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Water Research 36 (2002) 4902–4906

WATER RESEARCH

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Received 1 January 2002; accepted 1 April 2002

Abstract

Trihalomethanes (THMs), a by-product of the chlorination of natural waters containing dissolved organic carbon and bromide, are the focus of considerable public health concern and regulation due to their potential as a carcinogen by ingestion. This paper presents a promising new water treatment process that lowers the concentration of bromide in drinking water and thus, lowers the THM formation potential. Bromide is oxidized by electrolysis to bromine and then the bromine apparently volatilized. The electrolyzed water, when chlorinated, produces measurably lower amounts of THMs and proportionately fewer brominated THMs, which are of greater public health concern than the chlorinated THMs. Removing bromide should also reduce the formation of other disinfection by-products such as bromate and haloacetic acids. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Bromide; Disinfection by-products (DBPS); Trihalomethanes (THMS); Formation-potential; Electrolysis

1. Introduction

One of the greatest public health concerns in drinking water treatment today is the formation of trihalomethanes (THMs). THMs are formed by the interaction of natural organic matter, bromide, and chlorine [1,2]). The source of concern about disinfection by-products (DBPs), mainly the THMs which occur in the largest concentrations, has historically been chronic exposures resulting in cancers of the gastro-intestinal tract (e.g. [3–6]). Recent epidemiological studies have also suggested that THMs may have negative acute reproductive effects, including spontaneous abortion, birth defects, and stillbirths [7,8]. The most current toxicological and some epidemiological studies have suggested that the brominated THMs pose the greatest concern [6]. Lowering the bromide concentrations of source water would have significant effect on the amount of THM formed and how brominated those THMs would be. Also, limiting source water bromide would limit bromate production during any ozonation process. Bromate is a limiting contaminant for the use of ozone in water treatment [9].

Bromine was historically manufactured by electrolyzing high bromide brines (0.2–6 g/L) in a process identical to that used to manufacture chlorine [10]. The Wunsche process used mono-polar carbon electrodes and a diaphragm to separate the anode and the cathode compartments, while the Kossuth process used the dipolar carbon electrodes without a diaphragm. In both the processes, at the anode bromide was oxidized to bromine and then the bromine was volatilized by heating and air stripping the analyte [10].

The 1/2 cell reaction is [11]

$$2Br^- \rightarrow Br_2 + 2e^-, \quad E^o = -1.1\ V. \tag{1}$$

This 1/2 cell reaction competes with the oxidation of water:

$$2H_2O \rightarrow 4e^- + O_2(g) + 4H^+, \quad E^o = -1.23\ V. \tag{2}$$

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PII: S0043-1354(02)00210-5

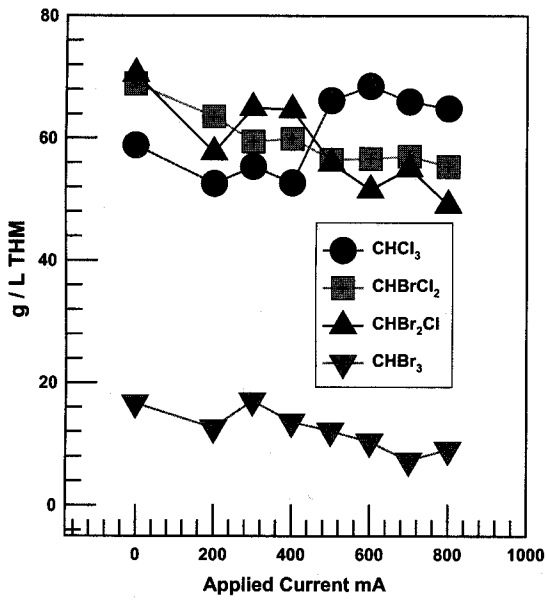

Fig. 3. THMFP of electrolyzed Castaic Lake water as a function of applied potential and current at a flow of 500 mL/min.

HOBr and OBr^- and was slightly incorporated into THMs. The reaction rate was directly proportional to the applied current where there was free bromide to react. A linear regression of bromide concentration versus applied current produced a regression coefficient (r) of 0.986 ($p<0.0001$) when the 800 mA results are excluded. The 800 mA results were excluded as it was not different from the 700 mA results, i.e. >99% oxidation.

The total mass of bromine atoms in all molecular forms was consistently within 15% of the initial bromide concentration. It is hypothesized that there was some loss of bromine due to volatilization of Br_2 caused by the action of oxygen bubbles and very low pH around the anode. This experiment indicates that this process will oxidize bromide to bromine but the bromine will primarily form HOBr and OBr—away from the low pH around the anode.

3.3. Experiment 3

The amount of THMs formed in this experiment decreased with increasing applied current. This is due to the oxidation of bromide to bromine and the volatilization of bromine by the carbon dioxide. Carbon dioxide was used as it would reduce the pH to 5. This would shift any hypobromite to hypobromous acid and bromine, which are uncharged and more volatile. What is more, the amount of bromide incorporated into THMs declines with increasing applied current. This clearly shows that the amount of bromide in the water was lowered and was not incorporated into THMs (Fig. 3).

The overall reduction in THMFP is not large (from about 210 to 180 μg/L) as there was an increase in concentration of $CHCl_3$ but there were significant reductions in the brominated THMs, $CHBr_2Cl$ and $CHBr_3$ in particular. The $CHBr_3$ dropped from 17 to 7 μg/L. The total mass of bromide incorporated into THMs decreased from 102 to 72 μg/mL of electrolyzed water. What is clear is that the stripping with CO_2 did remove the bromine from the electrolyzed water, although not completely. This may reflect the air stripping efficiency of the gas wash bottle used.

4. Summary and conclusion

A hybrid electrolytic cell of Wunsche and Kossuth processes can oxidize even very small concentrations of bromide (~200 μg/L) to bromine in low ionic strength water (<0.02 M). Some amount of volatilization seems to have occurred during electrolysis at the anode due to low pH shifting hypobromous acid to bromine and the effect of oxygen bubbles formed there. The bromine dissolved in solution can in turn be volatilized with carbon dioxide, although this was not efficiently done in this experiment. The future work needs to confirm the air-borne bromine in both electrolysis and carbon dioxide sparging. This process has the effect of lowering the formation potential of the water and of the brominated species in particular [14]. This is a preliminary study with very small volumes so the implications for water treatment are not conclusive but it does show promise as a technique to reduce brominated THMs. It may also prove useful for other brominated DBPs such as haloacetic acids and bromate. Nonetheless, the results are suggestive of a need to examine this process more closely.

Acknowledgements

The author would like to thank the Castaic Lake Water Agency for funding this research, Majid Langroodi and Howard An of the CLWA Laboratory, Paul Rowley and Larry Patellis of the CLWA Maintenance Department for their assistance.

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different settings from 0 to 800 mA. The reactor was allowed enough time for the potential to stabilize. The influent and effluent flows were equal. Then at least three reactor volumes were wasted (240 s) before samples were taken so that the samples will represent steady-state condition. The bromide, bromine in solution (as HOBr), and THM (formed from the chlorine formed during electrolysis) were determined for each applied current at a constant potential. It should be noted that bromine gas that may volatilize from solution during electrolysis was not measured.

2.6. Experiment 3—constant flow, variable current, THM formation potential

This experiment was conducted just as it was in Experiments 1 and 2. Just as with the other experiments three reactor volumes were wasted between a change in the applied current and when samples were taken. 500 mL samples were collected from the top of the reactor. This was sparged with carbon dioxide in a gas wash bottle at a flow of 3 L/min for 15 min, which lowered the pH to about 5. The samples then had the pH adjusted to 8.4 with sodium hydroxide. The chlorine concentration was adjusted to 5 mg/L (as Cl_2) using sodium hypochlorite. The samples were incubated for 24 h and then dechlorinated with STS and analyzed for THMs.

3. Results and discussion

3.1. Experiment 1

In both the Wunsche and Kossuth processes, brominated brines are electrolyzed at constant current and potential, oxidizing bromide to bromine. Experiment 1, summarized in Fig. 1, shows that this reactor produces a constant potential rapidly under constant current conditions. The potential initially spiked and then slowly declined but did not vary more than 1% in the 600 s of the experiment. Almost all of that 1% variability occurred within the first 90 s. From this it can be seen that, if samples were collected after three volumes had passed through (1650 mL over 236 s) then the potential would be constant for the sample that would be analyzed.

3.2. Experiment 2

Figs. 2 and 3 shows that the bromide ended up in four different molecular forms immediately after electrolysis; bromide (Br^-), bromine gas, hypobromous acid or hypobromite ion (HOBr or OBr^-), and as brominated THMs ($CHBrCl_2$, $CHBr_2Cl$, an $CHBr_3$). The residual bromine in the aqueous phase immediately becomes

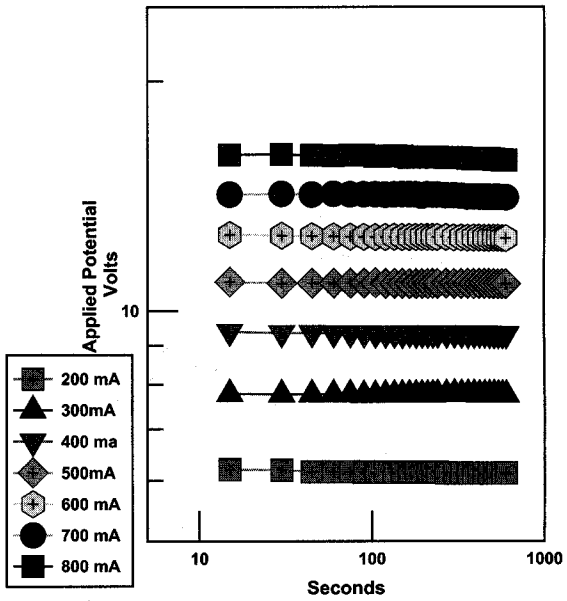

Fig. 1. Change in applied potential over time at different constant applied currents in Castaic Lake raw water flowing at 500 mL/min through an electrolytic cell.

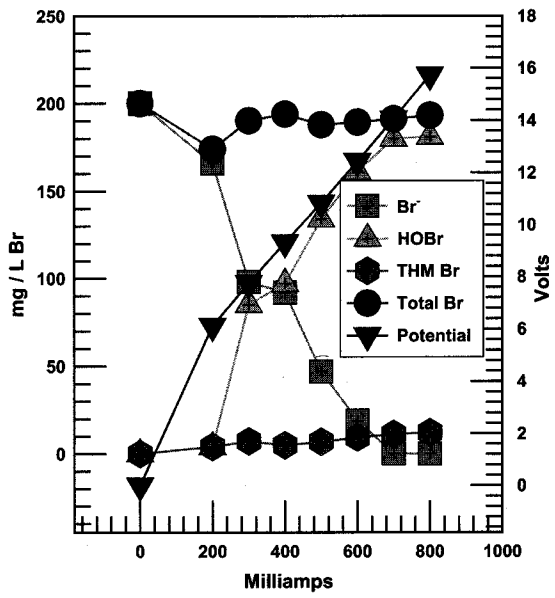

Fig. 2. Aqueous concentrations of Br^-/Br_2 during electrolysis of Castaic lake water at constant flow and variable applied current at a flow of 500 mL/min.

HOBr and OBr^-. The THMs are presented as the equivalent mass of bromide based on the mole fraction of bromide in the molecule. As can be seen, the bromide was converted mainly to bromine in the aqueous form of

At the cathode water is reduced to hydrogen and hydroxide ion:

$$2H_2O + 2e^{-2} \rightarrow OH^- + H_2, \quad E^o = -0.83\,V. \qquad (3)$$

Typical bromine production potentials used today is a high voltage (400 V) and a high currents (100,000 A range) process [12].

The purpose of this paper is to examine the possibility of using a similar process as a method to remove bromide from drinking water. The Wunsche and Kossuth processes use feedstock of bromide concentrations in the range 0.2–6 g/L Br and overall ionic strengths of 1 M. The "feed-stock" used in these experiments, i.e. sources for drinking water, is comparatively low in bromide (<1 mg/L) and at an ionic strength of <0.02 M. While fundamental mechanistic and kinetic issues will need to be resolved, this paper presents an initial bench-scale feasibility evaluation of this promising new process to remove bromide from drinking water sources.

2. Experimental section

2.1. Study design

A flow-through bench-top reactor similar to that used in the Kossuth and Wunsche processes is used. The electrodes are mono-polar like the Kossuth process but the cell is not divided by a diaphragm as in the Wunsche process. The flow-through reactor was used to electrolyze Castaic Lake raw water (CLRW) at a constant current which, after stabilization develops a constant potential. Water collected from the reactor was sampled for bromide and THMs (chlorine was also produced by electrolysis, so some THMs were formed). A different aliquot was sparged with carbon dioxide to remove the bromine formed. The aqueous phase of bromine is in the form of HOBr or OBr^- as a function of pH. This was done at several different applied constant currents and potentials. Castaic Lake water was used as it is known to have significant THM formation potential and high bromide concentrations (70–300 μg/L between 1990 and 2001 and an ionic strength of <0.02 M).

2.2. Analytical techniques

(1) Bromide was measured by ion chromatography (DIONEX DX-500) using USEPA Method 300.0 (1994) with a reporting limit of 5 μg/L. The bromine cannot be measured directly by this method. However, by adding sodium thiosulfate (STS) to the sample, bromine was reduced to bromide. Samples that had STS added could be analyzed by this method and the bromide concentration would represent $Br^- + HOBr$. Samples analyzed by this method with no STS added would only represent Br^-. By sampling in duplicate, and adding STS to one sample and not to the other, and then subtracting the difference, the amount of HOBr was determined.

(2) THMs were measured by gas chromatography combined with electrolytic conductivity detector (ELCD or Hall Detector) on a Varian 3400 using USEPA Method 502.2.

(3) THM formation potential (based on [13]) was determined by collecting 250 mL of sample, adding 5 mg/L of sodium hypochlorite and allowing the sample to incubate for 24 h. The bottle was then quenched with STS and analyzed for THMs by the above method.

2.3. Materials and equipment

A electrolytic flow-through reactor was constructed which consisted of a PVC tube with an inside diameter of 5 cm and a volume of 550 mL. On the inside walls three carbon rod cathodes (EDM-3, Electrodes Inc. Santa Fe Springs, CA), 30.5 cm (12 in) in length and 6.25 mm (1/4 in) in diameter, were placed at equal distance from each other and held in place by nylon binders. Three dimensionally stable anodes (DSAs), (titanium rods coated with a proprietary coating of RuO_2 and TiO_2 (EC-600), (ELTECH Systems Corporation, Fairport Harbor, OH) [12] of dimensions equivalent to the carbon cathodes were placed in a similar fashion between the cathodes. A fourth DSA was placed in the center of the reactor supported by inert material. All the rods were connected to a direct-current power source in parallel (PS-1850D, Instek Laboratories Inc., Los Angeles, CA). CLRW (total dissolved solids = 314 mg/L, specific conductance = 520 μS) was fed into the bottom of the reactor and allowed to flow up between the electrodes. Samples were collected from the top of the reactor.

2.4. Experiment 1—constant flow, constant current, variable potential over time

CLRW was fed into the reactor at a flow rate of 500 mL/min and an electrolysis time of about 80 s. The applied current was adjusted to a fixed current from 10 to 800 mA. For each applied current the potential was recorded every 15 s for 10 min. The amount of electrolysis time needed for constant potential was determined by this method.

2.5. Experiment 2—constant flow, variable potential, constant current

CLRW was fed into the reactor at a flow rate of 420 mL/min. The applied current was set at nine

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