Monochloramine Microelectrode for In-Situ Application Within Chloraminated Distribution System Biofilm

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Abstract
A monochloramine microelectrode with a tip size between 5 and 15 μm and using platinum wire was successfully designed, fabricated and characterized for in-situ monochloramine measurement within chloraminated distribution system biofilm. The monochloramine microelectrode showed sensitivity toward monochloramine concentrations (0.54 to 16.1 mg Cl_2/L) at an applied potential of +550 mV (Ag/AgCl reference electrode) at pH 8.0 and 23°C. The monochloramine microelectrode has successfully measured monochloramine microprofiles with high spatial resolution (50 μm) without biofilm structure disruption during measurements. Ultimately, this research will lead to a better understanding of the monochloramine microelectrode for in situ application within a chloraminated drinking water system biofilm, and along with other microelectrodes (e.g., ammonia, pH, DO) under development, elucidate nitrification phenomena occurring in the biofilm.

Introduction
As a result of the implementation of the Stage 1 and Stage 2 Disinfectants and Disinfection Byproduct Rules, chloramine use as a secondary disinfectant in the United States is predicted to increase to 57% of all surface and 7% of all ground water treatment systems [1]. A recent survey suggests that an additional 12% of drinking water utilities are contemplating a switch to monochloramine in the future [2]. For utilities that use monochloramine or have source water ammonia, nitrification is an undesirable side effect that may result in water quality degradation, and subsequent non-compliance with existing regulations. In order to elucidate nitrification phenomena within distribution system biofilm, microelectrode techniques are under development to profile the chemical constituents that lead to nitrifier growth and inactivation.

In the current research, monochloramine microelectrodes using platinum wire were fabricated and evaluated for use in *in-vivo* environmental analysis of monochloramine as the disinfectant within chloraminated water distribution system biofilm. Several researchers have reported the electrochemical behavior of monochloramine sensors using a platinum or gold disk (or electrode) with a flow injection technique [3, 4, 5]. However, these electrodes are too large to apply at the small scale (~10 μm), and there is currently no commercial or developed microelectrode for application to biological analyses, including direct measurement of biofilm monochloramine penetration. This study developed monochloramine microelectrodes and investigated their biological applicability, determining biofilm monochloramine profiles. The monochloramine microelectrode was fully examined using cyclic voltammetry, allowing determination of the appropriate applied potential for monochloramine measurement, and was evaluated for its application to various environmental conditions.

Materials and Methods

The monochloramine microelectrode was patterned after a chlorine microelectrode [6]. The platinum (Pt) wire (0.127 mm diameter, 99.99% purity, Aldrich Chemical Co.) was cut into 4 to 5 cm length sections. The tip of the Pt wire was etched in a 6 M potassium cyanide (KCN) solution with 5 V potential. After pulling a lead glass micropipette (O.D.: 1.5 mm, I.D.: 0.75 mm, 15 cm length, World Precision Instruments), the etched Pt wire was sealed in a glass capillary as described previously [7, 8, 9]. Subsequently, the sealed tip was beveled to expose the Pt surface and the glass was resealed by heating the tip. Finally, the Pt tip was recessed 5 to 6 μm and coated with 10 % (wt/vol) cellulose acetate in acetone for 30 sec. The tip diameters of the resulting microelectrodes were between 5 and 15 μm. Finished microelectrodes were evaluated before biofilm parameter profiling. Cyclic voltammetry tests were performed to check the appropriate applied potential for monochloramine using a Potentiostat (Diamond General Corp., Product No 1231) and pocket PC (Palm Instruments BV-2004) for sensing and data analysis.

Biofilm samples were analyzed in a specially designed flow chamber at 23°C. Figure 1 shows the experimental apparatus for microprofile measurements using the microelectrode, while Figure 2 shows an expanded view of microprofile measurements within the flow chamber. A mixed culture biofilm was grown on glass slides in a 4-L Sequencing Batch Reactor (SBR) with high substrate concentrations (200 mg COD/L, 7.5 mg P/L, and 20 mg N/L). Biofilm slides were taken from the reactor and mounted in the flow chamber to measure the monochloramine microprofiles. Microprofile measurements were carried out in a 50 mM phosphate buffer (PB) at pH 8.0, and chlorine and ammonia were supplemented to produce the target monochloramine concentration of 10 mg/L Cl_2/L (4:1 Cl_2:N). The flow rate in the flow chamber was 15 mL/min. Monochloramine measurement was performed vertically at 50 μm intervals in the biofilm using a micromanipulator (Figure 1) under a stereo microscope with a CCD camera inside a Faraday cage, which minimizes electrical interferences. Before and after microprofile measurement, the monochloramine concentration in the bulk fluid was measured using a colorimetric test kit (Hach-8167) and a DR/2010 spectrophotometer (Hach Co.). In these initial experiments, total chlorine was assumed to represent the monochloramine concentration because, at pH 8.0, monochloramine should be the dominant chloramine species in the bulk solution [10].

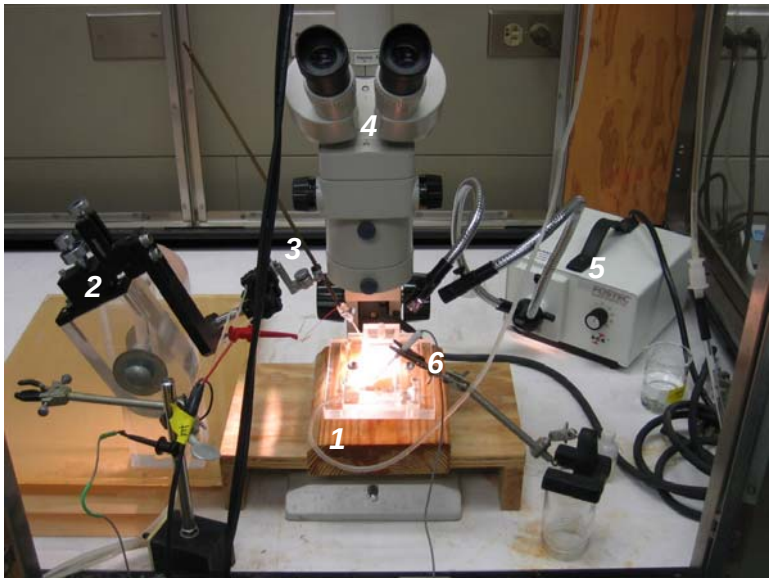

Figure 1. Microelectrode experimental apparatus. 1) Flow chamber ; 2) 3-D manipulator; 3) Microelectrode; 4) Microscope; 5) Light source; 6) Ag/AgCl reference electrode.

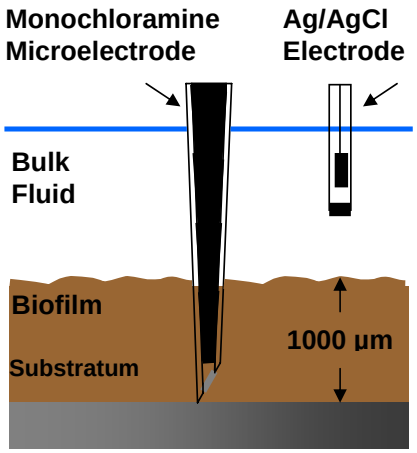

Figure 2. Microprofile measurement in a flow chamber

Results and Discussion

A monochloramine microelectrode with a tip diameter between 5 and 15 μm and a 45° tip angle was fabricated using platinum wire. The following three reactions have been proposed [3], whereby a platinum oxide layer forms on the platinum surface of the microelectrode tip and reacts with monochloramine, to explain the electro-chemical behavior of the electrode:

$$2\ NH_2Cl \rightarrow N_2 + 2\ Cl^- + 4\ H^+ + 2\ e^- \quad (1)$$

$$2\ Pt + 2\ OH^- \rightarrow 2\ PtOH + 2\ e\text{-} \quad (2)$$

$$2\ PtOH + 2\ NH_2Cl \rightarrow N_2H_4 + 2\ HCl + O_2 + Pt \quad (3)$$

These reactions affect the electrode response (pA), and monochloramine concentration can be measured. Current-potential curves were obtained for monochloramine electro-reaction in 50 mM PB solution at pH 8.0 through cyclic voltammogram tests. At +550mV, the signal increased proportionally to the monochloramine concentration with high stable and selective electrode response. In Figure 3, the monochloramine microelectrode showed sensitivity toward monochloramine concentrations (0.54 to 16.1 mg Cl_2/L) at an applied potential of +550 mV (Ag/AgCl reference electrode) at pH 8.0 and 23°C. The calibration curve indicated a linear response between current and monochloramine concentration with an R^2 of 0.99. The response time was less than 30 sec. The pH and ion interference in the typical drinking water pH range (6-9) was demonstrated to be minor (data not shown). Although dissolved oxygen (DO) shifted the electrode response, a good linear relationship existed with monochloramine concentration even at high DO concentrations (data not shown).

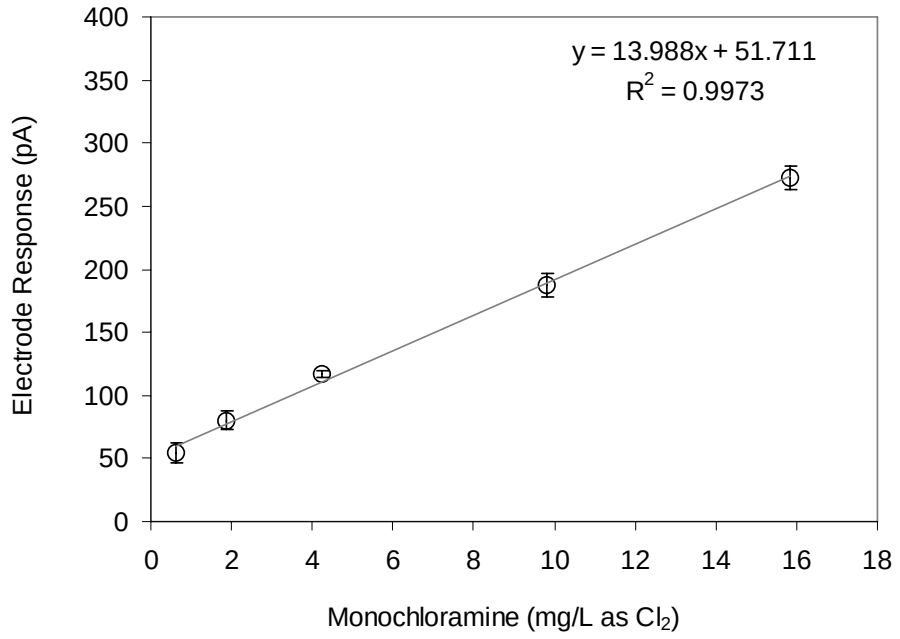

Figure 3. Calibration curve for the monochloramine microelectrode in 50 mM PB solution at pH 8.0.

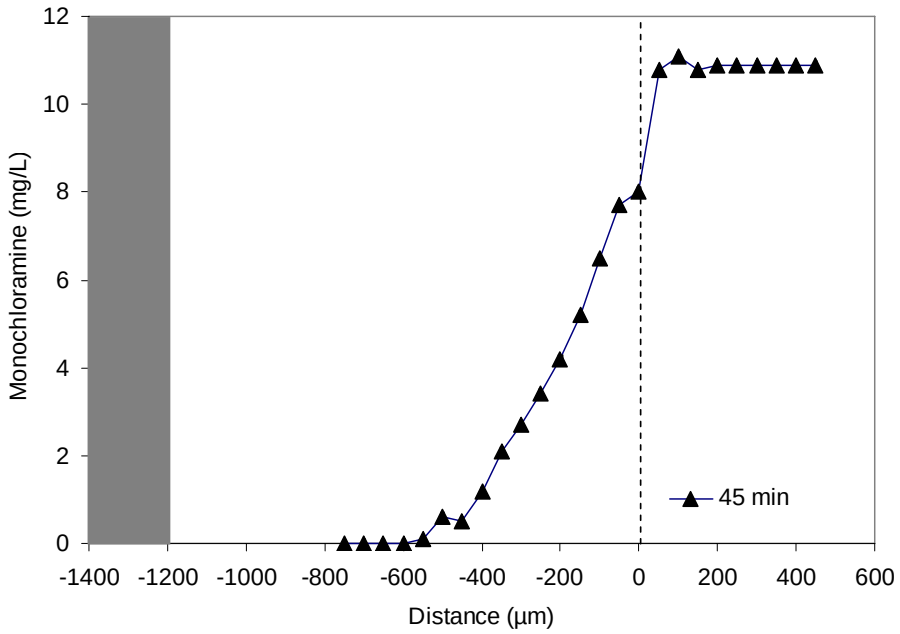

Figure 4. Monochloramine concentration microprofile within a biofilm after 45 min exposure to 10.9 mg/L monochloramine.

Figure 4 shows a monochloramine concentration microprofile within a biofilm after 45 min exposure to 10.9 mg/L monochloramine. The zero on the *x*-axis corresponds to the biofilm surface and bulk fluid interface with a negative sign indicating distance (µm) from the biofilm surface into the biofilm. The biofilm thickness was 1,200 µm. During the measurement, the monochloramine concentration was maintained at 10.9 mg/L (4:1 Cl_2:N) in 50 mM PB solution at pH 8.0 in the bulk solution. The monochloramine concentration decreased with biofilm depth indicating the characteristics for a chemical that is undergoing reaction and diffusion simultaneously [6]. The monochloramine microelectrode with a small tip (5 to 15 µm) successfully measured monochloramine microprofiles with high spatial resolution (50 µm), preventing biofilm structure disruption during measurements.

Conclusions

Monochloramine microelectrodes (tip size 5 to 15 µm) were fabricated using platinum, and were fully characterized and evaluated in various environmental conditions. Monochloramine measurements using these newly developed monochloramine microelectrodes exhibited fast, repeatable response times and good stability at an applied potential of +550mV. This research provides fundamental information to gain a better understanding of the monochloramine microelectrode for in-situ applications measuring biofilm monochloramine microprofiles. Combining these profiles with other biofilm constituent profiles will allow evaluation of the

microbial activity in the biofilm during the disinfection process, including nitrification in chloraminated drinking water distribution systems.

Acknowledgment

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