Rejection of Bromide and Bromate Ions by a Ceramic Membrane

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Received: February 28, 2012

Accepted in revised form: July 28, 2012

Abstract

Effects of pH and the addition of calcium chloride (CaCl_2) on bromate (BrO_3^-) and bromide (Br^-) rejection by a ceramic membrane were investigated. Rejection of both ions increased with pH. At pH 8, the rejection of BrO_3^- and Br^- was 68% and 63%, respectively. Donnan exclusion appears to play an important role in determining rejection of BrO_3^- and Br^- . In the presence of CaCl_2 , rejection of BrO_3^- and Br^- ions was greatly reduced, confirming the importance of electrostatic interactions in determining rejection of BrO_3^- and Br^- . The effect of Ca^{2+} is so pronounced that in most natural waters, rejection of both BrO_3^- and Br^- by the membrane would be extremely small.

Key words: bromate; bromide; ceramic membrane; rejection

Introduction

A MAJOR CONCERN in the treatment of drinking waters using ozone is the formation of bromate (BrO_3^-). The bromide ion (Br^-) is found naturally in many water supplies, and the ozonation of water containing Br^- leads to the formation of BrO_3^- , a potential human carcinogen. BrO_3^- is regulated by the U.S. Environmental Protection Agency (U.S. EPA, 1998) and the Ministry of the Environment, Canada (Ministry of the Environment, Canada, 2002). The typical means of controlling BrO_3^- formation are to adjust the pH, add ammonia, or reduce the ozone dosage (Pinkernell and von Gunten, 2001). A reduction in the ozone dosage can have a negative impact on pathogen inactivation (Gerba *et al.*, 2003) or the control of disinfection by-product formation during chlorination (Singer, 1994). Adjusting the pH or adding ammonia can be expensive as well as add to the total dissolved solids of the finished water. The use of activated carbon (Sanchez-Polo *et al.*, 2006) and other techniques for BrO_3^- removal, such as UV photocatalysis (Zhang *et al.*, 2009) and biological reduction (Matos *et al.*, 2008), has been investigated. Listiari *et al.* (2010) discussed the limitations of each of these treatment methods, and they concluded that existing BrO_3^- removal techniques are not cost effective and there is a need to develop new treatment technologies.

Reverse osmosis (RO) can remove Br^- and BrO_3^- (Gyparakis and Diamadopoulos, 2007), but it is an expensive process, as membrane fluxes are low and high operating pressures are needed. Listiari *et al.* (2010) re-

ported that polyamide nanofiltration (NF) membranes are not very effective at Br^- or BrO_3^- removal. The removal of Br^- and BrO_3^- ions by the NF membranes tested ranged from 1% to 7% and from 6% to 19%, respectively.

Ceramic membrane filtration has the potential to reduce BrO_3^- levels in drinking water. The surface of ceramic membranes is typically charged, as the surface of metal oxides from which they are made are usually charged, due to the amphoteric nature of the surface hydroxyl groups on the metal oxide surface (Tsuru, 2001). Previous studies have shown that due to their surface charge, ceramic ultrafiltration (UF) or NF membranes can reject ions, even though the pore size of the membrane is much larger than the size of the ions (Combe *et al.*, 1997; Fievet *et al.*, 2002; Labbez *et al.*, 2003; Skluzacek *et al.*, 2006). Charge effects are largely responsible for the rejection of the ions. If a charged membrane is in contact with an electrolyte solution, electrostatic repulsion will result in a lower concentration of ions with the same charge as the membrane (referred to as co-ions) near the membrane surface and within the membrane pores. On the other hand, counterions, which have an opposite charge to that of the membrane surface, are attracted to the membrane, and the concentration of these ions within the membrane and at its surface is higher than that in bulk solution. Models have been developed that describe the rejection of ions by charged membranes based on the Donnan, steric, and dielectric exclusions at the interfaces (Escoda *et al.*, 2011). In these models, the extended Nernst-Planck equation is used to describe transport within the pores of the membrane (Escoda *et al.*, 2011).

Due to their ability to reject ions, ceramic UF membranes could potentially be used to reduce BrO_3^- levels in drinking water and because of their greater permeability, UF membranes could be operated at higher membrane fluxes and/or

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lower transmembrane pressures than NF or RO membranes (U.S. EPA, 2005). This would result in considerable savings in operating and/or capital costs. In this study, we have measured the rejection of Br^- and BrO_3^- by a ceramic UF membrane. Rejection by the membrane was studied at various pH. The influence of the addition of calcium chloride (CaCl_2) was also studied, as the presence of Ca^{2+} is likely to affect the rejection of Br^- or BrO_3^- , as it will interact more strongly with the membrane than monovalent ions, such as Na^+ . In addition, since it is a divalent ion, Ca^{2+} will have a greater shielding effect than monovalent ions (Labbez *et al.*, 2003).

Materials and Methods

Experimental setup

The apparatus employed is shown in Fig. 1 and is described in greater detail in Moslemi *et al.* (2011). The system was operated at a transmembrane pressure of 138 kPa (20 psi). The average permeate flux was 6.5 mL/min. The cross-flow was 200 mL/min. The bleed flow rate was held at 5.0 mL/min. In order to duplicate the hydrodynamic conditions used in the hybrid ozonation-membrane filtration experiments (Moslemi *et al.*, 2011), oxygen was injected into the water stream flowing into the retentate loop through a Tee fitting at a flow rate of 50 mL/min. The temperature of the water inside the system was kept constant at $20^\circ\text{C} \pm 0.1^\circ\text{C}$. Tubular ceramic ultrafiltration membranes (TAMI North America) with molecular weight cutoffs of 5 kDa were used in these experiments. These membranes have a titania support and a filtration layer. The membrane had three channels and a total filtering surface area of 41.2 cm^2 .

Analytical methods and reagents

Br^- and BrO_3^- concentrations in the retentate and permeate streams were measured by high-performance liquid chromatography (Moslemi *et al.*, 2011). pH was measured using a pH meter (pHTestr 30, Eutech Instruments). Milli-Q water with a resistivity of greater than $18\text{ M}\Omega$ was used to prepare all solutions and reagents. In order to obtain the desired concentrations of Br^- and BrO_3^- ions in the feed water, Milli-Q water was spiked with appropriate amounts of sodium bromate (NaBrO_3 , 99.7 + %, Fisher Scientific) or sodium bromide

(NaBr , 99.995% metals basis, Fluka). Phosphoric acid (H_3PO_4) (99.99%, Sigma-Aldrich) and/or sodium hydroxide (NaOH) (98.0 + %, Fluka) was used to adjust the water pH.

The data reported are averages of the results obtained in triplicate experiments, and the error bars represent the standard deviations of the results for the triplicate experiments.

Accumulation of ions in the retentate loop

Since there is no reaction, the accumulation in the retentate loop can be calculated using the mass balance equation:

$$\text{Accumulation} = \text{Input} - \text{Output} \quad (1)$$

Our experimental results indicated that the adsorption of BrO_3^- and Br^- by the system at the various pHs examined (3.0, 6.0, and 8.0) was negligible (less than 1%). Thus, the mass balance equation can be written as follows:

$$V \frac{dC_R}{dt} = Q_{in}C_{in} - Q_P C_P - Q_B C_R, \quad (2)$$

where

V = total volume of water in the system (1500 mL)

C_{in} = concentration of the ion in the inflow into the system (μM)

Q_{in} = inlet flow rate (mL/min)

Q_P = permeate flow rate (mL/min)

Q_B = bleed flow rate (mL/min)

t = time (min)

After rearrangement, Equation (2) can be written as follows:

$$dC_R = \frac{(Q_{in}C_{in} - Q_P C_P - Q_B C_R)dt}{V} \quad (3)$$

The amount of BrO_3^- and Br^- that accumulated in the system after 180 min can be calculated by integrating both sides of Equation (2) over the course of the experiment (180 min). In order to obtain the accumulation from Equation (2), the discretization method was used to calculate the areas underneath the concentration versus the time graphs derived from the experimental data.

$$\text{Accumulation} = \frac{\int_{t=0}^{t=180} (Q_{in}C_{in} - Q_P C_P - Q_B C_R) \cdot dt}{V}, \quad (4)$$

where Q_{in} is the flow rate, and C_{in} is the concentration entering the membrane; Q_P and C_P pertain to the permeate; and Q_R and C_R pertain to the reject stream.

Results and Discussion

Figures 2–4 present the results for BrO_3^- and Br^- concentrations in the permeate and retentate streams, obtained at pH values of 3.0, 6.0, and 8.0, respectively. As shown in Fig. 2, at pH 3.0, the Br^- and BrO_3^- concentrations are constant, and the concentrations of these ions in the permeate and retentate are nearly identical, indicating that the rejection of this ions is negligible. However, at pH 6.0 and 8.0 (Figs. 3 and 4), BrO_3^- and Br^- ions were rejected by the ceramic membrane. The ions cannot be rejected due to sieving. The pore size of the

FIG. 1. Schematic of the experimental setup.

FIG. 2. Bromate (BrO_3^-) and bromide (Br^-) concentration vs. time. Membrane: 7 channel-5 kDa, $[\text{BrO}_3^-]_o$: $7.8 \mu\text{M}$ (1 mg/L), $[\text{Br}^-]_o$: $12.5 \mu\text{M}$ (1 mg/L), $[\text{CaCl}_2]_o$: $0 \mu\text{M}$, pH: 3.0.

membrane was estimated to be 4 nm using the following relationship:

$$d = 0.09 (\text{MWCO})^{0.44}, \quad (5)$$

where d is the pore size in nm, and MWCO is the nominal molecular weight cutoff of the membrane in Daltons (Howe and Clark, 2002). The radii of hydrated BrO_3^- and Br^- ions are 0.35 and 0.33 nm, respectively (Nightingale, 1959); so, they are much smaller than the pore size of the membrane. Donnan exclusion appears to play an important role in determining the rejection of BrO_3^- and Br^- . The filtration layer of the membrane consists of TiO_2 , which has a pH of zero point of charge (pH_{zpc}) in the range of 4.1–7.2 (with a median 6.0) (Kosmulski, 2009). At pH 8, the surface charge of the membrane would be negative. The rejection of ions by this membrane at higher pH can be explained by the repulsive interactions between the negatively charged membrane and the BrO_3^- and Br^- ions (Labbez *et al.*, 2003). In order to maintain electroneutrality in the retentate and permeate streams, the counter ion in this feedwater solution, Na^+ ,

FIG. 3. BrO_3^- and Br^- concentration vs. time. Membrane: 7 channel-5 kDa, $[\text{BrO}_3^-]_o$: $7.8 \mu\text{M}$, $[\text{Br}^-]_o$: $12.5 \mu\text{M}$, $[\text{CaCl}_2]_o$: $0 \mu\text{M}$, pH: 6.0.

FIG. 4. BrO_3^- and Br^- concentration vs. time. Membrane: 7 channel-5 kDa, $[\text{BrO}_3^-]_o$: $7.8 \mu\text{M}$, $[\text{Br}^-]_o$: $12.5 \mu\text{M}$, $[\text{CaCl}_2]_o$: $0 \mu\text{M}$, pH: 8.0.

would also be rejected by the membrane; however, no measurements were made of Na^+ levels in the retentate or permeate to confirm that this occurred. H_2PO_4^- , the predominant phosphate species at pH 3, will sorb onto the titania surface (Kang *et al.*, 2011). Previous studies have shown that phosphate is strongly sorbed on TiO_2 at pH 3 (Kang *et al.*, 2011), and spectroscopic evidence indicates that phosphate sorbed onto TiO_2 forms inner-sphere complexes with the Ti atom (Connor and McQuillan, 1999; Kang *et al.*, 2011). In pure water, the surface charge of the TiO_2 membrane would be positive at pH 3; however, the minimal rejection of the Br^- and BrO_3^- at pH 3 suggests that at this pH, Donnan exclusion is minimal, as the sorption of phosphate significantly reduces the surface charge on the TiO_2 surface.

The concentration of BrO_3^- and Br^- ions in the retentate increases with time, as these ions are retained within the recycle loop. The rejection, R , can be calculated using the expression:

$$R = 1 - \frac{C_P}{C_R}, \quad (6)$$

where

C_P = the concentration of the ion in the permeate (μM)

C_R = the concentration of the ion in the system (retentate) (μM)

For all the experiments conducted, R is essentially independent of time. Table 1 shows the values of R for Br^- and

TABLE 1. REJECTION COEFFICIENTS AT 180 MIN

pH	$[\text{CaCl}_2]$ μM	Rejection coefficient (%)	
		BrO_3^-	Br^-
3.0	0	1.4	0.6
6.0	0	41	33
8.0	0	68	63
6.0	10	13.3	7.6
6.0	250	4.2	1.2
6.0	500	3.4	1.1
6.0	1000	2.5	1.1

BrO_3^- ions at the end of each experiment. The rejection of BrO_3^- is slightly greater than that for Br^- , and the rejection of both ions increases with pH.

As shown in Table 1, the presence of CaCl_2 greatly reduces the rejection of both Br^- and BrO_3^- . At pH 6 and a Ca^{2+} concentration of $10\text{ }\mu\text{M}$ (0.4 mg/L), there is a 70%–80% decrease in the retention of Br^- and BrO_3^- . Typical Ca levels in freshwaters range from 0.5 to 100 mg/L (12.5 – $2,500\text{ }\mu\text{M}$) (Manahan, 1991); so, in most natural waters, the Ca^{2+} levels would be sufficiently high that the rejection of both BrO_3^- and Br^- by the membrane would be extremely small. Zhao *et al.* (2005) showed that the addition of CaCl_2 shifts the isoelectric point of a ceramic membrane to a higher pH value. In the presence of CaCl_2 , the surface charge of the membrane is more positive. The lower rejection of BrO_3^- and Br^- seen in CaCl_2 solutions can also be explained by the shielding of the surface charge in the presence of CaCl_2 (Labbez *et al.* 2003).

Accumulation

Due to their rejection, BrO_3^- and Br^- accumulated in the retentate recirculation loop over the course of the experiment (180 min). The accumulation of these ions in the retentate loop is presented in Figs. 5 and 6. The insets in these figures depict the accumulation normalized with regard to the initial concentration of the ions in the system. As can be seen, regardless of pH, BrO_3^- is accumulated in the reactor to a slightly greater degree than Br^- . This is because the rejection of BrO_3^- was slightly greater than the rejection of Br^- .

Conclusions

The rejection of Br^- and BrO_3^- increased with pH. At pH 8, the rejection of BrO_3^- and Br^- was 68% and 63%, respectively. Donnan exclusion appears to play an important role in determining the rejection of BrO_3^- and Br^- . In the presence of CaCl_2 , the rejection of BrO_3^- and Br^- ions was greatly reduced, confirming the importance of electrostatic interactions in determining the rejection of BrO_3^- and Br^- . As such, membrane filtration can be used to reduce bromate levels in drinking water. If ozonation is used, the BrO_3^- levels in the treated water can be reduced by using membrane filtration to remove Br^- before ozonation or by removing BrO_3^- after ozonation.

FIG. 5. BrO_3^- and Br^- accumulation in the system after 180 min at various pHs. Membrane: 7 channel-5 kDa, $[\text{BrO}_3^-]_0$: $7.8\text{ }\mu\text{M}$, $[\text{Br}^-]_0$: $12.5\text{ }\mu\text{M}$, $[\text{CaCl}_2]_0$: $0\text{ }\mu\text{M}$.

FIG. 6. BrO_3^- and Br^- accumulation in the system after 180 min at various CaCl_2 concentrations. Membrane: 7 channel-5 kDa, $[\text{BrO}_3^-]_0$: $7.8\text{ }\mu\text{M}$, $[\text{Br}^-]_0$: $12.5\text{ }\mu\text{M}$, pH: 6.0.

When ozonation is used in combination with membrane filtration, as was accomplished in this hybrid system, fouling can be controlled (Karnik *et al.*, 2005b) and the formation of disinfection by-products after chlorination can be reduced (Karnik *et al.*, 2005a). In very soft waters, the combined use of ozonation and ceramic membrane may lead to significant decreases in BrO_3^- levels in the product water; however, in most natural waters, the Ca^{2+} levels would be high enough such that the rejection of both BrO_3^- and Br^- by the membrane would be extremely small.

Acknowledgments

The authors acknowledge financial support of this work from the National Science Foundation Research (Grant No. CBET-0506828) and from the Natural Sciences and Engineering Research Council of Canada Discovery Grant Program.

Disclosure Statement

No competing financial interests exist.

References

- Combe, C., Guizard, C., Aimar, P., and Sanchez, V. (1997). Experimental determination of four characteristics used to predict the retention of a ceramic nanofiltration membrane. *J. Membrane Sci.* 129, 147.
- Connor, P.A., and McQuillan, A.J. (1999). Phosphate adsorption onto TiO_2 from aqueous solutions: An *in situ* internal reflection infrared spectroscopic study. *Langmuir* 15, 2916.
- Escoda, A., Deon, S., and Fievet, P. (2011). Assessment of dielectric contribution in the modeling of multi-ionic transport through nanofiltration membranes. *J. Membrane Sci.* 378, 214.
- Fievet, P., Labbez, C., Szymczyk, A., Vidonne, A., Foissy, A., and Pagetti, J. (2002). Electrolyte transport through amphoteric nanofiltration membranes. *Chem. Eng. Sci.* 57, 2921.
- Gerba, C.P., Nwachuku, N., and Riley, K.R. (2003). Disinfection resistance of waterborne pathogens on the United States Environmental Protection Agency's Contaminant Candidate List (CCL). *J. Water Supply Res. Technol. Aqua* 52, 81.
- Gyparakis, S., and Diamadopoulos, E. (2007). Formation and reverse osmosis removal of bromate ions during ozonation of groundwater in coastal areas. *Separation Sci. Technol.* 42, 1465.

- Howe, K.J. and Clark, M.M. (2002). Fouling of microfiltration and ultrafiltration membranes by natural waters. *Environ. Sci. Technol.* 36, 3571.
- Kang, S. A., Li, W., Lee, H. E., Phillips, B. L., and Lee, Y. J. (2011). Phosphate uptake by TiO_2 : Batch studies and NMR spectroscopic evidence for multisite adsorption. *J. Colloid Interface Sci.* 364, 455.
- Karnik, B.S., Davies, S.H., Baumann, M.J., and Masten, S.J. (2005a). The effects of combined ozonation and filtration on disinfection by-product formation. *Water Res.* 39, 2839.
- Karnik, B.S., Davies, S.H.R., Chen, K.C., Jaglowski, D.R., Baumann, M.J., and Masten, S.J. (2005b). Effects of ozonation on the permeate flux of nanocrystalline ceramic membranes. *Water Res.* 39, 728.
- Kosmulski, M. (2009). Compilation of PZC and IEP of sparingly soluble metal oxides and hydroxides from literature. *Adv. Colloid. Interface Sci.* 152, 14.
- Labbez, C., Fievet, P., Thomas, F., Szymczyk, A., Vidonne, A., Foissy, A., and Pagetti, J. (2003) Evaluation of the "DSPM" model on a titania membrane: measurements of charged and uncharged solute retention, electrokinetic charge, pore size, and water permeability. *J. Colloid Interface Sci.* 262, 200.
- Listiarini, K., Tor, J.T., Sun, D.D., and Leckie, J.O. (2010). Hybrid coagulation-nanofiltration for removal of bromate and humic acid in water. *J. Membrane Sci.* 365, 154.
- Manahan, S.E. (1991). *Environmental Chemistry*, 5th ed. Chelsea, MI: Lewis Publishers.
- Matos, C.T., Velizarov, S., Reis, M.A.M., and Crespo J.G. (2008). Removal of bromate from drinking water using the ion exchange membrane bioreactor concept. *Environ. Sci. Technol.* 42, 7702.
- Ministry of the Environment, Canada (2002). Ontario drinking-water quality standards. Safe Drinking Water Act, Ontario Regulation 169/03.
- Moslemi, M., Davies, S.H., and Masten, S.J. (2011). Bromate formation in a hybrid ozonation-ceramic membrane filtration system. *Water Res.* 45, 5529.
- Nightingale, E.R. (1959). Phenomenological theory of ion solvation. Effective radii of hydrated ions. *J. Phys. Chem.* 63, 1381.
- Pinkernell, U., and von Gunten, U. (2001). Bromate Minimization during ozonation: Mechanistic considerations. *Environ. Sci. Technol.* 35, 2525.
- Sanchez-Polo, M., Rivera-Utrilla, J., Salhi, E., and von Gunten, U. (2006). Removal of bromide and iodide ions from drinking water by silver activated carbon aerogels. *J. Colloid Interface Sci.* 300, 437.
- Singer, P.C. (1994). Control of disinfection by-products in drinking-water. *J. Environ. Eng. ASCE*, 120, 727.
- Skluzacek, J.M., Tejedor, M.I., and Anderson, M.A. (2006). An iron-modified silica nanofiltration membrane: Effect of solution composition on salt rejection. *Microporous Mesoporous Mater.* 94, 288.
- Tsuru, T. (2001). Inorganic porous membranes for liquid phase separation. *Separation Purifi. Technol.* 30, 191.
- U.S. EPA. (1998) National primary drinking water regulations: Disinfection and disinfection byproducts, Federal Register 63, 69390–69476.
- U.S. EPA. (2005). Membrane filtration guidance manual. EPA 815-R-06-009. Office of Ground and Drinking Water, Cincinnati, OH.
- Zhang, X., Zhang, T., Ng, J., Pan, J.H., and Sun, D.D. (2009). Transformation of bromine species in TiO_2 photocatalytic system. *Environ. Sci. Technol.* 44, 439.
- Zhao, Y., Xing, W., Xu, N., and Wong, F.S. (2005). Effects of inorganic electrolytes on zeta potentials of ceramic micro-filtration membranes. *Separation Purifi. Technol.* 42, 117.