores that allow ions to permeate. EDR is a modification of the ED process, where electrode polarity is periodically reversed during the treatment process to reduce scaling and clean membrane surfaces (AWWA, 1995; Valero, 2010). EDR has been successfully used for desalination, waste treatment, treatment of boiler feed and process water, and hardness removal, providing a reliable and economical alternative to RO of brackish waters (Spiegler and El-Sayed, 2001; van der Hoek et al., 1998). The EDR process is used as a ‘finishing’ treatment for desalting brackish water with TDS concentrations of up to 4000 mg/L. After 4000 mg/L the energy costs dramatically increase, reducing its competitiveness with other membrane techniques such as RO (Seneviratne, 2007). The halide rejection of ED and EDR has been summarised (Table 7).

Recently, Valero and Arbós (Valero and Arbós, 2010) conducted a 28 month pilot plant study of EDR, as well as a study of the implementation of EDR in Llobregat’s desalination drinking water treatment plant (DWTP) in Barcelona, Spain. The pilot plant study utilised the same source water as is treated at Llobregat’s DWTP. Anthropogenic activities severely impact the quality of this source water, which consequently has substantial concentrations of salts, NOM and

micropollutants, causing elevated concentrations of DBPs during the drinking water treatment process ( $160 \pm 40 \mu\text{g/L}$  THMs). EDR was incorporated into the water treatment system after granular activated carbon (GAC) treatment, in both pilot and full scale studies. On average the pilot study achieved over 75% bromide, 60% chloride, 65% electrical conductivity (EC), 58% total alkalinity (TAC), 30% TOC, 75%  $\text{NO}_3^-$ , 70%  $\text{SO}_4^{2-}$ , 80%  $\text{Ca}^{2+}$ , 70%  $\text{K}^+$  and 80%  $\text{Mg}^{2+}$  reduction, while maintaining over 90% water recovery. The improved chemical quality of the water resulted in a decrease in THMs formation potential (THMs-FP) to  $64 \pm 60 \mu\text{g/L}$ , which was below the regulated concentration of  $100 \mu\text{g/L}$ . During the trial the systems' performance was highly robust and reliable with no operational problems experienced (Valero and Arbós, 2010). Llobregat's DWTP (with full-scale application of EDR) has the capacity to produce an average of  $200,000 \text{ m}^3/\text{day}$ , making it the world's largest desalination plant using this technology. The plant obtained water quality parameters and THM-FP consistent with the pilot study values. Optimisation of the plant achieved a maximum of 80% bromide and 80% EC reduction, while maintaining over 94% water recovery. Furthermore, Valero and Arbós showed EDR treatment allows the control of THM speciation as a result of  $\text{Br}^-$  removal, resulting in a reduction of brominated species in favour of chlorinated species.

Van der Hoek *et al.* (van der Hoek et al., 1998) investigated the possibilities of applying EDR as an alternative for RO filtration in three integrated membrane systems (IMS) that use ozone for disinfection. The IMS-1 system used pre-treated (coagulation/sedimentation/filtration) Rhine River water and further treated sequentially with ozonation, biologically activated carbon filtration, slow sand filtration and RO; IMS-2 treatment was the same as IMS-1, however the RO step was replaced with an EDR step; IMS-3 took pre-treated Rhine River water then treated

sequentially with EDR, ozonation, biologically activated carbon filtration and slow sand filtration. IMS-1 and IMS-3 were able to achieve compliance with bromate regulation, however, IMS-2 could not. IMS-3 reduced bromide concentrations by 72% (prior to the disinfection step), thus reducing bromate formation to 5 µg/L after ozonation (van der Hoek et al., 1998), in compliance with the European Union drinking water standard (Lenntech Water, 2009 ). The authors found IMS-3 (using EDR) had lower energy and chemical consumption and thus lower operational costs when compared to IMS-1 (using RO) however, RO provided a dual barrier for disinfection and removal of organic compounds such as NOM and pesticides, which is an advantage over the EDR process (van der Hoek et al., 1998). EDR membranes AR204-SZRA (anion) and CR67-HMR (cation) both manufactured by Ionics were used in this study.

Permselectivity of ions is determined by ion exchange selectivity and mobility selectivity (steric and membrane density effects) with a membrane (Sata, 2004). Generally, ions with higher valence and a smaller hydrated radius have a higher permeability in an ion exchange membrane than ions with lower valence and larger hydrated radius. Hann *et al.* (Hann et al., 1983) found the permselectivity counterion exchange sequence of an anion-exchange membrane containing quaternary ammonium groups as fixed charges was:  $\text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$ . Sata and colleagues have also conducted several studies on the effect of hydrophilicity of anion-exchange membranes on the permselectivity of specific anions in ED (Sata, 1994, 2000; Sata et al., 1998a; Sata et al., 1998b). The group showed that permselectivity of specific anions is mainly dependent on the balance between hydration energy of anions with hydrophilicity of the membranes. Specifically, the more hydrophobic membranes have a higher permselectivity for less hydrated (higher hydration energy) ions. In keeping with this, increasing hydrophobicity of the strongly



basic anion-exchange membrane enhanced the permeation of bromide and iodide, while decreasing the permeation of fluoride ions. As expected, increasing the hydrophilicity of the membranes reversed this trend.

Inoue *et al.* has carried out several investigations into the removal of radioactive iodide ion ( $^{125}\text{I}$ ) from wastes using ED with anion-exchange paper membranes (Inoue, 2001, 2002, 2003, 2004; Inoue and Kagoshima, 2000; Inoue et al., 2004). These membranes were found to be electroconductively more permeable to iodide than to chloride ions, allowing iodide to be concentrated from the feed stream (Inoue and Kagoshima, 2000). In a further project, covalent linking of glucose and urea to membranes was reported to increase the membrane/solution distribution of iodide, however the diffusion process of iodide within the membrane was not significantly altered, relative to the unmodified membrane (Inoue, 2001). Inoue *et al.* also worked on membrane separation control using three different anion-exchange groups bound to a pulp/ cellulose fibre matrix: trimethylhydroxypropylamino, diethylaminoethyl and 50% saturated quaternary diethylaminoethyl (Inoue, 2002). It was observed that the membrane permeability for iodide was higher than chloride in all three cases. Notably, trimethylhydroxypropylamino groups improved the iodide diffusion process, whereas 50% quaternary diethylaminoethyl groups improved the iodide solution/membrane distribution process. High iodide permselectivity was achieved in membranes with the trimethylhydroxypropylamino quaternary amine anion-exchange group, due to electrostatic effects (Inoue, 2003; Inoue et al., 2004).

#### **2.1.4 Relative advantages and disadvantages of the membrane techniques**

The ED/EDR processes are not commonly used in drinking water treatment plants although examples of successful implementation do exist (Pequignot and Rigau, 2007; Valero and Arbós, 2010). The main advantages of ED compared to other membrane techniques are; minimal pre-treatment of feed water is required, higher water recovery can be achieved than for RO, although process recoveries for EDR should be similar to NF (Valero, 2010). EDR membrane life would be expected to be higher than RO membrane life (7-10 years for EDR membranes versus 5-7 years for RO membranes) (Valero, 2010). EDR has several technical and economic limitations, including high energy consumption and high capital cost (Strathmann, 2010). ED/EDR has the potential to be widely applied to brackish and anthropogenic impacted waters to enable the utilisation of alternative sources of water, however, more research is needed in the membrane development and in the optimization of ED/EDR for large scale drinking water treatment plants. A limitation of ED/EDR processes is that unlike RO and NF, they do not remove organic DBP precursors, they exclusively remove ionic species, i.e., hardness, halides, and other salts. Therefore, the use of this technology without an additional organic matter removal step may decrease the level of bromination/iodination of organic DBP precursors during disinfection, but may not decrease the total concentration of DBPs (e.g. total THMs) formed. Furthermore, ED and EDR do not provide any disinfection, unlike NF and RO, however, these techniques can be used in the presence of a chlorine residual, thereby enabling disinfection and reducing biological fouling of membranes.

## **2.2 Electrochemical techniques**

Electrochemical techniques have been successfully used to remove contaminants from various industrial wastewaters and environmental waters (Pletcher and Walsh, 1990; Rajeshwar and

Ibanez, 1997). Electrochemical techniques comprising electrolysis and capacitive deionization (CDI) are briefly discussed in the following sections.

### **2.2.1 Electrolysis**

Electrolysis is a process that uses the passage of an electric current through a solution to induce chemical decomposition (Hale, 2008). Historically, electrolysis processes have been used to produce bromine from brines containing bromide (Black & Veatch Corporation, 2010; Kimbrough and Suffet, 2002; Society for Mining Metallurgy and Exploration US, 2006). Kimbrough and Suffet (Kimbrough and Suffet, 2002) examined the feasibility of using electrolysis to remove bromide from drinking water sources (Table 8). Carbon rod cathodes and dimensionally stable anodes (DSA) were used in the electrolysis cell. Electrolysis of raw water oxidised bromide to a mixture of hypobromite, hypobromous acid and bromine gas. Degassing this solution with carbon dioxide caused a decrease in the solution pH, driving the conversion of hypobromite to hypobromous acid, which was then volatilised, along with bromine gas, leading to a decrease in the solution concentration of bromide. The rate of bromide removal is dependent on the applied current and effectiveness of air stripping. Upon chlorination the electrolysed water produced lower THMs concentrations and decreased the proportion of brominated THMs formed. The authors suggest that the removal of bromide should also reduce the formation of other brominated DBPs.

An electrolytic process that combines disinfection with the removal of bromide from raw water was patented by Bo (Table 8) (Bo, 2008). Electrolysis cells used silver cathodes and DSA arranged in parallel fashion. During electrolysis chloride was oxidised to chlorine gas, providing

disinfection, while bromide ions were oxidised to bromine gas which volatilised without requiring stripping. High bromide removal efficiency is achieved due to the high silver conductivity and large electrode surface contact area coupled with several passes of the solution through the electrolysis cell. The effectiveness of this process is dependent upon the chloride:bromide ratio, the magnitude of the electrical current, ionic strength of the water, distance between electrodes, water residence time in the cell and electrode material. Bromide removal efficiency decreased with lower influent bromide concentrations. At low bromide concentrations ( $<125\text{ }\mu\text{g/L}$ ) the process achieved between 48%-62% removal, but at high bromide ( $>200\text{ }\mu\text{g/L}$ ) concentrations bromide removal increases to between 47%-79%. Brominated THMs concentrations (generated by THM formation potential test (THM FP)) were reduced by 27% after the initial bromide concentration was reduced from  $461\text{ }\mu\text{g/L}$  to  $48\text{ }\mu\text{g/L}$  during the treatment. This reduction in Br-THMs may be expected to be greater, given the excellent bromide removal reported, however, the authors report losing chlorine residual during the THM FP of the high bromide sample, so they may not have formed a maximum of Br-THMs during the experiment. Additionally, several electrolysis processes that remove bromide by producing bromine gas from different aqueous sources, including brines, bittern and waste effluents have been patented (Blum, 1999; Bonnick, 2002; De Nora, 1983; Hawley, 1994; Howarth, 1995; Kroon, 2003; Nidola, 1978; Ramachandraiah, 2004; Sharma, 1978; Williams, 1993).

Although electrolysis has been shown to remove bromide reasonably on a small scale the feasibility of large scale application to drinking water treatment has not been assessed. Further development of electrodes would be required as part of working toward larger scale treatment.

### 2.2.2 Capacitive deionization

Capacitive deionization (CDI) is a recently developed electrolysis technology for removing ionic species from aqueous solutions using porous activated or aerogel carbon electrodes (Figure 3) (Gabelich et al., 2002; Ying et al., 2002). The deionisation process occurs by an induced electrical potential difference across an aqueous solution, which flows in between oppositely charged porous electrodes. As a result of the applied electrical potential, ions are adsorbed in the electrodes, deionising the product stream (Oren, 2008). Although CDI technology is in its infancy, it has the potential to develop into a feasible low-cost alternative to membrane and thermal desalinisation of brackish waters (Table 9) (TDA Research, 2010; Welgemoed and Schutte, 2005; Xu et al., 2008b). The CDI process operates at ambient conditions of temperature and pressure, requires minimum pre-treatment, does not require chemicals for scaling control or chemical cleaning, has low voltage requirements and a low fouling/scaling potential (Xu et al., 2008b). The adsorption capacity of carbon aerogels is dependent upon the surface characteristics of the electrodes, including; surface area, size and microstructure of pores, electrical conductivity, chemical composition and electrical double-layer capacity (Gabelich et al., 2002; Yang et al., 2001; Ying et al., 2002). Halides are usually removed from solution by electrostatic attraction within the electrode, whereas large polyvalent oxyanions, heavy metals, and colloidal impurities can be removed by means of chemi/physisorption, electrodeposition, electrophoresis, double-layer charging and possibly faradaic reactions, as well as simple electrostatic interactions (Pekala et al., 1994; Yang et al., 2001). Electrode polarity is reversed after saturation to regenerate carbon aerogel electrodes (TDA Research, 2010; Tran, 2004; Welgemoed and Schutte, 2005).

Gabelich *et al.* (Gabelich et al., 2002) and Ying *et al.* (Ying et al., 2002) report that an ion's hydrated radius may regulate the ionic species' sorption capacity into carbon aerogel electrodes. Monovalent ions with smaller hydrated radii were preferentially removed from solution over multivalent ions. Additionally, counterion valency appears to have a strong influence on an individual ion's sorption capacity (Gabelich et al., 2002). Experiments conducted with natural waters showed the sorption capacity of carbon aerogels was significantly lower when a high concentration of NOM was present. The authors suggest pre-treatment for NOM removal would increase effectiveness of CDI in treating natural waters (Gabelich et al., 2002). CDI was found to increase in total capacity for anion removal in the order of  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ , thus this technique could be used most effectively to selectively recover iodide from solutions (Ying et al., 2002). Ying *et al.* (Ying et al., 2002) theorised this effect was due to iodide ions having a partial charge-transfer coefficient larger than bromide and chloride ions. The adsorption capacity of the carbon aerogel electrodes was shown to increase with increasing solution concentration of ionic species, voltage, and surface area of the electrodes. Due to its selectivity, this technique has the potential (with further development) to be applied in the removal of halides from drinking water sources.

Welgemoed and Schutte (Welgemoed and Schutte, 2005) developed an industrial CDI bench scale prototype (MK-8A) and evaluated the module's performance for coal-bed methane brackish water desalination. The module achieved high ionic species reduction in artificial brackish water, reducing the feed stream from 1000  $\mu\text{S}/\text{cm}$  to 23.4  $\mu\text{S}/\text{cm}$  at a flow rate of 50 mL/min. Interestingly, in the artificial system bromide had the highest reduction percent of all ions monitored (86.11%). The prototype was then tested on naturally occurring brackish water

from the natural gas industry in Wyoming, USA. It reduced the feed stream conductivity from 2095  $\mu\text{S}/\text{cm}$  to  $<1000 \mu\text{S}/\text{cm}$  at approximately 70% water recovery rate. Rinse brine was recycled, reducing the volume of waste brine produced. Furthermore, the authors compared the costs of RO, EDR and CDI for brackish water desalination to a potable water standard. CDI could be significantly cost effective compared to RO for brackish water applications (CDI: US\$0.11/1000 L, RO: US\$0.35/1000 L). CDI could also reduce brackish water desalination costs by 70% when compared to existing EDR technologies. A water recovery rate of 70% while still retaining quite a high conductivity (2095  $\mu\text{S}/\text{cm}$  to  $<1000 \mu\text{S}/\text{cm}$ ) is, however, quite inferior to what could be achieved with RO, i.e. organic precursor removal and disinfection, as well as halide removal.

The viability and ion selectivity of CDI technology in treating brackish water generated during natural gas mining for water reuse and iodide recovery has been investigated (Xu et al., 2008b). CDI testing units used in this study were provided by CDT Systems, Inc. The anion sorption capacity of the carbon aerogel (in mol/g aerogel) was dependent upon initial ion concentrations in the feed water. That is, the ions present in the greatest concentration were adsorbed to a greater extent, following the order  $\text{Cl}^- \geq \text{Br}^- > \text{I}^-$ . However, the maximum percentage of removal for these anions followed the opposite trend;  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ , which the author's attributed to iodide's higher partial charge-transfer coefficient compared to the other anions, and intermolecular interactions with the carbon-aerogel electrodes, resulting in a higher sorption capacity. In concurrence with the findings of Ying *et al.* (Ying et al., 2002), bench scale tests showed preferential sorption of iodide from brackish water even in the presence of dominant coexisting ions. The removal of iodide reached 69% and removal of bromide reached 50% in

artificial water (Xu et al., 2008b). During the regeneration phase, 77-107% of sorbed iodide was recovered from the carbon aerogels (a recovery >100% was attributed to the desorption of iodide from the previous run). The authors found bench scale and pilot scale CDI cells exhibited similar sorption capacities. During the pilot study the maximum removals observed were 83% of UV<sub>254</sub>, 77% of I<sup>-</sup>, 62% of Br<sup>-</sup>, 40% of Ca<sup>2+</sup>, 40% of alkalinity (as CaCO<sub>3</sub>), 34% of Mg<sup>2+</sup>, 18% of Na<sup>+</sup> and 16% of Cl<sup>-</sup>. However, field experiments employing a three stage CDI treatment could not meet the water quality standards for reuse due to high total dissolved solids (TDS) concentrations. To resolve this issue additional CDI stages were applied to simulate a multi-stage desalination treatment. Ten CDI stages were needed to reduce TDS to an acceptable level for reuse.

Shiue *et al.* (Shiue et al., 2005) have enhanced the efficiency of CDI by using spiral wound electrodes (activated carbon coated on titanium foil) in combination with online electrolytic ozonation. This allows the reduction of uncharged constituents and disinfection of water by ozone, in addition to the removal of charged species by CDI. Ozone was produced by low-voltage electrolysis of water. The electricity retrieved at the discharging of CDI operation could be harnessed for use in producing ozone, thus increasing energy efficiency.

CDI technology is a promising alternative for brackish water desalination, although the operational performance and sorption capacity of the electrodes may need further development before the technology becomes economically feasible (Xu et al., 2008b).

### **2.2.3 Membrane Capacitive Deionization**



Membrane Capacitive Deionization (MCDI) is a modification of the CDI process, in which ion-exchange membranes are added onto a CDI system (Figure 4) (Biesheuvel and van der Wal, 2009; Li, 2008). Ion-exchange membranes are positioned in front of their corresponding charged electrodes. MCDI has several advantages over CDI namely; the membranes inhibit ions from leaving the electrode region, thereby increasing the salt removal efficiency of the process, and ion release from the electrode region (during electrode regeneration) is more efficient (Biesheuvel and van der Wal, 2009). Both Lee *et al.* and Li found that MCDI had a higher salt removal rate than traditional CDI systems, with 19% and 49% higher rejection found, respectively (Lee et al., 2006; Li, 2008). Although no specific studies on bromide and iodide removal were found using this process, MCDI would be expected to produce improved halide removal efficiency to that experienced with CDI, and is thus an area of potential future research.

#### **2.2.4 Relative advantages and disadvantages of the electrochemical techniques**

The CDI and MCDI processes are not currently used in the treatment of drinking water. The CDI process is both robust and energy efficient, although MCDI may be expected to be able to remove halides with greater efficiency than CDI. With further development CDI has the potential to be applied to drinking water, wastewater, boiler water and coal seam gas water deionisation, as well as brackish water desalination (Oren, 2008). Conversely, the potential for large-scale application of electrolysis to halide removal during water treatment may be limited, due to difficulties in scaling up the process, although this has not yet been explored. Areas in which further development would be expected prior to wide-spread use of CDI technology are related to the optimisation of deionisation, commercial development of aerogels, full scale application and commercialisation of the technique.

## **2.3 Adsorption techniques**

Although membrane techniques can successfully reduce bromide and iodide concentrations in water, surface sorption methods form a major component of halide reduction research and application because of their ease of application and low cost. Recent research has continued to explore the development of low cost, effective, bromide and iodide adsorbents. Sorption techniques comprising; hydrous oxides, activated carbons, silver-doped activated carbons and carbon aerogels, ion-exchange resins, aluminium based adsorbents and soils, are briefly discussed in the following sections.

### **2.3.1 Hydrous oxides**

#### **2.3.1.1 Layered double hydroxides**

Layered double hydroxides (LDHs) (also called hydrotalcite-like compounds (HTCs)) are attracting considerable attention for their ability to selectively remove contaminants in aqueous systems (Barriga et al., 2002; Das et al., 2003; Das et al., 2004; Duan and Evans, 2006; Inacio et al., 2001; Lv et al., 2007; Mandal and Mayadevi, 2008; Pavan et al., 2000; Seida and Nakano, 2002; Villa et al., 1999; Yang et al., 2005; You et al., 2001). LDHs consist of positivity charged metal hydroxide layers, with interstitially located anions and water molecules (Goh et al., 2008; Mandal and Mayadevi, 2008; Reichle, 1986). They have large surface areas and numerous sites for anion exchange, making them ideal ion-exchangers and adsorbents. Additionally, LHDs are produced from low-cost precursors that can be easily regenerated (Das et al., 2003; Mandal and Mayadevi, 2008; Pavan et al., 2000). A summary of studies investigating halide removal using LDH's is reported (Table 10).

Curtius and Kattilparampil (Curtius and Kattilparampil, 2005) studied the application of Mg-Al-Cl LDH for  $^{135}\text{I}$  removal from radioactive wastes. It was found that the adsorption of iodide was independent of pH between 3.5 and 8.5. In the test parameters studied the sorption capacity for iodide decreased with increasing chloride concentrations. A Kentjono *et al.* (Kentjono et al., 2010) study using Mg-Al-(NO<sub>3</sub>) LHD found that the optimum pH for iodide removal was 9.0–9.2. The maximum iodide adsorption capacity achieved was 10.1 mg/g at a LDH dose of 20 g/L and pH of 9.2. The optimum pH for iodide adsorption coincides with that of boron adsorption, however they do not compete with each other's adsorption, indicating that this LDH could be used to simultaneously remove both boron and iodide. The iodide removal capacity of thiosulfate intercalated Zn-Al LDH has been reported by Thomas and Rajamathi (Thomas and Rajamathi, 2009). Approximately 60% of iodide ions were intercalated in the interstitial layer of the LDH, making it a potentially useful treatment for the removal of iodide from drinking waters.

The Lv group investigated the influence of LDH calcination temperatures and the Mg:Al molar ratio on the adsorption of bromide from water by Mg-Al LDHs (Lv and Li, 2007; Lv et al., 2008). The bromide and iodide adsorption capacity of calcined LDHs is higher than that of uncalcined LDHs. Adsorption capacity of bromide and iodide increased with increasing calcination temperature between 200 °C and 500 °C, however it drastically decreased with calcination temperatures from 500 °C to 800 °C. A maximum bromide and iodide adsorption capacity of 94.0 mg/g and 96.1 mg/g, respectively, was achieved with LHD calcination at 500 °C. It was found that a Mg:Al molar ratio of 4 had the highest capacity to remove bromide and iodide from aqueous solution (Table 10). Additionally, the group found that increasing adsorbent

concentrations from 0.2 g/L to 1.0 g/L significantly increased bromide removal from 73.4% to 91.6%, after which the removal plateaus off to a maximum of 94% using 5 g/L (Lv et al., 2008). Similarly, adsorbent concentrations from 0.2 g/L to 1.0 g/L significantly increased iodide removal from 39.4% to 96.5%, after which the removal plateaus with a maximum of 97.6% using 4 g/L (Lv and Li, 2007). LHDs maintained similar bromide removal capacities after five regeneration cycles (Lv and Li, 2007; Lv et al., 2008).

A preliminary study on the effect of layered hydroxides metal composition on iodide sorption was conducted by Pless *et al.* (Pless et al., 2007) Uncalcined layered hydroxides containing  $\text{Cu}^{2+}$  exhibited the highest sorption for iodide, followed by  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . The authors found calcination decreased the sorption of iodide, however calcination temperatures were only 550°C for 1 or 24 hours and only a limited number of layered hydroxides were tested.

Echigo's group investigated the removal of bromide from a real water matrix by LDH's to control the formation of brominated DBPs in the drinking water treatment process (Echigo et al., 2007). Two LDH's, Mg-Fe-LDH (ratio 4:1) and Mg-Al-Fe-LDH (ratio 8:1:1) were compared to a commercially available gel-type polystyrene-divinylbenzene quaternary amine anion-exchange resin; Diaion SA10A. An approximately 60% reduction in bromide using a real water matrix was achieved using both LDH's, whereas an approximately 73% reduction in bromide was achieved with the Dianion resin. The LDH's selectivity sequence was shown to be  $\text{HCO}_3^- \gg \text{NO}_3^- > \text{Br}^- > \text{SO}_4^{2-}$  and hence LDH's were found to be better for bromide removal in a water matrix with high sulfate ion and low bicarbonate and nitrate concentrations due to their selectivity for bromide under these conditions and faster ion exchange reactions in comparison to Diaion SA10A.

However, in the presence of bicarbonate, bromide removal was impaired due to the LDH's preferential adsorption of this anion rather than bromide. This may limit the extent to which these LDH's could be used in bromide removal from drinking water sources, since they would not be expected to be useful under high bicarbonate conditions. Organic carbon (measured as TOC) was not removed by either LDH, indicating it was rejected by the ion-sieve effect of the LDH's. This is important since organic carbon comprises many DBP precursors, so although bromide may be efficiently removed (in low alkalinity conditions), the organic DBP precursors would be expected to remain. The performance of LDH's was found to be comparable to Diaion SA10A in terms of the treatment volume and the bromide uptake before breakthrough for low alkalinity waters. The authors conclude that the application of LDH in the drinking water treatment process would provide similar performance to organic resins such as Dianon SA10A without the potential for secondary contamination.

A Zn-Al LDH adsorbed approximately 14% of iodide from a deionised solution but almost none from a mineralised solution containing 1 mM  $\text{Cl}^-$ , 15 mM  $\text{SO}_4^{2-}$ , and 5 mM  $\text{HCO}_3^-$  at an initial KI concentration of 0.01M at both pH 7 and 10 (Kaufhold et al., 2007). Thus, in a multi-ion solution LDH exhibited preferential selectivity to bicarbonate and sulfate over iodide, in agreement with several other studies (Israeli et al., 2000; Kaufhold et al., 2007; Miyata, 1983). The usefulness of LDHs for halide removal from water is therefore dependent on the nature of the other anionic species present in solution.

Despite this limitation, LDHs have been shown to effectively remove bromide and iodide from real water matrices (Table 10). Several LDHs' anion sorption performance was comparable to

commercially available resins in terms of the treatment volume and anion adsorption before breakthrough. Additionally, ion exchange reactions were shown to be faster using LDH's than commercial ion-exchange resins, and no concerns about secondary contamination when using LDH's have been raised, unlike many commercial ion-exchange resins. The preferential adsorption of bicarbonate over bromide ions, and both sulfate and bicarbonate over iodide ions, for particular LDH's is an important imitation, however, further investigation into the large scale application of promising LDH's is warranted, given they are a prospective low-cost treatment technology, which has the potential for widespread application in drinking water treatment.

#### **2.3.1.2 Sol-gel double hydrous oxide**

In a recent development, the sol-gel method was used to synthesize an inorganic ion exchanger based on a double hydrous oxide ( $\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) (Chubar et al., 2005). Adsorption behaviour of fluoride, chloride, bromide, and bromate ions was investigated by varying experimental parameters including time, pH and adsorbant concentrations. The ion exchanger exhibited both cation and anion-exchange capacity, which reached values of 1.38 and 1.8 mEq/g, respectively. Adsorption of selected anions was observed over the pH range 3 - 8.5, with maximum bromide adsorption occurring at  $\text{pH} < 5$ . Kinetic data on bromide sorption fit a pseudo-second-order model, with a rate coefficient of  $0.16 \text{ min}^{-1}$ . Within the first 10 min of treatment 50% of the bromide ions were adsorbed. The maximum bromide sorption capacity achieved was 80 mg/g at bromide concentrations of 200 mg/L (Table 11). Investigation into competitive adsorption of  $\text{Br}^-$  and  $\text{BrO}_3^-$  at equal concentrations found that at concentrations over 40 mg/L bromide and bromate, competition for adsorption sites favoured bromide, whereas for lower concentrations of bromide and bromate, bromate dominated adsorption. A number of other

novel sol-gel double hydrous oxides have recently been developed, and have been shown to have bromide removal capability (Chubar, 2011) (Table 11).

Further investigation into the ion-exchange interactions with organic matter and complex water matrices under field conditions is needed before the suitability of these adsorbents for drinking water treatment can be more thoroughly evaluated. Further research should also include the development and study of new types of sol-gel double hydrous oxides.

### **2.3.2 Carbon**

Porous carbon materials have been widely used in water treatment to remove various contaminants because of their large surface area and high adsorption capacity.

#### **2.3.2.1 Coal and activated carbon**

Balsley *et al.* (Balsley et al., 1998) studied the iodide adsorption capacity of lignite and sub-bituminous coal. Adsorption of iodide onto coal was found to be highly pH-dependent. Lignite achieved a maximum sorption of 34% at pH 3.9, and above that pH iodide adsorption capacity rapidly decreased. In contrast, sub-bituminous coal exhibited higher adsorption capacity over a wider pH range, with a maximum iodide sorption of 46% at pH 6.2. However, further investigation showed the adsorption capacity of coal decreases over time. Kaufhold *et al.* reported a 13-21% sorption capacity of a Merck activated carbon for the removal of iodide (Kaufhold et al., 2007). Sorption capacity was slightly higher at pH 7 than pH 10. Interestingly, investigation into competitive adsorption showed iodide sorption was not affected by competing anions. Maes' group also investigated adsorption of iodide on activated carbon under aerobic and anaerobic conditions (Maes et al., 2004). Results showed the dissociation constant ( $K_d$ ) values

decreased from 2000 mL/g under aerobic conditions to 70 mL/g under anaerobic conditions. Due to the well-documented high affinity of iodine towards activated carbon (Juhola, 1975; Mianowski et al., 2007; Yang et al., 1993), the authors concluded that iodide removal is facilitated by the oxidation of iodide to iodine by dissolved oxygen, which is subsequently adsorbed by the activated carbon. Hence, the effectiveness of activated carbon in iodide removal is dependent on dissolved oxygen concentrations (Maes et al., 2004). Some studies on halide adsorption using coal and activated carbon have been summarised (Table 12).

Use of activated carbons in the water industry has been increasing due to increasing environmental regulations and its ability to adsorb a wide range of contaminants. Price varies depending on demand, quality and cost of production. Although activated carbon is widely used in the water industry (primarily for organics removal) this technique is not generally utilised for bromide/iodide removal, due to limited efficiency in this context.

#### **2.3.2.2 Silver impregnated activated carbon**

Hoskins *et al.* (Hoskins et al., 2002) investigated two bituminous coal-based silver-impregnated granular activated carbons (AgAC) (0.05 and 1.05 wt% Ag) and their unimpregnated counterparts (GAC) in their ability to remove iodide from aqueous solutions by a series of batch sorption and leaching experiments. Silver impregnation did not significantly alter the texture and pore structure of unimpregnated GAC. Interestingly, iodide sorption onto AgAC was independent of pH until silver became saturated with iodide, after which iodide sorption increased with decreasing pH indicating a more positively charged surface and less competition from hydroxide ions at lower pH values. The authors concluded iodide sorption is initially



controlled by precipitation of silver iodide, and subsequent removal occurs as a result of adsorption onto the GAC, which is a pH-dependent phenomenon. The 0.05% AgAC sorption behaviour closely resembled its unimpregnated GAC, due to the small silver concentration relative to total iodide concentration. In contrast, the 1.05% AgAC exhibited noticeably greater iodide sorption than its unimpregnated GAC at pH values of 7 and 8, while their performances were comparable at a pH of 5 (Table 13). At a dose of 1 g/L sorbent, at pH 8 with an initial iodide concentration of 425  $\mu\text{M}$ , approximately 390  $\mu\text{mole/g}$  of  $\text{I}^-$  was sorbed onto the AgAC. Several silver impregnated activated carbon treatment processes that remove iodide from drinking water have been patented (Doumas, 1980; Quinn, 1952; Renn, 1966).

#### **2.3.2.3 Silver chloride impregnated activated carbon**

Ho and Kraus demonstrated pre-treatment of activated carbon with silver (20 wt% Ag) and chloride, to form a silver chloride impregnated activated carbon (AgClAC), caused a large increase in the uptake of iodide, relative to unimpregnated activated carbon (Ho and Kraus, 1981). The iodide-chloride concentration ratio did not significantly affect the efficiency of iodide absorption. Long term experiments with tracer iodide solutions ( $10^{-7}$  M) passed over small columns ( $<0.5 \text{ cm}^3$ ) achieved over 98% iodide removal after several thousand column volumes of treatment. The authors hypothesized that ion exchange of chloride for iodide is due to the differences in solubility between silver chloride and silver iodide ( $K_{\text{sp}} 10^{-10}$  and  $10^{-17}$ , respectively). More recently, Karanfil *et al.* (Karanfil et al., 2005) demonstrated that in streams of low iodide concentrations AgClAC could be used instead of AgAC to reduce silver leaching. Both AgClAC and AgAC (1.05 wt% Ag) exhibited relatively similar iodide sorption, independent of pH, however, under acidic conditions silver leaching from AgClAC was

significantly lower than from AgAC (6% and 50%, respectively). Experiments conducted using a groundwater contaminated with  $^{129}\text{I}$  showed similar iodide sorption using both AgAC and AgClAC as adsorbants.

Silver impregnated activated carbons have widespread applications in domestic drinking water, beverage and food industry, mineral water bottling, and laboratories (Marsh and Rodríguez-Reinoso, 2006). They provide a means for water purification without a large infrastructure burden and are also a safe and effective method of controlling/preventing bacterial growth. This technique has the potential for widespread application in the drinking water industry, since both NOM and halides may be lowered using this method, thereby lowering DBPs formation. However, further development is required in the areas related to; effects of competing anions, efficiency in complex water matrices, and the optimisation of the technique for large scale water treatment plants. Leaching of silver from these materials can be controlled by a dedicated silver-impregnation process, therefore ensuring the safety of the product for drinking water use. For example, Norit 18x40 AG 1 has a silver content of 0.1% by mass, and a water-extractable silver concentration of 0.01 mg/L (Norit, 2010). Individual commercially available silver-impregnated activated carbons will vary in the extent of silver leaching, and information on this is available in the specifications for the individual materials.

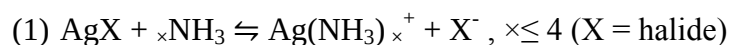
#### **2.3.2.4 Silver doped carbon aerogels**

Sánchez-Polo and colleagues have conducted several studies into the effectiveness of silver doped activated carbon aerogels for bromide and iodide removal from drinking water (Sánchez-Polo et al., 2006a, 2007a; Sánchez-Polo et al., 2006b, 2007b) (Table 14). Halide adsorption onto

silver-doped carbon aerogels was significantly higher than for activated carbon (Sánchez-Polo et al., 2007a). The maximum adsorption capacity for chloride, bromide, and iodide were 7.32, 3.01, and 1.98  $\mu\text{mol/g}$ , respectively, using a silver-doped carbon areogel with a surface area of  $428 \pm 30$  ( $\text{m}^2/\text{g}$ ), characterised by an elevated surface acidity ( $\text{pH} = 4.5 \pm 0.1$ ), high concentration of surface oxygen ( $\text{O} = 21 \pm 1\%$ ), and a wide dispersal of  $\text{Ag}^+$  covering  $10 \pm 1\%$  of the aerogel surface. The initial study showed that an increase in the silver concentration reduced the surface area of the aerogel and increased mesopore and macropore volumes. However, halide adsorption capacity increased with silver concentrations on the aerogel surface. The adsorption capacity of the adsorbent increased with decreasing radius size of the halide ion (adsorption capacity and halide affinity decreased in the order;  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ ), indicating steric hindrance in the sorption of larger ionic radius halides on silver-doped aerogels. The presence of chloride and NOM reduces the efficiency of silver-doped aerogels in removing bromide and iodide from aqueous solution. High concentrations of chloride (40 mg/L) reduced the adsorption capacity of bromide and iodide to 36% and 33%, respectively, from 3.01 and 1.98  $\mu\text{mol/g}$  in the absence of chloride to 1.91 and 1.33  $\mu\text{mol/g}$  in the presence of chloride.

The affects of carbonization and activation of silver-doped aerogels on bromide and iodide removal has also been studied (Sánchez-Polo et al., 2006a). Carbonization and activation of silver-doped aerogels increased the surface area, and mesopores and macropores volumes slightly decreased. Carbonization and activation treatments significantly increased the aerogels adsorption capacity of bromide and iodide, due to increased microporosity as well as electrostatic interactions. Activation treated aerogels increased bromide and iodide sorption capacity by 92% and 154%, respectively, compared to the untreated silver aerogel. Although carbonization and

activation treated aerogels exhibited higher adsorption capacity than the untreated silver-aerogel, all adsorption capacities were considerably lower in natural waters. The authors conclude the reduced sorption capacity is a result of organic matter blocking pores and the presence of competing anions. The anion affinity for silver-doped aerogels is quite high in comparison to aerogels that do not include silver, indicating that in addition to chemisorption, electrostatic interactions contribute to halide adsorption in silver-doped aerogels. Additional research examined the adsorption of bromide and iodide under dynamic conditions chosen to simulate a water treatment plant using Lake Zurich water (Sánchez-Polo et al., 2007b). This study also examined the regeneration of exhausted aerogels. Results showed aerogel columns have a high removal efficiency of iodide and bromide from synthetic water (60 - 71%), however, these values decreased to 31 - 56% when natural waters were tested. This agrees with the reports discussed above and may be a consequence of the presence of NOM and competing anions. Regeneration with  $\text{NH}_4\text{OH}$  results in the replacement of the halide ions with ammonia to form a silver–ammonia complex, which transforms adsorption sites from  $\text{Ag}^+$  to  $\text{Ag}(\text{NH}_3)_x^+$  according to equation (1) (Sánchez-Polo et al., 2006b, 2007b).



Regeneration of the columns enabled the recovery of approximately 100% of the initial adsorptive capacity of the aerogel, with no significant changes in the adsorption characteristics after three adsorption/regeneration cycles. Investigation into the possible leaching of organic polymer precursors from the aerogels found that these are not released in high concentrations ( $>0.1 \text{ mg/L}$ ). The number of surface silver adsorption sites is not significantly altered after

regeneration. Silver-doped aerogels have also been shown to exhibit strong, long-term antibacterial activity against *E. coli* and *S. aureus* (Zhang et al., 2004).

Silver-doped activated carbon aerogels are a promising technique to remove bromide and iodide from drinking water, thereby lowering DBPs formation. Metal-doped carbon aerogels may also find application in the treatment of wastewater. The high cost of production at this time has been the main limitation of this technology. Additionally, research has been limited to lab-scale studies. Further research and development to lower the cost of aerogel production will be integral to the expansion of carbon aerogel technology into large-scale treatment processes.

### **2.3.3 Ion exchange resins**

#### **2.3.3.1 MIEX®**

Orica Watercare's MIEX® (Magnetic Ion EXchange) resin was developed specifically for the removal of NOM from natural waters (Boyer and Singer, 2005, 2006; Hsu and Singer, 2010; Johnson and Singer, 2004). MIEX® is a strong base anion-exchange resin with iron oxide integrated into a macroporous polyacrylic matrix, which provides the resin with magnetic characteristics, aiding the agglomeration and settling of the resin. MIEX® resin beads are 2-5 times smaller than traditional resins ( $\phi \approx 180 \mu\text{m}$ ), resulting in an increased surface area to volume ratio that allows rapid ion exchange kinetics (Bourke et al., 2001; Cadee et al., 2000). A review of the literature reveals that in addition to NOM removal it is capable of removing bromide (Bourke et al., 2001; Boyer and Singer, 2005, 2006; Boyer et al., 2008; Cadee et al., 2000; Hsu and Singer, 2010; Johnson and Singer, 2004; Mergen et al., 2008; Singer and Bilyk, 2002) (Table 15). Several studies have shown MIEX® efficiently reduces NOM concentrations,

consequently reducing THMs precursors and oxygen demand (Boyer and Singer, 2005, 2006; Hsu and Singer, 2010; Johnson and Singer, 2004; Morran, 2004; Singer, 2007; Singer and Bilyk, 2002). The charge density of NOM isolates have been shown to have the most significant effect on NOM affinity with MIEX® (Boyer et al., 2008; Singer, 2007). Removal of bromide by MIEX® resin is highly dependent on the alkalinity of the water and competing ion concentrations (Boyer and Singer, 2005, 2006; Hsu and Singer, 2010; Johnson and Singer, 2004; Singer, 2007; Singer and Bilyk, 2002). Under optimal conditions MIEX® was able to reduce bromide concentrations by approximately 93%, however under less favourable conditions reductions in the order of 60% were typically achieved (Singer and Bilyk, 2002). Boyer's study showed that the ion-exchange capacity of regenerated MIEX® resin was significantly lower than virgin MIEX® (20-28%) (Boyer, 2008). In high alkalinity waters, bromide is unable to compete effectively against bicarbonate ions for the exchange sites on the strong base anion-exchange resin (Johnson and Singer, 2004; Singer, 2007; Singer and Bilyk, 2002). Therefore, in high alkalinity waters where bromide removal is less efficient, subsequent chlorination of MIEX® treated water can still cause significant concentrations of brominated THMs and HAAs to be formed (Ates, 2008; Boyer and Singer, 2005).

MIEX® resin is a proven and highly successful NOM removal technology. However, the simultaneous removal of bromide in addition to NOM is often not efficient when treating a raw drinking water matrix. There is potential to apply MIEX® for bromide removal in low alkalinity waters, however, further research is required to understand the conditions under which this will provide an efficient bromide-reduction treatment, as well as to understand the affinity of MIEX® with iodide.

### 2.3.3.2 Other anion-exchange resins

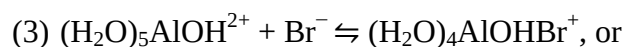
Any strong anion-exchange resin could be expected to display some bromide and iodide absorption capacity under favourable conditions. Hsu *et al.* (Hsu and Singer, 2010) compared Ionac A-641 and Amberlite IRA910 polystyrene resins to MIEX® and found that the polystyrene resins were more efficient for bromide removal while MIEX® was more effective at NOM removal. A number of commercially available resins have been compared (Tables 16, 17 and 18).

Ion-exchange resins have been used widely in many applications of drinking and wastewater treatment. Ion-exchange is a moderately expensive water treatment. Commercially available strong anion-exchange resins that are capable of adsorbing both bromide and iodide are available, however, their application to drinking water treatment is limited due to cost and reduced removal efficiency in complex matrices. Generally, as concentrations of competing anions and NOM increase in the water matrix, the adsorption of bromide and iodide decreases. There is potential to apply strong anion-exchange resins for bromide and iodide removal after pre-treatment to remove NOM and/or competing anions. Many patented resins are modified with metals, which increases cost and the potential for leaching, therefore lowering suitability for potable water treatment. Most have not been applied on a large scale, however, with more research they have the potential for specific wastewater applications. Further research investigating the affinity of strong anion-exchange resins for iodide would be beneficial, since most studies reviewed focussed on bromide adsorption (Hsu and Singer, 2010; Humbert et al., 2005; Lokhande et al., 2009a; Singare and Lokhande, 2009). Further investigation into the risk of

leaching from various resin types as well as improved cost-effectiveness would also be beneficial.

#### 2.3.4 Aluminium coagulation

Ge and Zhu (Ge and Zhu, 2008) reported that bromide sorption by aluminium coagulation can occur via three possible pathways (equations 2-4):



Ge *et al.* (Ge *et al.*, 2007) showed that in synthetic water, 93.3–99.2% removal efficiency of bromide was achieved by coagulation with aluminium chloride ( $AlCl_3 \cdot 6H_2O$ ) in the absence of humic acids. In the presence of humic acids, bromide removal was decreased by approximately 20% to 73.2% at a dose of 3 mg/L aluminium chloride (Table 19). In a natural water, 87.0% of bromide was removed using a significantly higher coagulant dose (15 mg/L). Bromide removal efficiency was relatively stable from pH 4–8, however at pH 9 removal efficiency drastically decreased to 44.2%. The effects of coexisting ions on removal of bromide by aluminium coagulation was also investigated (Ge and Zhu, 2008). It was observed that bromide removal decreased from 82.8–99.2% in deionized water to 62.1–87.0% in raw water, indicating bromide removal was significantly affected by coexisting ions and humic acids, present in natural water (Ge and Zhu, 2008). Humic acid was also found to be adsorbed by aluminium coagulation, and the efficiency of this was diminished in the presence of 0.2 mg/L bromide in raw water (92.3%



as compared to 97.0% in deionized water). Both experiments were conducted with 15 mg/L coagulant at pH 6. The addition of  $\text{NO}_3^-$  (10 mg/L),  $\text{HCO}_3^-$  (250 mg/L),  $\text{Cl}^-$  (250 mg/L),  $\text{SO}_4^{2-}$  (250 mg/L) and  $\text{H}_2\text{PO}_4^-$  (250 mg/L) to deionised water decreased bromide removal efficiency by 8.0%, 11.5%, 14.6%, 21.2% and 40.8% respectively. The authors did not investigate the compounding effects a mixture of competing anions would have on bromide removal.

The aluminium coagulation of bromide is inhibited by the presence of organic matter and anions in natural source waters. Although the authors show reasonable bromide reductions with small volumes of natural waters, this required large coagulant doses, in order to compensate for the inhibitions effects from competing anions and NOM. Further investigation into halide adsorption optimisation and potential to be used in conjunction with other techniques to improve halide removal would be of interest.

### **2.3.5 Soils**

Several research groups have studied the adsorption of iodide on soil, with particular emphasis on radioactive iodide (Dai et al., 2004; Dai et al., 2009; Gu and Schulz, 1991; Hu et al., 2005; Kaplan et al., 1999; Muramatsu et al., 1990; Sheppard et al., 1996; Sheppard et al., 1995; Yoshida et al., 1992) (Table 20). Dai *et al.* (Dai et al., 2009) studied iodide adsorption using soil from China. It was shown that iodide sorption exhibited a linear relationship with soil organic matter concentration, a polynomial relationship with free iron oxide content and a logarithmic relationship with cation exchange capacity.  $K_d$  for iodide sorption onto these soil samples ranged from 0.78 to 6.59 mg/kg. Dai *et al.* deduced that higher sorption capacity was due to the higher proportion of ferric oxides and aluminum oxides in soils. Similarly, Whitehead (Whitehead,

1973, 1974), Sheppard *et al.* (Sheppard et al., 1996) and Gu and Schulz (Gu and Schulz, 1991) observed that iodide adsorption by soil was dependent on ferric oxides, aluminum oxides and soil organic matter. Common soil components (Kaolinite, bentonite, quartz sand,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and humic acids') iodide sorption capacities from water were investigated by Muramatsu *et al.* (Muramatsu et al., 1990). Quartz sand,  $\text{Al}_2\text{O}_3$ , kaolinite and bentonite had limited or no sorption capacity. Humic acid was shown to sorb approximately 70% of iodide out of a synthetic water solution. Sorption of iodide by  $\text{Fe}_2\text{O}_3$  was very high (~ 80%) from deionised synthetic water, however, in a complex system with competing molecules  $\text{Fe}_2\text{O}_3$  would not be expected to contribute significantly to iodide adsorption. Couture and Seitz reported that 30% of iodide was sorbed from water by hematite ( $\text{Fe}_2\text{O}_3$ ) and less than 5% was sorbed by Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) (Couture and Seitz, 1983). Sheppard *et al.* (Sheppard et al., 1995) found iodide adsorption significantly decreased in the presence of competing anions.

The investigation of Kaplan *et al.* (Kaplan et al., 1999) into soil isolates found illite had a significant iodide adsorption capacity ( $K_d = 15.14 \pm 2.84 \text{ mL/g}$ ), which was pH dependent. Desorption experiments showed that  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $^{127}\text{I}$  displaced  $^{125}\text{I}$  that was sorbed onto illite, by  $43 \pm 3\%$ ,  $45 \pm 0\%$ ,  $52 \pm 3\%$ , and  $83 \pm 1\%$  respectively. Desorption was shown to increase from 43% to 83% with increasing size of the competing anion, indicating  $\text{I}^-$  is weakly associated by anion or ligand exchange with the illite structure. Yoshida *et al.* (Yoshida et al., 1992) studied the adsorption of iodide from deionised water by Japanese Andosols and Kanuma soils. Approximately 99% and 55% of iodide was adsorbed from aqueous solution at pH 4 by Andosols and Kanuma soils respectively. Anion sorption can occur on positive charges on either free hydroxides of iron and aluminium or on the edges of aluminosilicate clay mineral lattices

(Whitehead, 1974). Yoshida *et al.* (Yoshida et al., 1992) reported that the sorption of iodide on Kanuma soil increased with decreasing pH and was described by Henry isotherms, suggesting that iodide was electrostatically adsorbed on the described positive charges. The observed relationship between  $I^-$  and pH on Kanuma soil was in agreement with Whitehead's (Whitehead, 1974) and Musicć's (Musicć, 1979) studies on iodide sorption onto ferric hydroxide and aluminum hydroxide. Balsley *et al.* (Balsley et al., 1998) showed imogolite-bearing soil have significant iodide sorption between pH 4 and 5.5.

The potential application of soils appears to be an economical and efficient method for halide removal for potable water treatment, assuming organic matter concentration of water was not increased by the process. Further research to evaluate the practical applications of different soils and their components on DBPs precursor removal is warranted.

### **2.3.6 Relative advantages and disadvantages of adsorptive techniques**

Adsorptive techniques for halide removal are generally cheaper and more easily implemented than membrane or electrochemical techniques, however, their adsorption efficiency is often adversely impacted by the presence of competing anions and NOM in natural waters. Although activated carbons and MIEX® are used in drinking water treatment, they are employed for organic matter adsorption, rather than for halide removal. Development of adsorptive techniques that effectively removed NOM and halides in the presence of competing anions would represent an important step forward in DBPs precursor removal.

## **3.0 Comparison of the three classes of halide removal techniques**

The specific experimental conditions of the reviewed research varied greatly, making quantitative comparisons of bromide and iodide removal difficult. Discussion of each removal technique's potential for commercial application in drinking water treatment is intended to guide further research, rather than to conclusively indicate which technology is preferable, due to the lab-scale nature of much of the research reviewed.

Evaluating bromide and/or iodide removal efficiency of each technique requires the consideration of all experimental conditions, including water type, flow rate, pressure, current, adsorbent load, adsorption capacity, initial anion concentration, pH, contact time, system regeneration, effects of competing anions, ease of application and overall cost. Not all authors report these experimental conditions, making comparison between different removal technologies challenging. The overall bromide and iodide removal capacity of the three removal technique categories, taking these many parameters into account to the extent that it is possible, is discussed herein (Table 21).

In general, membrane techniques have the highest bromide and iodide removal for natural drinking water matrices, and offer the additional benefits of NOM removal and disinfection. Electrochemical techniques were found to be preferable over adsorption techniques because their halide removal efficiencies were higher in natural drinking water matrices. Despite several lab-scale studies finding that adsorbents achieved high bromide and iodide removals, generally their adsorption capacity was greatly diminished in the presence of competing anions and NOM in natural drinking waters, thus, adsorption techniques are likely to be the least applicable to halide removal in drinking water treatment at this stage in the development of the technology. With this

in mind, however, the cost-effectiveness and ease of applicability of adsorbent techniques suggest that this will continue to be an important area of research, and with further development to circumvent the current limitations, surface sorption methods still may have the greatest potential in widespread DBP management.

In terms of efficiency of halide removal, RO is the optimal membrane technique of those discussed here. NF is also excellent in achieving halide removal, however, the performance of this technique is lower than that of RO. ED and EDR are not as well-developed in accomplishing optimal halide removal as RO and NF, although excellent removals can still be attained.

Membrane technologies have the highest bromide and iodide removal capacity of all the techniques discussed here, but they are also the most expensive. Despite this, with increasingly stringent regulations on water quality and a movement to increased utilisation of alternative water sources, membrane filtration is emerging as an economically viable alternative to conventional methods for removal of a wide array of microbial and chemical contaminants, including halides.

In natural drinking water matrices, the electrochemical techniques discussed here have shown high bromide and iodide removal capacity. Although CDI is at an early stage of its development, it has a greater likelihood of applicability to the drinking water treatment industry for halide removal than electrolysis, due to the difficulty of increasing electrolysis to a water treatment plant scale. With further development and research CDI could be widely applied to the water industry, rivalling membrane techniques.

Adsorption processes are promising methods for the removal of bromide and iodide for DBPs minimisation in terms of cost effectiveness and simplicity of design and operation. However, for use in environmental water matrices, further development of these techniques is required in order to overcome the detrimental effect of competing anions and NOM present in potable water sources on halide adsorption.

#### **4.0 Research directions**

Several areas in which additional research is needed to assess the bromide and iodide reduction capacity of treatment technologies have been identified. The main areas relevant to DBPs management in drinking water by removing halide precursors are: optimisation of technologies such as EDR, electrolysis, LDHs, silver-doped aerogels and resins for the water treatment plant scale; adaptation for commercial production/application of resins, soils and aerogels; minimising the effects of competing anions and NOM on adsorptive techniques for halide removal; improving energy efficiency of membrane techniques and development of improved membranes for EDR; studying bromide and iodide removals by MCDI and optimising the deionisation achievable by CDI; decreasing production costs of resins and silver-doped aerogels; developing understanding of optimal silver-doping for best cost/benefit in silver-doped activated carbons.

There is a general need for further development of halide removal techniques able to be used in commercial water treatment applications. Most halide removal studies have investigated removals of specific anions in isolation from other halides and other potentially competing anions. There is a need to assess halide reduction methods with respect to both bromide and iodide, as well as competing anions. Removal of both halides and NOM simultaneously

represents the ideal solution for DBP control by precursor removal, however, in general the membrane techniques are the only processes of those reviewed here that are efficient in doing this. Further potential is in the development of hybrid techniques from the combination of less efficient/limited techniques, to achieve this ultimate goal, of efficient NOM and halide removal for DBP minimisation.

## **5.0 Conclusions**

The increasing demand on water resources will inevitably require increasing use of impaired and alternative water sources, including salinity impacted waters, for potable water supply.

Increasing stringency on potable water quality may also be expected to occur, to increase global alignment with World Health Organisation suggested water quality guidelines. These combined pressures may create a need for the implementation of effective bromide and iodide removal technologies in order to control known and emerging DBPs. The important advantage of DBPs precursor removal over other DBP management strategies is that removing precursors minimises the formation of all DBPs, both known and unknown, regulated and unregulated. Since there are innumerable individual DBP species and they cannot feasibly all be monitored and regulated, this approach would be expected to be simple and effective in the reduction of the entire suite of brominated and/or iodinated DBPs.

Bromide and iodide removal techniques have been broadly classified into three categories; membrane, electrochemical and adsorption techniques. Membrane techniques (RO, NF, MCI) were found to have excellent halide removal efficiencies, although these techniques can be expensive and energy inefficient. Electrochemical techniques (electrolysis, CDI and MCDI) can

also have good halide removal abilities, although unlike the membrane techniques, they do not remove NOM, which is also essential for controlling DBP formation. CDI and/or MCDI may be suitable for application to drinking water treatment with further development of this technology. Studies on bromide and/or iodide removal using adsorption techniques (LDH's, silver impregnated activated carbons, carbon aerogels, ion-exchange resins, aluminium coagulation, and soils) showed varied results, with the primary limitation being interference from competing anions and NOM causing lowering of halide adsorption. Despite this limitation, adsorptive techniques continue to be a promising area of research due to the relatively low cost and ease of application of these technologies.

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**Table 1.** Examples of levels of bromide and iodide in different source waters.

|                      | Bromide (µg/L)                                           | Iodide (µg/L)                    |
|----------------------|----------------------------------------------------------|----------------------------------|
| Seawater             | 65000 (Stumm, 1996)                                      | 35.8 – 51.1<br>(Duranceau, 2010) |
| Desalinated seawater | 650 (Magara et al., 1996;<br>Obolensky and Singer, 2005) | <4 (Duranceau, 2010)             |
| US rivers (median)   | 35 (Amy and Siddiqui, 1998)                              | 0.5-212 (Moran et al.,<br>2002)  |
| US ground water      | 16 (Davis, 2004)                                         | 30 (Land, 2004)                  |

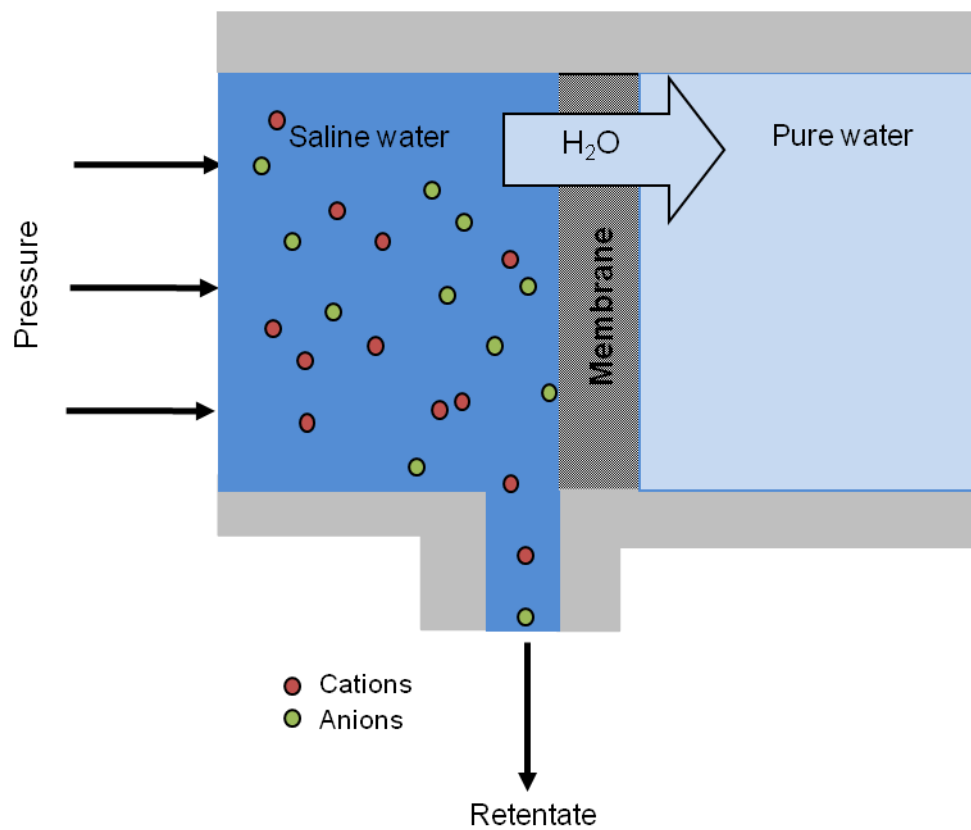
**Table 2.** Rate constants for bromide and iodide oxidation by common disinfectants.

|                                              | Chlorine                                                                 | Monochloramine                                                                            |
|----------------------------------------------|--------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| $\text{Br}^- \rightleftharpoons \text{HOBr}$ | $1.5 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ (Kumar and Margerum, 1987) | $0.014 \text{ M}^{-1}\text{s}^{-1}$ (Trofe, 1980)                                         |
| $\text{I}^- \rightleftharpoons \text{HOI}$   | $4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Nagy, 1988)               | $2.4 \times 10^{10} \times [\text{H}^+] \text{ M}^{-2}\text{s}^{-1}$ (Kumar et al., 1986) |

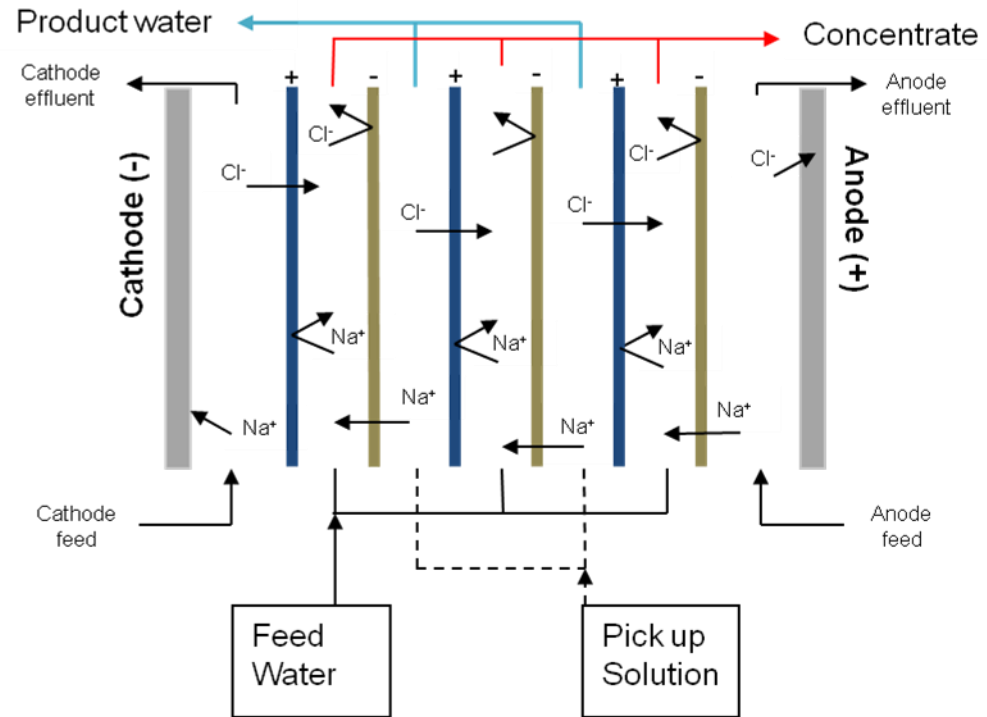
**Table 3.** Rate constants of HOI and HOBr reaction with common disinfectants.

|      | Chlorine                                                        | Monochloramine                                                                   |
|------|-----------------------------------------------------------------|----------------------------------------------------------------------------------|
| HOBr | $2.95 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ (Farkas, 1949)   | $2.86 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (Gazda et al., 1995)              |
| HOI  | $52 \text{ M}^{-1}\text{s}^{-1}$ (Bichsel and von Gunten, 1999) | $<2.0 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ (Bichsel and von Gunten, 1999) |

**Figure 1** Schematic of the RO process. Note that while this illustrates the desalination process, other contaminants present in water including NOM and small organic molecules can also be rejected by RO membranes.



**Figure 2** Schematic of the ED process (example using NaCl solution).



**Table 4** Bromide and iodide rejection capacity for a number of RO membrane types.

| Membrane        | Type                | Initial anion concentration |                       | Competing anions present | Water type* | Rejection capacity  |                    | Pressure (kPa) | Flow rate (L/min) | pH      | Temp (°C) | Reference              |
|-----------------|---------------------|-----------------------------|-----------------------|--------------------------|-------------|---------------------|--------------------|----------------|-------------------|---------|-----------|------------------------|
|                 |                     | Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (mg/L) |                          |             | Br <sup>-</sup> (%) | I <sup>-</sup> (%) |                |                   |         |           |                        |
| SWC4+           | Composite Polyamide | 71                          | -                     | Y                        | N, SW       | 99.8                | -                  | 6480           | 63.2              | 7.9     | 20        | (Bartels et al., 2009) |
| SWC5            | Composite Polyamide | 64.4                        | -                     | Y                        | N, SW       | 99.34               | -                  | 5065           | 11933             | 8.0     | 25.1      | (Bartels et al., 2009) |
| SWC6            | Composite Polyamide | 64.4                        | -                     | Y                        | N, SW       | 99.34               | -                  | 5065           | 11933             | 8.0     | 25.1      | (Bartels et al., 2009) |
| SWC4+b          | Composite Polyamide | 71                          | -                     | Y                        | N, SW       | 99.8                | -                  | 6480           | 63.2              | 7.9     | 20        | (Bartels et al., 2009) |
| SWC6            | Composite Polyamide | 64.4                        | -                     | Y                        | N, SW       | NS                  | -                  | 5065           | 11933             | 8.0     | 25.1      | (Bartels et al., 2009) |
| Trisep X-20®    | Composite polyamide | >0.160                      | -                     | Y                        | N, WW       | ~ 90%               | -                  | -              | 60 –90            | -       | -         | (Khan et al., 2005)    |
| Multiple tested | NS                  | -                           | 0.0358 - 0.0511       | Y                        | N, SW       | -                   | 89                 | -              | -                 | 7.1-7.6 | 26.1-38.5 | (Duranceau, 2010)      |
| TFC-HR          | TFC® polyamide      | 51.3                        | 49.9                  | Y                        | N, OB       | 90.7                | 92                 | 558.8          | 0.5               | 6       | 11±1      | (Drewes et al., 2009)  |
| TMG-10          | Cross Linked Fully  | 51.3                        | 49.9                  | Y                        | N, OB       | 100                 | 87                 | 558.8          | 0.5               | 6       | 11±1      | (Drewes et al., 2009)  |

|         |                                              |      |      |   |       |      |      |       |     |     |      |                          |
|---------|----------------------------------------------|------|------|---|-------|------|------|-------|-----|-----|------|--------------------------|
|         | Aromatic<br>Polamide<br>Composite            |      |      |   |       |      |      |       |     |     |      |                          |
| TFC-ULP | Proprietary<br>TFC®<br>polyamide             | 51.3 | 49.9 | Y | N, OB | 100  | 82   | 558.8 | 0.5 | 6   | 11±1 | (Drewes et al.,<br>2009) |
| XLE     | Polyamide<br>Thin-Film<br>Composite<br>(TFC) | 51.3 | 49.9 | Y | N, OB | -    | 80   | 558.8 | 0.5 | 6   | 11±1 | (Drewes et al.,<br>2009) |
| FT30    | polyamide<br>membrane                        | 3995 | 6345 | N | SW    | 99.6 | 99.4 | 2000  | -   | 6.8 | 25   | (Pontié et al.,<br>2003) |

\*Water type – N = Natural water, SW = seawater, WW = waste water, OB = oilfield brines. '–' = data not available.

**Table 5** Physical characteristics of the halide ions.

| Halide          | Atomic weight | Electronegativity<br>(Pauling scale) | Molar hydration enthalpies<br>(kcal/mol) (Weiss, 1995) | Non-hydrated radius<br>(Å) (Nightingale, 1959) | Hydrated radius (Å)<br>(Nightingale, 1959) |
|-----------------|---------------|--------------------------------------|--------------------------------------------------------|------------------------------------------------|--------------------------------------------|
| F <sup>-</sup>  | 18.99         | 3.98                                 | -98                                                    | 1.16                                           | 3.52                                       |
| Cl <sup>-</sup> | 35.45         | 3.16                                 | -79                                                    | 1.81                                           | 3.32                                       |
| Br <sup>-</sup> | 79.90         | 2.96                                 | -71                                                    | 1.95                                           | 3.30                                       |
| I <sup>-</sup>  | 126.90        | 2.66                                 | -62                                                    | 2.16                                           | 3.31                                       |

**Table 6** Bromide and iodide rejection capacity for a number of NF membrane types

| Membrane           | Type                              | Initial anion concentration |                       | Competing anions present | Water type* | Rejection capacity  |                    | Pressure (kPa) | Flow rate (L/min) | pH        | Temp °C | Reference               |
|--------------------|-----------------------------------|-----------------------------|-----------------------|--------------------------|-------------|---------------------|--------------------|----------------|-------------------|-----------|---------|-------------------------|
|                    |                                   | Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (mg/L) |                          |             | Br <sup>-</sup> (%) | I <sup>-</sup> (%) |                |                   |           |         |                         |
| NF-90 (200 Da)     | Polyamide TFC                     | 1030                        | 1                     | Yes                      | S           | 94-96               | 84-91              | 4000           | 1                 | 7.8 - 9.8 | 20      | (Harrison et al., 2007) |
| NE-90 (200 Da)     | Polyamide TFC                     | 1030                        | 1                     | Yes                      | S           | 94-97               | ~90                | 4000           | 1                 | 7.8 - 9.8 | 20      | (Harrison et al., 2007) |
| NF70-2540 (180 Da) | Polyamide TFC                     | -                           | 719.5                 | No                       | S           | -                   | 80                 | 1200           | -                 | -         | -       | (Lhassani et al., 2001) |
| NF45-2540 (200 Da) | Polyamide                         | -                           | 2538                  | No                       | S           | -                   | 56.785             | NS             | 1.16              | -         | 20      | (Pontie et al., 2003)   |
| NF45-2540 (200 Da) | Polyamide                         | -                           | 2538                  | No                       | S           | -                   | 56.785             | NS             | 1.16              | 6         | 20      | (Diawara et al., 2003)  |
| NF-70 (200 Da)     | TFC polyamide film active surface | 79.9                        | -                     | No                       | S           | >93                 | -                  | 2000           | 1.16              | 6.8       | 25      | (Pontié et al., 2003)   |
| NF-90 (200 Da)     | Polyamide TFC                     | 51.3                        | 49.9                  | Yes                      | N           | 80                  | 78.3               | 1241 - 1275    | 0.5               | 6         | 25      | (Drewes et al., 2009)   |
| TFC-S (200 Da)     | Polyamide TFC                     | 51.3                        | 49.9                  | Yes                      | N           | -                   | 69.5               | 1241 - 1275    | 0.5               | 6         | 25      | (Drewes et al., 2009)   |
| ESNA (200 Da)      | Polyamide TFC                     | 51.3                        | 49.9                  | Yes                      | N           | -                   | 55.6               | 1241 - 1275    | 0.5               | 6         | 25      | (Drewes et al., 2009)   |

\*Water type – N = Natural water, S= synthetic. '–' = data not available.

**Table 7** Parameters and halide rejection capacity for ED/EDR techniques.

| Exposure Time (h) | No. of Cell Pairs | Membrane Type            | Initial Anion Concentration |                      | Competing anions present | Water type* | Halide Rejection Capacity |                    | Current (V) | Flow rate (L/min) | Water recovery (%) | pH      | Temp (°C) | Reference                   |
|-------------------|-------------------|--------------------------|-----------------------------|----------------------|--------------------------|-------------|---------------------------|--------------------|-------------|-------------------|--------------------|---------|-----------|-----------------------------|
|                   |                   |                          | Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (g/L) |                          |             | Br <sup>-</sup> (%)       | I <sup>-</sup> (%) |             |                   |                    |         |           |                             |
| 0.5-1             | 600               | Mark III to Mark IV type | 0.5–1.2                     | -                    | Yes                      | N           | 75-80                     | -                  | -           | 138000            | 90-94              | 6.5-7.3 | 25        | (Valero and Arbós, 2010)    |
| NS                | 250               | AR204-SZRA and CR67-HMR  | 0.185                       | -                    | Yes                      | N           | 72                        | -                  | 180-190     | 233.3             | 92-93              | 7.6     | 25        | (van der Hoek et al., 1998) |
| 12                | 2                 | DE81                     | -                           | 1.2 - 12.7           | No                       | S           | -                         | 92–97              | -           | -                 | -                  | -       | 25        | (Inoue and Kagoshima, 2000) |

\*Water type – N = Natural water, S= synthetic. '–' = data not available

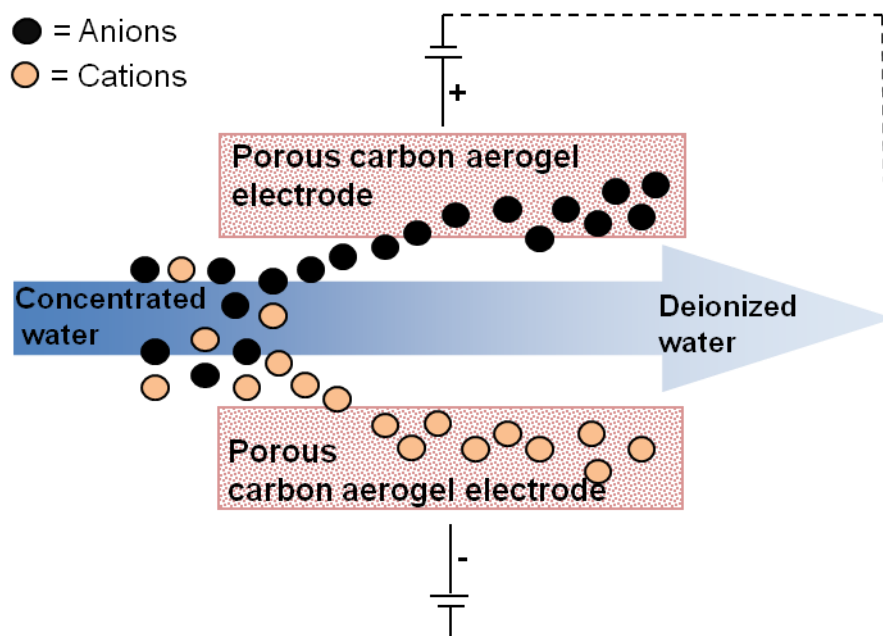
**Table 8** Parameters and bromide oxidation capacity of electrolysis methods (note iodide was not included in these studies).

| Br <sup>-</sup> (mg/L) | Competing anions present | Water type* | Br <sup>-</sup> oxidation capacity (%) | Flow rate (L/min) | Contact time (s) | Current               | pH   | Temp (°C) | Reference                    |
|------------------------|--------------------------|-------------|----------------------------------------|-------------------|------------------|-----------------------|------|-----------|------------------------------|
| 0.200                  | Yes                      | N           | >99                                    | 0.420             | 240              | 700 mA                | -    | -         | (Kimbrough and Suffet, 2002) |
| 0.461                  | Yes                      | S           | 79                                     | -                 | 39               | 14 mA/in <sup>2</sup> | ~7.5 | -         | (Bo, 2008)                   |

\*Water type – N = Natural water, S= synthetic. '–' = data not available.



**Figure 3** Schematic showing the capacitive deionisation (CDI) process.

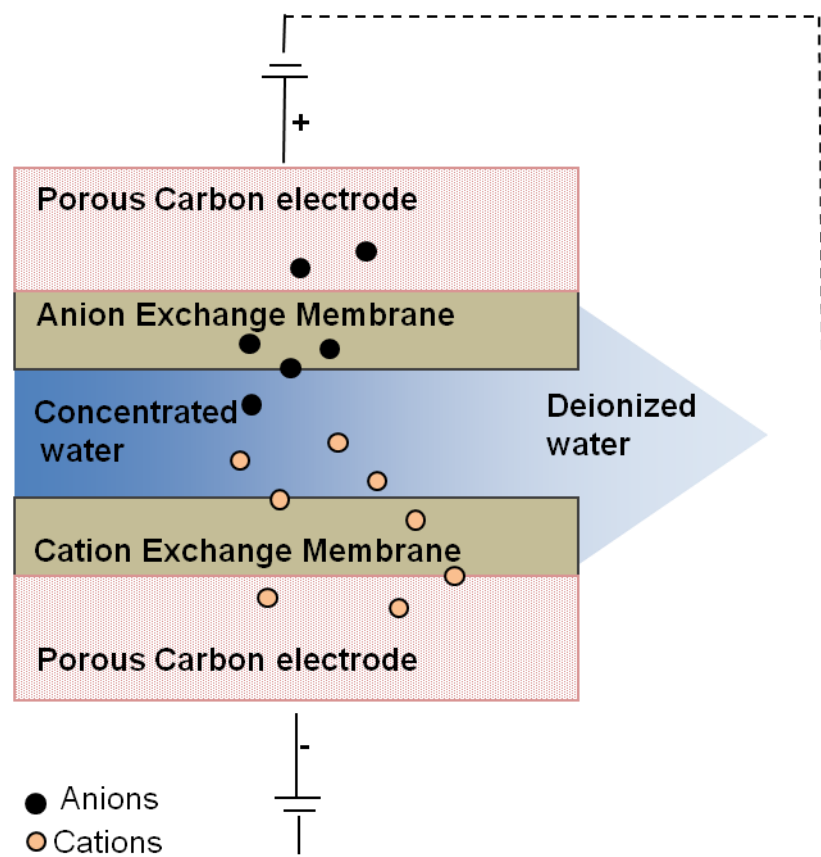


**Table 9** Parameters and halide removal capacity from CDI studies.

| Initial Anion Concentration |                       |                          |             | Halide Removal Capacity           |                           |                    |             |         |           |                               |
|-----------------------------|-----------------------|--------------------------|-------------|-----------------------------------|---------------------------|--------------------|-------------|---------|-----------|-------------------------------|
| Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (mg/L) | Competing anions present | Water type* | Br <sup>-</sup>                   | I <sup>-</sup>            | Flow rate (mL/min) | Current (V) | pH      | Temp (°C) | Reference                     |
| 399.5                       | -                     | No                       | S           | 0.13 and 0.18 mmol/g <sup>#</sup> | -                         | 100                | 1.4         | 7       | -         | (Gabelich et al., 2002)       |
| 79.9                        | 126.9                 | No                       | S           | 0.059 mmol/g <sup>#</sup>         | 0.063 mmol/g <sup>#</sup> | 10                 | 1.2         | -       | 25        | (Ying et al., 2002)           |
| 191.8                       | 304.56                | No                       | S           | 0.108 mmol/g <sup>#</sup>         | 0.154 mmol/g <sup>#</sup> | 10                 | 1.2         | -       | 25        | (Ying et al., 2002)           |
| 50.3                        | 49.5                  | No                       | S           | 50%                               | 69.7%                     | 250                | 1.3         |         | 23        | (Xu et al., 2008b)            |
| ~75                         | ~30                   | Yes                      | N           | 62.5%                             | 77%                       | 560                | 1.3         | 7.5-9.1 | 23        | (Xu et al., 2008b)            |
| 0.36                        | -                     | Yes                      | S           | 86.11%                            | -                         | 50                 | 1.3         | -       | -         | (Welgemoed and Schutte, 2005) |

\*Water type – N = Natural water, S= synthetic. ‘-’ = data not available. <sup>#</sup> Percent removals not available.

**Figure 4** Schematic showing the membrane capacitive deionisation (MCDI) process.



**Table 10** Summary of parameters for halide adsorption studies using LDHs.

| LDH Type                                           | Initial Anion Concentration |                       |             |                          | Halide Removal Capacity |                         |                      |          |          |         | Reference                           |
|----------------------------------------------------|-----------------------------|-----------------------|-------------|--------------------------|-------------------------|-------------------------|----------------------|----------|----------|---------|-------------------------------------|
|                                                    | Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (mg/L) | Water type* | Competing anions present | Br <sup>-</sup> (%)     | I <sup>-</sup> (%)      | Adsorbent dose (g/L) | Time (h) | pH       | Temp °C |                                     |
| Mg–Al-(NO <sub>3</sub> )                           | -                           | 342                   | N, WW       | Yes                      | -                       | 59                      | 20                   | 4        | 9.2      | 25      | (Kentjono et al., 2010)             |
| Zn-Al                                              | -                           | 330                   | S           | No                       | -                       | 60                      | -                    | -        | 7        | -       | (Thomas and Rajamathi, 2009)        |
| Mg-Al                                              | 100                         | -                     | S           | No                       | 27.5                    | -                       | 1                    | 24       | -        | 30      | (Lv and Li, 2007; Lv et al., 2008). |
| Mg-Al (molar ratio of 2)                           | -                           | 100                   | S           | No                       | -                       | 35                      | 1                    | -        | -        | 30      | (Lv and Li, 2007; Lv et al., 2008)  |
| Mg-Al (molar ratio of 3)                           | -                           | 100                   | S           | No                       | -                       | 88.4                    | 1                    | -        | -        | 30      | (Lv and Li, 2007; Lv et al., 2008)  |
| Mg-Al (molar ratio of 4, calcined at 500°C)        | 100                         | 100                   | S           | No                       | 94                      | 96.1                    | 1                    | 24       | -        | 30      | (Lv and Li, 2007; Lv et al., 2008)  |
| Cu <sub>6</sub> Al <sub>2</sub> (OH) <sub>18</sub> | -                           | 1                     | S           | Yes                      | -                       | 9600 mL/g <sup>#</sup>  | 10                   | 24       | -        | 25      | (Pless et al., 2007)                |
| Cu <sub>6</sub> Cr <sub>2</sub> (OH) <sub>18</sub> | -                           | 1                     | S           | Yes                      | -                       | 4,200 mL/g <sup>#</sup> | 10                   | 24       | -        | 25      | (Pless et al., 2007)                |
| Cu <sub>6</sub> Ga <sub>2</sub> (OH) <sub>18</sub> | -                           | 1                     | S           | Yes                      | -                       | 1,700 mL/g <sup>#</sup> | 10                   | 24       | -        | 25      | (Pless et al., 2007)                |
| Mg-Fe                                              | 0.2                         | -                     | N           | Yes                      | 60                      | -                       | 10                   | 0.16     | ~7-8     | -       | (Echigo et al., 2007)               |
| Mg-Al-Fe                                           | 0.2                         | -                     | N           | Yes                      | 60                      | -                       | 10                   | 0.16     | ~6.5-7.5 | -       | (Echigo et al., 2007)               |
| Zn-Al                                              | -                           | 1269                  | S           | Yes                      | -                       | 14                      | 10                   | 48       | 6        | -       | (Kaufhold et al., 2007)             |

\*Water type – N = Natural water, S= synthetic, WW = waste water. ‘-’ = data not available. <sup>#</sup>Adsorption coefficient (Kd) reported, percent removals not available.

**Table 11** Summary of halide adsorption studies using sol-gel double hydroxides (note, literature on iodide adsorption was not available).

| Type                                                                              | Initial Anion Concentration |             | Competing anions present | Halide Removal Capacity |                      | Time (h) | pH  | Temp (°C) | Reference             |
|-----------------------------------------------------------------------------------|-----------------------------|-------------|--------------------------|-------------------------|----------------------|----------|-----|-----------|-----------------------|
|                                                                                   | Br <sup>-</sup> (mg/L)      | Water type* |                          | Br <sup>-</sup> (%)     | Adsorbent dose (g/L) |          |     |           |                       |
| Fe <sub>2</sub> O <sub>3</sub> ·Al <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O | 120                         | S           | Yes                      | 80                      | 2                    | 48       | -   | <u>22</u> | (Chubar et al., 2005) |
| Mg–Al-(3a-1)–NaC                                                                  | 198.2                       | S           | Yes                      | 75.7                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | 13.1                    | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3a-1)–N                                                                    | 198.2                       | S           | Yes                      | 66.6                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | 77.7                    | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3a-1)–KC                                                                   | 198.2                       | S           | Yes                      | 78.7                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | -                       | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3b)–NaC                                                                    | 198.2                       | S           | Yes                      | 13.1                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | 12.1                    | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3b)–N                                                                      | 198.2                       | S           | Yes                      | 14.1                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | 15.1                    | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3b)–KC                                                                     | 198.2                       | S           | Yes                      | 13.1                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | 12.1                    | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3d-120)–NaC                                                                | 198.2                       | S           | Yes                      | 12.1                    | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   | 198.2                       | S           | Yes                      | 11.1                    | 2                    |          | 8.5 | <u>22</u> |                       |
| Mg–Al-(3d-160)–N                                                                  | 198.2                       | S           | Yes                      | 9                       | 2                    | -        | 4.5 | <u>22</u> | (Chubar, 2011)        |
|                                                                                   |                             |             |                          | 13.1                    | 2                    |          | 8.5 | <u>22</u> |                       |

\*Water type –S= synthetic. ‘-’ = data not available.

**Table 12** Iodide adsorption capacity of coal and activated carbon (note, studies on bromide adsorption were not available).

| Type                   | Initial Iodide Concentration |             |                          | Iodide Removal Capacity |                      |    | Time (h) | pH | Temp °C | Reference               |
|------------------------|------------------------------|-------------|--------------------------|-------------------------|----------------------|----|----------|----|---------|-------------------------|
|                        | I <sup>-</sup> (mg/L)        | Water type* | Competing anions present | I <sup>-</sup> (%)      | Adsorbent dose (g/L) |    |          |    |         |                         |
| Lignite                | 1.3                          | S           | Yes                      | 34                      | 1-20                 | 24 | 3.9      | 25 |         | (Balsley et al., 1998)  |
| Sub-bituminous coal    | 1.3                          | S           | Yes                      | 46                      | 1-20                 | 24 | 6.2      | 25 |         | (Balsley et al., 1998)  |
| Merck activated carbon | 1269                         | S           | No                       | 15                      | 10                   | 48 | 7        | -  |         | (Kaufhold et al., 2007) |
|                        | 1269                         | S           | No                       | 13                      | 10                   | 48 | 10       | -  |         | (Kaufhold et al., 2007) |
|                        | 1269                         | S           | Yes                      | 21                      | 10                   | 48 | 7        | -  |         | (Kaufhold et al., 2007) |
|                        | 1269                         | S           | Yes                      | 15                      | 10                   | 48 | 10       | -  |         | (Kaufhold et al., 2007) |

\*Water type –S= synthetic. ‘–’ = data not available.

**Table 13** Summary of studies investigating silver impregnated activated carbons' halide adsorption capacity. Note, studies specifically on bromide adsorption were not available.

| Initial Iodide concentration |                     |             |                          | Iodide removal capacity |                      |             |    |      |                        |
|------------------------------|---------------------|-------------|--------------------------|-------------------------|----------------------|-------------|----|------|------------------------|
| AgAC Type                    | I <sup>-</sup> (mM) | Water type* | Competing anions present | I <sup>-</sup> (μmol/g) | Adsorbent dose (g/L) | Time (days) | pH | temp | Reference              |
| AgAC (1.05 wt % of Ag)       | 0.008-1.58          | S           | No                       | 153.7–143.6             | 1                    | 7           | 5  | -    | (Hoskins et al., 2002) |
|                              | 0.008-1.58          | S           | No                       | 120.4–103.9             | 1                    | 7           | 7  | -    |                        |
|                              | 0.008-1.58          | S           | No                       | 93.4–83.0               | 1                    | 7           | 8  | -    |                        |
| AgAC (0.05 wt % of Ag)       | 0.008-1.58          | S           | No                       | 50.0–30.7               | 1                    | 7           | 5  | -    | (Hoskins et al., 2002) |
|                              | 0.008-1.58          | S           | No                       | 8.98–3.82               | 1                    | 7           | 7  | -    |                        |
|                              | 0.008-1.58          | S           | No                       | 3.93-3.10               | 1                    | 7           | 8  | -    |                        |
| AgAC (20 wt % of Ag)         | 1000                | S           | Yes                      | 98 %^                   | -                    | -           | -  | 20   | (Ho and Kraus, 1981)   |

\*Water type –S= synthetic. '–' = data not available. ^Adsorption in μmol/g was not reported, therefore a percent removal shown.

**Table 14** Halide adsorption by silver doped carbon aerogels under specific conditions.

| Type                             | Initial Anion Concentration |                       | Water type* | Competing anions present | Halide Removal Capacity  |                         | Adsorbent dose (g/L) | pH     | Flow rate (mL/min) | Temp (°C) | Reference                                                              |
|----------------------------------|-----------------------------|-----------------------|-------------|--------------------------|--------------------------|-------------------------|----------------------|--------|--------------------|-----------|------------------------------------------------------------------------|
|                                  | Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (mg/L) |             |                          | Br <sup>-</sup> (μmol/g) | I <sup>-</sup> (μmol/g) |                      |        |                    |           |                                                                        |
| Silver-doped aerogels            | 0.15                        | 0.15                  | S           | Yes                      | 3.01                     | 1.98                    | 3                    | 6.5- 7 | 1.5                | 25        | (Sánchez-Polo et al., 2006a, 2007a; Sánchez-Polo et al., 2006b, 2007b) |
| Carbonized silver-doped aerogels | 0.15                        | 0.15                  | S           | No                       | 4.68                     | 3.71                    | 3                    | 7      | 1.5                | 25        | (Sánchez-Polo et al., 2006a, 2007a; Sánchez-Polo et al., 2006b, 2007b) |
| Activated silver-doped aerogels  | 0.15                        | 0.15                  | S           | No                       | 5.78                     | 5.03                    | 3                    | 7      | 1.5                | 25        | (Sánchez-Polo et al., 2006a, 2007a; Sánchez-Polo et al., 2006b, 2007b) |

\*Water type –S= synthetic.



**Table 15** The bromide adsorption capacity of MIEX® resin is shown. Note, studies of iodide adsorption using MIEX are not yet available.

| Adsorbent/coagulant used | Initial Bromide Concentration |             | Competing anions present          | Bromide removal capacity |                   | Alum dose (mg/L) | Time (h) | pH  | Temp. (°C) | Reference                  |
|--------------------------|-------------------------------|-------------|-----------------------------------|--------------------------|-------------------|------------------|----------|-----|------------|----------------------------|
|                          | Br <sup>-</sup> (mg/L)        | Water type* |                                   | Br <sup>-</sup> (%)      | MIEX® Dose (mL/L) |                  |          |     |            |                            |
| MIEX®                    | 0.100                         | S           | Yes (NaCl and DOC)                | 35                       | 1                 | -                | 1        | 8   | 22         | (Hsu and Singer, 2010)     |
| MIEX®                    | 0.100                         | S           | Yes (NaCl and CaCO <sub>3</sub> ) | 29                       | 1                 | -                | 1        | 8   | 22         | (Hsu and Singer, 2010)     |
| MIEX®                    | 0.900                         | N           | Yes                               | 64                       | 8                 | -                | 1        | 8.1 | 15         | (Johnson and Singer, 2004) |
| Alum                     | 0.076                         | N           | Yes                               | 4                        | -                 | 60               | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| MIEX®                    | 0.076                         | N           | Yes                               | 28                       | 5                 | -                | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| MIEX® + Alum             | 0.076                         | N           | Yes                               | 26                       | 5                 | 16               | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| Alum                     | 0.083                         | N           | Yes                               | -2                       | -                 | 60               | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| MIEX®                    | 0.083                         | N           | Yes                               | 45                       | 2                 | -                | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| MIEX® + Alum             | 0.083                         | N           | Yes                               | 49                       | 2                 | 5                | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| Alum                     | 0.240                         | N           | Yes                               | 0                        | -                 | 60               | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| MIEX®                    | 0.240                         | N           | Yes                               | 17                       | 2                 | -                | 1        | 8   | 20         | (Boyer and Singer, 2005)   |
| MIEX® + Alum             | 0.240                         | N           | Yes                               | 21                       | 2                 | 4                | 1        | 8   | 20         | (Boyer and Singer, 2005)   |

|              |             |   |                                      |       |       |    |     |         |       |                          |
|--------------|-------------|---|--------------------------------------|-------|-------|----|-----|---------|-------|--------------------------|
| Alum         | 0.540       | N | Yes                                  | 2     | -     | 60 | 1   | 8       | 20    | (Boyer and Singer, 2005) |
| MIEX®        | 0.540       | N | Yes                                  | 15    | 4     | -  | 1   | 8       | 20    | (Boyer and Singer, 2005) |
| MIEX® + Alum | 0.540       | N | Yes                                  | 13    | 4     | 20 | 1   | 8       | 20    | (Boyer and Singer, 2005) |
| MIEX®        | 0.167-0.218 | N | Yes                                  | 20-28 | 0.224 | -  | 1   | 6.6-6.9 | 17-26 | (Boyer and Singer, 2006) |
| MIEX® + Alum | 0.0381      | N | Yes<br>(155 mg/L CaCO <sub>3</sub> ) | -0.7  | 6     | 12 | 1   | 8.2     | 25    | (Singer and Bilyk, 2002) |
| MIEX® + Alum | 0.0945      | N | Yes<br>(91 mg/L CaCO <sub>3</sub> )  | 43    | 8     | 45 | 1   | 7.3     | 25    | (Singer and Bilyk, 2002) |
| MIEX® + Alum | 0.163       | N | Yes<br>(20 mg/L CaCO <sub>3</sub> )  | 94    | 8     | 10 | 1   | 7.2     | 25    | (Singer and Bilyk, 2002) |
| MIEX® + Alum | 0.0137      | N | Yes<br>(4 mg/L CaCO <sub>3</sub> )   | BDL   | 2     | 10 | 1   | 6.1     | 25    | (Singer and Bilyk, 2002) |
| MIEX®        | 0.150       | N | Yes                                  | 83    | 8     | -  | 0.5 | 7       | 26    | (Humbert et al., 2005)   |

\*Water type – N = Natural water, S= synthetic. BDL = below detection limit. ‘-’ = data not available.

**Table 16** Commercially available water treatment resins – parameters for use and subsequent halide adsorption efficiency.

| Resin Type        | Initial Anion Concentration |                      |             |                          | Halide Removal Capacity |                    |                       |                  |    |           | Reference                                       |
|-------------------|-----------------------------|----------------------|-------------|--------------------------|-------------------------|--------------------|-----------------------|------------------|----|-----------|-------------------------------------------------|
|                   | Br <sup>-</sup> (mg/L)      | I <sup>-</sup> (g/L) | Water type* | Competing anions present | Br <sup>-</sup> (%)     | I <sup>-</sup> (%) | Adsorbent dose (g/L)^ | Contact Time (h) | pH | Temp (°C) |                                                 |
| Ionac A-641       | 0.300                       | -                    | S           | Yes                      | 76                      | -                  | 2 mL/L                | 5                | 8  | 22        | (Hsu and Singer, 2010)                          |
| Amberlite IRA910  | 0.300                       | -                    | S           | Yes                      | 73                      | -                  | 2 mL/L                | 5                | 8  | 22        | (Hsu and Singer, 2010)                          |
| Duolite A-161     | 159.8                       | -                    | S           | No                       | 56                      | -                  | 4                     | 3                | -  | 27        | (Lokhande et al., 2009b; Singare et al., 2010)  |
| Duolite A-162     | 7990                        | -                    | S           | No                       | **Log Kd 5.48           | -                  | 4                     | 3                | -  | 25        | (Singare et al., 2010)                          |
| Amberlite IRA-400 | 7990                        | 12.7                 | S           | No                       | **Log Kd 3.80           | **Log Kd 4.50      | 4                     | 3                | -  | 32.0      | (Singare and Lokhande, 2009)                    |
| Indion-850        | 2876.4                      | 5.1                  | S           | Yes                      | 66.6                    | 57.5               | 10                    | 4                | -  | 25        | (Lokhande et al., 2007)                         |
| Duolite A-116     | -                           | 0.51                 | S           | No                       | -                       | 50                 | 5                     | 3                | -  | 25        | (Lokhande et al., 2008)                         |
| Duolite A 101D    | 399.5                       | -                    | S           | No                       | 89                      | -                  | 2.5                   | 3                | -  | 25        | (Lokhande et al., 2010) (Lokhande et al., 2010) |
|                   | 399.5                       | -                    | S           | No                       | 96                      | -                  | 2.5                   | 3                | -  | 45        |                                                 |
| Duolite A 102D    | 399.5                       | -                    | S           | No                       | 86                      | -                  | 2.5                   | 3                | -  | 25        | (Lokhande et al., 2010) (Lokhande et al., 2010) |
|                   | 399.5                       | -                    | S           | No                       | 89                      | -                  | 2.5                   | 3                | -  | 45        |                                                 |
| Duolite A-113     | 3403.7                      | 5.3                  | S           | No                       | 54                      | 45.3               | 2.5                   | 4                | -  | 25        | (Lokhande et al., 2009a)                        |

|                    |       |   |   |     |      |   |        |     |         |   |                        |
|--------------------|-------|---|---|-----|------|---|--------|-----|---------|---|------------------------|
| DOWEX-MARATHON 11s | 0.110 | - | N | Yes | 87   | - | 8 mL/L | 0.5 | 7       | - | (Humbert et al., 2005) |
| DOWEX-MARATHON MSA | 0.110 | - | N | Yes | 90   | - | 8 mL/L | 0.5 | 7       | - | (Humbert et al., 2005) |
| Amberlite IRA-938  | 0.150 | - | N | Yes | 87   | - | 8 mL/L | 0.5 | 7       | - | (Humbert et al., 2005) |
| Diaion SA10A       | 0.204 | - | N | Yes | 73.5 | - | -      | 10  | 6.5-7.5 | - | (Echigo et al., 2007)  |

\*Water type – N = Natural water, S= synthetic. \*\*Percent removals were not reported, therefore Kd's have been included here. ^Units are g/L unless otherwise specified. '–' = data not available.

**Table 17** Commercially available water treatment resins and their halide removal efficiencies.

| Resin              | Uses                                                                                                                        | Type                                                   | Matrix                                 | Functional groups                                                  | Br <sup>-</sup> (%) | I <sup>-</sup> (%) | Reference                                      |
|--------------------|-----------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------|----------------------------------------|--------------------------------------------------------------------|---------------------|--------------------|------------------------------------------------|
| Amberlite IRA-400  | Demineralization, electroplating                                                                                            | Type 1 strong base anion exchange resin                | Cross linked polystyrene               | Quaternary amine                                                   | 87                  | -                  | (Singare and Lokhande, 2009)                   |
| Amberlite IRA910   | Treatment of highly saline solutions, sugar industry use in mixed bed polisher                                              | Type 2 strong base macroreticular anion exchange resin | Macroreticular crosslinked polystyrene | Dimethyl ethanol amine                                             | 73                  | -                  | (Hsu and Singer, 2010)                         |
| Amberlite IRA-938  | Deionization of water and removal of organics                                                                               | Strong base macroporous anion exchange resin           | Styrene                                | Quaternary amine                                                   | 87                  | -                  | (Humbert et al., 2005)                         |
| Diaion SA10A       | Desalination                                                                                                                | Strong base anion exchange resin                       | Gel, porous styrenic polymer           | Quaternary amine                                                   | 73.5                | -                  | (Echigo et al., 2007)                          |
| DOWEX™ 1           | Removal of uranium, perchlorate, hexavalent chromium and iodide. Purification of radiochemicals.                            | Type 1 strong base anion exchange resin                | Styrene-divinylbenzene copolymer, gel  | Quaternary amine                                                   | -                   | >90                | (DOW, 2011)                                    |
| DOWEX-MARATHON 11s | Multi-bed demineraliser - recommended for treating waters that contain naturally occurring organic matter                   | Type 1 strong base anion exchange resin                | Styrene-divinylbenzene copolymer       | Acrylic                                                            | 87                  | -                  | (Humbert et al., 2005)                         |
| DOWEX-MARATHON MSA | Demineralization of high organic matter waters, catalysis, and the extraction of heavy metals in the form of complex anions | Type 1 macroporous strong base anion exchange resin    | Styrene-divinylbenzene copolymer       | Quaternary amine                                                   | 90                  | -                  | (Humbert et al., 2005)                         |
| Duolite A-113      | Water demineralisation                                                                                                      | Type 1 strong base anion exchange resin                | Crosslinked polystyrene                | Quaternary amine (-N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> ) | 54                  | 45.3               | (Lokhande et al., 2009a)                       |
| Duolite A-161      | Production of ultrapure water                                                                                               | Type 1 macroporous strong base anion exchange resin    | Styrene-divinylbenzene copolymer       | Quaternary amine (-N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> ) | 56.3                | -                  | (Lokhande et al., 2009b; Singare et al., 2010) |
| Ionac A-641        | Demineralising high organic matter waters and catalysis, extraction of heavy metals.                                        | Strong base anion exchange resin                       | Polystyrene                            | Quaternary amine                                                   | 76                  | -                  | (Hsu and Singer, 2010)                         |
| Indion-850         | Two stage deionisation                                                                                                      | Macroporous weak base anion exchange resin             | Styrene-divinylbenzene copolymer       | Tertiary and quaternary amine groups                               | 66.6                | 57.5               | (Lokhande et al., 2007)                        |

**Table 18** Patented anion exchange resins with halide removal capacity.

| Patent Number | Resin Type                       | Unmodified Resin*                                                      | Functional group of final (patented) resin | Uses                                                       | Reference         |
|---------------|----------------------------------|------------------------------------------------------------------------|--------------------------------------------|------------------------------------------------------------|-------------------|
| 7588690       | Macroporous resin-               | Purolite® CT275, Purolite® CT276                                       | Ag                                         | Concentrating iodide from solvent                          | (Tsao, 2009)      |
| 5624567       | Strong-base anion exchange resin | -                                                                      | Trialkyl amine                             | Iodide removal from aqueous solutions                      | (Colombo, 1997)   |
| 6379556       | Strong-base anion exchange resin | Amberlite IRA-400<br>Amberlyst A-21.                                   | Quaternary amine                           | Recovery of iodide from chemical process wastewater        | (Venkat, 2002)    |
| 5366636       | Chelating resin (gel)            | Chelex 100<br>Chelex 20                                                | Ag                                         | Disinfection and halide removal                            | (Marchin, 1994)   |
| 3050369       | Strong-base anion exchange resin | Dowex 1<br>Dowex 2<br>Dowexx 11<br>Dowex 21A                           | Quaternary amine                           | Recovery of iodide from brines                             | (Mills, 1962)     |
| 2261021       | Anion exchange resin             | -                                                                      | Aryl/methylene                             | Recovery of halogens from fluids                           | (Findlay, 1941)   |
| 3352641       | Strong-base anion exchange resin | -                                                                      | -                                          | Iodide removal from brines and natural gas well waters     | (Hiromichi, 1967) |
| 5220058       | Macroreticular resin             | Mesoporous or macroporous                                              | Ag, Pd, Hg                                 | Removal of iodide impurities from acidic aqueous solutions | (Fish, 1993)      |
| 2945746       | Strong-base anion exchange resin | -                                                                      | Quaternary amine                           | Removal of iodide from natural brines                      | (Glenn, 1960)     |
| 4451375       | Strong-base anion exchange resin | Resins bearing picolylamine functionality (DOW XFS-43084 and xfs-4195) | Picolylamine ion                           | Iodide adsorption from acidic aqueous solutions            | (Grinstead, 1984) |

\*Resin from which patented (modified) resin was made.

**Table 19** Summary of data on bromide adsorption during aluminium coagulation. Note, data on iodide adsorption using this technique was not available.

| Initial bromide concentration |             |                                                  | Bromide removal capacity |                       |          |    |                                     |
|-------------------------------|-------------|--------------------------------------------------|--------------------------|-----------------------|----------|----|-------------------------------------|
| Br <sup>-</sup> (mg/L)        | Water type* | Competing anions present                         | Br <sup>-</sup> (%)      | Adsorbent dose (mg/L) | Time (h) | pH | Reference                           |
| 2.0                           | S           | No                                               | 30.4                     | 7                     | 2 ½      | 6  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | No                                               | 98.8                     | 7                     | 2 ½      |    |                                     |
| 0.2                           | S           | Yes                                              | 98.4                     | 15                    | 2 ½      | 6  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | (6 mg/L humic acid)                              | 73.2                     | 3                     | 2 ½      | 6  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | N           | Yes                                              | 87.0                     | 15                    | 2 ½      | 6  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | N           | Yes                                              | 74.5                     | 15                    | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | N           | Yes                                              | 62.1                     | 15                    | 2 ½      | 8  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | N           | Yes                                              | 62.3                     | 7                     | 2 ½      | 6  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | N           | Yes                                              | 55.9                     | 7                     | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | N           | Yes                                              | 43.5                     | 7                     | 2 ½      | 8  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | Yes                                              | 94.5                     | 15                    | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | Yes<br>(250 mg/L HCO <sub>3</sub> <sup>-</sup> ) | 83.8                     | 15                    | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | Yes<br>(250 mg/L SO <sub>4</sub> <sup>2-</sup> ) | 74.5                     | 15                    | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | Yes<br>(250 mg/L Cl <sup>-</sup> )               | 80.7                     | 15                    | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |
| 0.2                           | S           | Yes<br>(10 mg/L NO <sub>3</sub> <sup>-</sup> )   | 87.0                     | 15                    | 2 ½      | 7  | (Ge et al., 2007; Ge and Zhu, 2008) |

\*Water type – N = Natural water, S= synthetic.

**Table 20** The iodide adsorption capacity of soils. Note, data on bromide adsorption onto soils was not available.

| Type              | Initial Iodide concentration |             |                          | Iodide removal capacity |                      | Time (h) | pH   | Temp (°C) | Reference                |
|-------------------|------------------------------|-------------|--------------------------|-------------------------|----------------------|----------|------|-----------|--------------------------|
|                   | I <sup>-</sup> (mg/L)        | Water type* | Competing anions present | I <sup>-</sup> (%)      | Adsorbent dose (g/L) |          |      |           |                          |
| Udic Ferrisols    | 4                            | S           | No                       | 57.5                    | 100                  | 40       | 5.05 | 25        | (Dai et al., 2009)       |
| Perudic Ferrisols | 4                            | S           | No                       | 13.2                    | 100                  | 40       | 5.45 | 25        | (Dai et al., 2009)       |
| Udic Isohumisols  | 4                            | S           | No                       | 12.8                    | 100                  | 40       | 7.95 | 25        | (Dai et al., 2009)       |
| Usdic Luvisols    | 4                            | S           | No                       | 11                      | 100                  | 40       | 7.85 | 25        | (Dai et al., 2009)       |
| Orthic Aridisols  | 4                            | S           | No                       | 10.9                    | 100                  | 40       | 8.51 | 25        | (Dai et al., 2009)       |
| Field soil        | -                            | S           | No                       | >90                     | 100                  | 24       | 5.4  | 23        | (Muramatsu et al., 1990) |
| Paddy soil        | -                            | S           | No                       | >90                     | 100                  | 24       | 5.7  | 23        | (Muramatsu et al., 1990) |
| Sandy soil        | -                            | S           | No                       | >70                     | 100                  | 24       | 5.5  | 23        | (Muramatsu et al., 1990) |
| Japanese Andosols | -                            | S           | No                       | >99                     | 100                  | 48       | 4    | 23        | (Yoshida et al., 1992)   |
| Japanese Kanuma   | -                            | S           | No                       | >55                     | 100                  | 48       | 4    | 23        | (Yoshida et al., 1992)   |

\*Water type – S= synthetic. ‘-’ = data not available.



**Table 21** Qualitative comparison of bromide and iodide removal techniques for use in drinking water treatment.

| Technology class | Treatment method             | Applicability to full-scale drinking water treatment | Br <sup>-</sup> removal (%)                        | I <sup>-</sup> removal (%)                         | Halide removal in drinking water matrix | Cost | Available on Commercial scale for water treatment |
|------------------|------------------------------|------------------------------------------------------|----------------------------------------------------|----------------------------------------------------|-----------------------------------------|------|---------------------------------------------------|
| Membrane         | RO                           | H                                                    | 90-99.8                                            | 80-92                                              | H                                       | H    | P                                                 |
|                  | NF                           | H                                                    | 93-97                                              | 55-91                                              | H                                       | H    | P                                                 |
|                  | ED/EDR                       | H                                                    | 72-80                                              | 92-97                                              | H                                       | H    | P                                                 |
| Electrochemical  | Electrolysis                 | L                                                    | 79-99                                              | -                                                  | M                                       | H    | N/A                                               |
|                  | CDI                          | ML                                                   | 50-86.1                                            | 69.7-77                                            | M                                       | H    | FD                                                |
| Adsorption       | LDH                          | MH                                                   | 27-94                                              | 14-96                                              | M                                       | L    | FD                                                |
|                  | Sol-gel double hydrous oxide | MH                                                   | 9-80                                               | -                                                  | M                                       | ML   | FD                                                |
|                  | Coal and Activated Carbon    | M                                                    | -                                                  | 13-46                                              | L                                       | L    | P*                                                |
|                  | AgAC                         | U                                                    | -                                                  | -                                                  | U                                       | M    | FD                                                |
|                  | Silver doped carbon aerogels |                                                      | 3.01-5.78 $\mu\text{mol/g}$ adsorbent <sup>#</sup> | 1.98-5.03 $\mu\text{mol/g}$ adsorbent <sup>#</sup> | U                                       | MH   | FD                                                |
|                  | MIEX                         | M                                                    | 2-83                                               | -                                                  | L                                       | MH   | P*                                                |
|                  | Other resins                 | M                                                    |                                                    |                                                    | M                                       | MH   | P*                                                |
|                  | Aluminium coagulation        | M                                                    | 34-98                                              | -                                                  | L                                       | L    | FD                                                |
|                  | Soils                        | M                                                    | -                                                  | 11-99                                              | U                                       | L    | FD                                                |

H- High, MH- medium/high, M-Moderate, ML- medium/low, L-Low, N/A- Not applicable, FD- further development needed for bromide and iodide reduction application, P- proven technology in drinking water treatment, U- unknown

\*Not used specifically for halide removal, in practice they are used for NOM removal during drinking water treatment. <sup>#</sup>Percent removals were not available.