Electrochemical dehalogenation of dibromomethane and 1,2-dibromoethane to non-toxic products using a carbon fiber brush electrode

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Abstract

The electrochemical dehalogenation of 1,2-dibromomethane (DBM) and 1,2-dibromoethane (DBA), two brominated contaminants often detected in groundwater, was studied at different cathode potentials (-0.8, -1 and -1.2 V versus Standard Hydrogen Electrode) in aqueous solution using an inexpensive graphite fiber brush electrode. The degradation followed first-order kinetics with respect to the nominal concentration of the brominated compounds and the kinetic constant increased concomitantly with the decrease of the cathode potential. The amount of bromide ion released during electrochemical dehalogenation, for the range of cathode potentials tested, was 96% and 99% of the maximum bromide concentration expected if DBM and DBA were fully dibrominated, respectively. In accordance with these results, the non-brominated compounds methane and ethene were the main products detected during DBM and DBA electrochemical degradation. In addition, minor amounts of formic acid and acetic acid were also detected for each contaminant respectively. The non-toxicity of the effluent was confirmed by a Microtox test. These results open the door to the application of a simple and non-toxic electrochemical approach to the treatment of aliphatic brominated compounds from aquifers and other water sources.

Keywords

Dibromomethane; 1,2-Dibromoethane; Electrochemistry; Remediation, Reductive debromination

1 Introduction

Dibromomethane (DBM) and 1,2-dibromoethane (DBA) are brominated volatile compounds, which are utilized in a wide range of industrial applications, such as petrochemical and pharmaceutical processes, and have been used as agricultural pesticides [1,2]. Due to their extensive usage and accidental events, their presence has been detected in natural environments, including groundwater sources [2,3]. Both compounds have adverse effects on human health, and are considered probable/potential carcinogens [4]. Based on a combination of frequency of occurrence, toxicity, and potential for human exposure, DBA has been ranked 39th on the 2017 ATSDR Priority List of Hazardous Substances [5].

Several degradation techniques have been studied to degrade these brominated compounds in aqueous media, including chemical reduction or oxidation [6–9] and aerobic or anaerobic biodegradation [4,6]. Electrochemical techniques have been tested within a broad range of halogenated contaminants, but mostly include chloroalkanes and pesticides [10–14]. With regards to the electrochemical degradation of brominated compounds, Radjenović et al. (2012) [15] reported the successful simultaneous electrochemical reduction of 17 contaminants, including several bromoiodomethanes, bromochloromethanes and bromoform, using resin-impregnated carbon-brushes. Electrocatalysis of halogenated compounds can involve either oxidation or reduction reactions, but electrochemical reduction is promising for the degradation of simple halogenated contaminants because enables the cleavage of the carbon – halogen bond and their further transformation to innocuous compounds (i.e. methane and ethane) [16,17]. The main advantages of the electrochemical degradation over biological techniques are i) the short reaction time, ii) the ability to treat streams even with high concentrations of contaminant and iii) the ability to work in complex mixtures of different pollutants in which the growth of microorganisms may

be inhibited [18]. On the other side, the main drawbacks of electrochemical techniques are i) the high cost of the precious metals (i.e. Ag, Al, Au, Cu, Ni, Pd, Ti) required to catalyze the electrochemical reactions [16,19], ii) the need of a high external energy input, and iii) the need of specific medium compositions (as low pH or non-aqueous electrolytes), which may complicate its field application [16,20]. In any case, there is a need to find cheaper and novel efficient technologies to treat efficiently halogenated pollutants that can be found in groundwater.

The aim of this study is to demonstrate the feasibility of the reductive dehalogenation of DBM and DBA in lab-scale electrochemical cells using an inexpensive and untreated graphite brush electrode under non-aggressive electrolytic conditions. The effect of the electrode potential on reaction rates and degradation efficiencies was studied together with the identification of the byproducts and the toxicity of the treated effluent.

2 Materials and methods

2.1 Electrochemical cells description

The electrochemical cells consisted of two 165 mL glass vessels separated by a cation-exchange membrane (CMI-7000, Membranes International INC, USA), with an aperture diameter of 4 cm. The membrane was hydrated prior to its use by maintaining it in a 5% wt sodium chloride solution for 24 hours at room temperature. A titanium sheet was used as the anode. The cathode was a graphite fiber brush (35 mm length x 30 mm diameter, 7.2 µm fiber diameter, Millrose Co., USA) providing a surface area of 0.132 m^2 and a ratio of electrode surface : reaction volume of 802 m^2/m^3. A power source (Quad Potentiostat, Whistonbrook Software) was used to obtain the desired cathode potentials. The cathode potential versus an Ag/AgCl reference electrode (RE-1B, BAS Inc., +197 mV vs SHE) was measured with a digital multimeter (Hayoue DT830B). The potential

values are reported as V vs SHE, if not otherwise stated. The cathode vessel was sealed with a Teflon cap in order to prevent the loss of volatile compounds. A Teflon-coated butyl rubber stopper sealed with an aluminium crimp cap was used as a sampling port for liquid extraction in the cathode.

2.2 DBM and DBA electrochemical reduction experiments

Before each experiment, anodic and cathodic chambers were filled with an anoxic bicarbonate-buffered aqueous solution (50 mM) with a pH value adjusted to 7 and a conductivity of 3.85 mS/cm. The catholyte was spiked with DBM (Sigma-Aldrich, 99% purity) or DBA (Sigma-Aldrich, ≥98% purity) and vigorously mixed with a magnetic stirrer during all the experiment length. The degradation of both pollutants was tested by triplicate at three different cathode potentials (-0.8, -1 and -1.2 V vs SHE). Open circuit experiments with each contaminant in the same experimental conditions were performed to discard spontaneous degradation of both compounds. During the experiments, liquid samples were withdrawn periodically from the catholyte in order to monitor the degradation of the pollutants and the formation of byproducts. Experiments were conducted at room temperature (25±3 °C).

The maximum degradation rate for each contaminant at the different cathode potentials was calculated from the contaminant degradation profile during the application of potential. In addition, a first-order kinetic model (equation 1) was fitted to describe the contaminant degradation rate ($\mu M \cdot h^{-1}$) under different applied potentials:

$$Degradation\ rate = -k \cdot [Contaminant] \quad (1)$$

where k is the first order rate constant (h^{-1}) and [Contaminant] is the remaining concentration of DBM or DBA in the cathode.

2.3 Coulombic efficiency and energy consumption

The coulombic efficiency (CE) for each degradation experiment at the cathode was calculated using equation 2:

$$CE = \frac{2 \cdot V \cdot F \cdot [Br^-]}{\int I(t)dt} \quad (2)$$

where 2 is the number of electrons required to release a mole of bromide ion, V is the cathodic liquid volume (L), F is Faraday's constant (96485 $A \cdot s \cdot mol^{-1}$), $[Br^-]$ is the concentration of released bromide ions (μM) and $\int I(t)dt$ is the integration of the measured intensity data along the experimental time.

Additionally, the energetic input (EI) required for each experiment was calculated as follows:

$$EI = \frac{V_A \cdot \int I(t)dt}{V \cdot [Br^-]} \quad (3)$$

where V_A is the voltage applied in the system (V).

2.4 Analytical methods

The volatile halogenated contaminants, methane and ethene were identified by static headspace gas chromatography. The liquid samples (1 mL) from the cathode were transferred to 10 mL vials containing 5.5 mL water. The vials were sealed with Teflon-coated butyl rubber stoppers and aluminum crimp caps, placed in a headspace sampler (Agilent 7964) and heated to 85 ºC for 15 min. Subsequently, 1 mL headspace gas sample from the vials was injected automatically into an Agilent 6890N gas chromatograph equipped with an Agilent DB-624 column (30 m × 0.32 mm

with 0.25 μm film thickness) and a flame ionization detector following a method described elsewhere [21].

To identify nonvolatile compounds produced from the electrochemical degradation of DBA and DBM, 400 mL of aliquot derived from these experiments were mixed with 200 mL of D_2O (99.96 % D, Cortecnet, Voisins-le-Bretonneux, France) in a 5-mm-diameter NMR tube. A Bruker Avance II 600 nuclear magnetic resonance spectrometer (Bruker Biospin, Rheinstetten, Germany) equipped with a 5 mm TBI probe with Z-gradients, operating at a 1H NMR frequency of 600.13 and at 298.0 K of temperature, was used for the NMR experiments. 1D 1H NMR spectra were acquired using the noesy1dpr pulse sequence to suppress the H2O signal. An acquisition time of 1.70 s and a relaxation delay of 2 s were used. The data were collected into 32 K computer data points, with a spectral width of 9615 Hz and as the sum of 2048 transients. Identification of compounds was done comparing results with those reported in literature and gathered in NMR spectral data bases [22,23].

Bromide ions were quantified from filtered (0.22 μm PVDF filters) liquid samples (1 mL) using ion chromatography with conductivity detection (Dionex ICS-2000 with an Ultimate 3000 Autosampler) as described elsewhere [21].

2.5 Toxicity Analysis

A Microtox bioassay was performed before and after the electrochemical treatment to detect possible toxic intermediates. A Microtox model 500 analyser (Azur Environmental) was used and the 81.9% basic test (adequate for samples with expected low toxicity) was selected. The bioluminescence of the model bacterium *Aliivibrio fischerii* was measured 5 and 15 minutes after exposition to experiment samples and compared to the bioluminescence produced by the control

tests (i.e without exposition to the contaminant). The tubes were sealed with a rubber septum to prevent the loss of volatile contaminants during the assay.

3 Results and discussion

3.1 DBM and DBA electrochemical reduction experiments and identification of byproduts

The electrochemical reduction of DBM and DBA was evaluated at different cathode potentials (-0.8, -1 and -1.2 V vs SHE). The degradation of DBM and DBA was only observed when cathodes were poised at the desired value and not under open circuit conditions (Fig. 1), indicating that DBM and DBA degradation was electrochemically mediated.

In the case of DBM, the time needed to obtain a contaminant decrease higher than 95% was 7, 3 and 1 h for the potentials of -0.8, -1 and -1.2 V, respectively (Fig. 1A). Time-course degradation experiments showed a correlation between the DBM degradation rate and the cathode potential (Fig. 1A), the degradation rate being the highest (786.7 ± 50.6 $\mu M \cdot h^{-1}$) at the lowest cathode potential (-1.2 V) tested. At cathode potentials of -1.0 and -0.8 V, degradation rates of 213.5 ± 31.7 $\mu M \cdot h^{-1}$ and 102.5 ± 26.5 $\mu M \cdot h^{-1}$ were obtained, respectively.

A lower percent degradation was achieved for DBA for the same time point experiments and cathode potentials tested for DBM (Fig. 1C). Again, the more negative the cathode potential, the higher the maximum degradation rate. The obtained values were 677.0 ± 107.4, 177.1 ± 18.3 and 76.3 ± 10.9 $\mu M \cdot h^{-1}$ for the potentials of -1.2, -1.0 and -0.8 V, respectively. Although there is a difference among the percentages of degradation between both contaminants, the comparison between the maximum degradation rates obtained for each potential shows a difference lower than

167 26%. Electrochemical DBM degradation has not been previously studied and DBA degradation
168 has only been reported with boron-doped diamond and dropping mercury electrodes at cathode
169 potentials around -1.5 V (vs SHE) [17,24]. In our study, less negative cathode potentials were
170 successfully used due to the high surface area per reaction volume of the graphite brush used as
171 the electrode.

172 The chromatographic analyses of headspace samples indicate that DBM and DBA degraded was
173 mostly transformed to methane and ethene, respectively (data not shown). In addition, liquid
174 samples from DBM and DBA at potential of -1.2 V experiments at time point 60 min were
175 analyzed by ^{1}H NMR spectroscopy to identify any possible nonvolatile degradation compound.
176 Spectra from DBM and DBA presented some very low intense peaks, in form of singlets, which
177 differed from the blank (Fig. 2a). This blank consisted in a sample derived from the cathodic
178 chamber that was electrochemically operated for 60 min at the same electric potential but without
179 brominated compounds spiked. These signals were difficult to identify due to their singlet nature
180 and to their low intensity (i.e. compounds in very low concentration), which hampered the
181 performance of other NMR experiments like ^{13}C based experiments. However, two compounds
182 were identified due to their typical resonance frequencies at the experimental conditions used. In
183 sample derived from DBM degradation, a small singlet at 8.45 ppm corresponding to formic acid
184 was observed (Fig. 2c). In DBA sample, which presented a cleaner spectrum than the equivalent
185 for DBM, a very low intense singlet at the resonance frequency of acetic acid, 1.92 ppm, was
186 detected (Fig. 2b) [22,23]. Also, increasing amounts of bromide ions were released during the
187 dehalogenation of both brominated compounds (Fig. 1B and 1D). No product generation was
188 detected in the open circuit experiments, ensuring that the generation of these substances was
189 directly correlated with the contaminant degradation.

The amount of bromide ion released from DBM degradation was 96.8% of the maximum bromide concentration expected if all the degraded DBM was fully dibrominated (Fig. 3A). Hydrogenolysis of DBM was discarded as a pathway for degradation because no bromomethane was detected by GC analyses during the experiments (detection limit 1 μM). Similarly, DBA degradation yielded a molar ratio of bromide to DBA of 1.995, which means that 99.8% of the expected bromide was released, considering that all the DBA degraded was completely debrominated (Fig. 3B). In contrast, incomplete electrochemical debromination of DBA (ratio between bromide released and DBA degraded of 1.56 and 1.78) was reported at cathode potentials around -1.5 V (vs SHE) in previous studies [17]. Tokoro et al. (1986) hypothesized that carbanion was generated as reaction intermediate and it was further transformed to bromoethane [17]. In our study, neither vinyl bromide nor bromoethane (formed during dehydrohalogenation or hydrogenolysis of DBA, respectively) were detected in the catholyte by GC analyses (detection limit 1 μM).

The Microtox toxicity bioassay was applied to evaluate the toxicity of the electrolyte before and after treatment. Our results showed that the samples analyzed were not sufficiently toxic to produce any effect on the bioluminescence from *A. fischeri*, indicating that electrochemical degradation of DBM and DBA did not result on the accumulation of major toxic products.

3.2 Coulombic efficiency and energy consumption

The values of coulombic efficiency and energy consumption were calculated for each experiment based in the measured intensities and voltages (Table 1). All the potentials tested showed similar values of coulombic efficiency for both contaminants (between 60 and 77%). No correlation was found among the different potentials. Alternative cathodic reactions presumably lowering the coulombic efficiency include e.g. the reduction of oxygen (leaking to the cathode from the anode through the cation exchange membrane) and electrochemical hydrogen production. Despite this

similarity, the energetic consumption adopted higher values in the -1.2 V due to the more negative voltages applied. These results show that the use of carbon brush electrodes can grant high efficiency values despite its simplicity when they are involved in the cleavage of the bromide-carbon bond.

Table 1. Coulombic efficiencies (CE) and Energetic Inputs (EI) for DBM and DBA degradation at different potentials.

Contaminant	Applied potential (V vs SHE)	Voltage (V)	CE (%)	EI ($kWh \cdot mol^{-1}$)
DBM	-0.8	-1.9	69.8 ± 3.6	0.15 ± 0.01
	-1.0	-2.3	76.3 ± 0.8	0.16 ± 0.01
	-1.2	-4.0	68.6 ± 1.8	0.31 ± 0.01
DBA	-0.8	-1.9	65.3 ± 8.3	0.16 ± 0.02
	-1.0	-2.3	67.2 ± 0.5	0.18 ± 0.01
	-1.2	-4.0	60.7 ± 14.7	0.37 ± 0.10

3.3 Kinetics of transformation

The degradation of DBM and DBA followed first-order kinetics with respect to the nominal concentration. The rate constants were estimated by fitting the data to a first-order kinetic model (Fig. S1), obtaining R^2 values ranging from 0.92 to 0.97. The dependence of the rate constants for both brominated contaminants on the cathode potential is illustrated in Fig. 4. For both compounds, the first order kinetic constant statistically increases when the electric potential adopts more

227 negative values. These results are in agreement with the maximum degradation rates discussed in
228 the previous results section.

229 In a previous study reporting electrochemical reduction of DBA at -1.5 V (vs SHE) with a boron
230 doped diamond electrode and 22 mL of a 30 % methanol containing aqueous medium, a kinetic
231 constant value of 0.44 h^{-1} was obtained [24]. This value is 80 % lower than the one obtained in this
232 study at potential of -1.2 V, while our experiments were performed in a 7.5-fold higher reaction
233 volume. This higher degradation rate is mainly due to the high ratio between electrode surface area
234 and catholyte volume provided by the graphite brush, being two orders of magnitude higher. This
235 indicates that an efficient degradation can be reached with cheaper electrode materials and simpler
236 medium compositions. Further research is needed to assess the optimal conditions and the
237 suitability of the degradation process in a larger scale setup. The kinetic constants obtained in other
238 reports on electrochemical degradation of similar compounds as Radjenović et al. (2012) [15] are
239 difficult to compare due to the complexity of their systems or the use of several simultaneous
240 contaminants.

241 ## 4 Conclusions

242 This study demonstrates the feasability of electrochemical systems to fully debrominate DBA and
243 DBM using inexpensive and environmentally friendly carbon fibers as electrode materials. The
244 short operation time did not lower the coulombic efficiency of the process, maintaining similar
245 efficiency values even in the experiments with higher energetic inputs. The first order kinetic
246 model proposed fits acurately the obtained data and allows to statistically confirm a relationship
247 between the applied cathode potential and the rate of contaminant degradation. The treated effluent
248 was not toxic according to the Microtox bioassay, which is in accordance to the nonhalogenated

byproducts identified during the electrochemical degradation of DBM and DBA by NMR.. Further investigation is required to assess the application of this methodology on environmental contaminated sites.

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The authors declare no conflict of interest.

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Figure legends

Figure 1. Time-course of the electrochemical degradation of DBM (a) and DBA (c) and their respective bromide generation (b and d) in aqueous medium at different cathode potentials (●: -0.8 V, ■: -1 V, ▼: -1.2 V, ◆: Open Circuit). Solid symbols and open symbols refer to contaminant and bromide mean concentrations, respectively. No bromide generation was detected in open circuit experiments. Bars indicate deviation for triplicate experiments.

Figure 2. 1D ^{1}H NMR spectra of liquid samples taken after 60 min of the electrochemical degradation process of DBA (Panel B) and DBM (Panel C) at -1.2 V (vs SHE). Panel A shows the 1D ^{1}H NMR spectra of a blank that accounted for an electrochemical cell without brominated compounds. The spectra were acquired with suppression of the water signal (noesy1dpr), at 25 ºC and at a magnetic field of 600 MHz.

Figure 3. Fitted curve of bromide released in the liquid medium per DBM (a) or DBA (b) degraded. Values were obtained from the experiments plotted in Figure 1.

Figure 4. Dependence of first-order kinetic constants for DBM and DBA reductions on cathode potential using a graphite fibre brush cathode. Shown are means for triplicate assays ± standard deviations.