Research Article

Development of a Gold Microelectrode and its Application for Evaluating Free Chlorine Consumption by Metal Surfaces

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Abstract

An amperometric gold microelectrode for in situ free chlorine measurement was newly fabricated, characterized, and successfully applied for evaluating free chlorine consumption by ductile iron coupons at the micro level in a simulated drinking water distribution system. The developed gold microelectrode showed a linear relationship with various free chlorine concentrations (0–4 mg Cl_2/L) at an applied potential of +150 mV vs. Ag/AgCl. The response time was less than 5 seconds and the limit of detection was 0.08 ± 0.008 mg Cl_2/L. However, the gold microelectrode showed a pH interference on free chlorine measurement, requiring construction of calibration curves at different pHs. After measuring pH and free chlorine concentration micro profiles simultaneously at the same depth, pH was compensated for determining accurate free chlorine concentrations. Two examples of pH compensation were demonstrated with increasing pH and decreasing pH conditions near the metal surface. The well-defined pH compensated free chlorine micro profiles provided more accurate corrosion kinetic parameters such as flux (J), reaction rate (k), and free chlorine concentration at the metal surface (Cs). The developed gold microelectrode will be a useful experimental tool for evaluating localized corrosion processes.

Keywords: Copper; Drinking water distribution system; Ductile iron; free chlorine; Gold microelectrode; Metal pipes

Introduction

Free chlorine is a strong oxidant which has been used as a secondary disinfectant in drinking water distribution systems for decades in order to provide safe and potable water [1,2]. Chlorine residuals should be maintained in the drinking water system to control the potential bacterial activity, but metal corrosion can occur on the surface of the piping materials by reacting with the oxidant in the system. Studies have shown that metal corrosion like copper pitting [3,4], cast iron leaching [5], and lead pipe corrosion [6] are related to the presence of chlorine species in distribution systems. Although conceptual theories regarding the surface chemistry reactions of corroding metals exist, metal corrosion reactions are complex and their mechanisms, particularly pitting corrosion, still remain unknown. Water parameters such as free chlorine, dissolved oxygen (DO), pH, temperature, and flow velocity have great impact on the corrosion process [7]. Previous research shows that there is a complex cycle of events in which free chlorine may contribute to contribute to corrosion and the build-up of corrosion products on the metal pipe walls [8]. The study pointed out that corrosion products may consume free chlorine before the disinfectant can penetrate the biofilm to destroy the microorganisms, requiring higher doses of free chlorine, which in turn would increase corrosion and subsequent chlorine residual loss in the system [8,9]. To understand the effect of free chlorine on localized metal corrosion and bacterial inactivation, a direct monitoring of free chlorine concentration gradients from the bulk to the metal surface is needed. The results will also provide better understanding of in situ chemistry dynamics on the metal surface and corrosion mechanism.

Several studies on electrochemical free chlorine determinations have been conducted using new materials (e.g., pyrolytic-graphite) or precious metals (e.g., platinum) [10-13]. However, for localized corrosion application, a microelectrode with a tip diameter on the order of several microns (e.g., 10 μm) is required to provide the required high spatial resolution. Although Kodera et al. [10] conducted a very thorough study of free chlorine anodic oxidation using commercially available electrodes (i.e., 1.6 mm platinum and gold disk, and 1.0 mm glassy carbon disk), these electrode diameters are over two orders of magnitude (e.g., 2,000 μm vs. 10 μm) too large for the intended application (i.e., localized metal corrosion and free chlorine consumption at metal surface).To address this constraint, the current research developed a simple fabrication method to construct a 10–15 μm tip diameter amperometric free chlorine microelectrode. de Beer et al. (1994) developed a platinum microelectrode to directly measure free chlorine biofilm penetration [14]. The platinum microelectrode has been modified to detect monochloramine at different applied potentials [15,16]. The platinum microelectrode showed a good selectivity and sensitivity toward free chlorine in water and inside biofilms; however, the pH interference was reported during free chlorine measurement [14]. Despite expecting pH changes within biofilm less than 1 pH unit, pitting corrosion may involve in high-pH waters [17] as well as acidic condition (i.e., pH 4) [18]; however, the pH effect on free chlorine measurement has not been properly evaluated or fully interpreted.
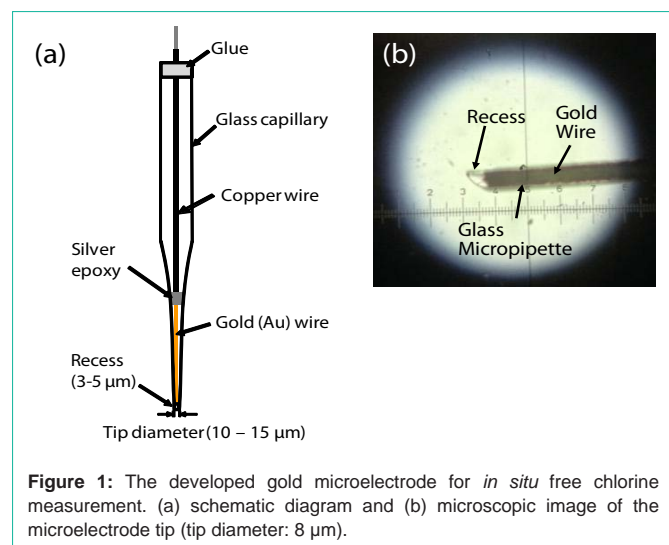
Figure 1: The developed gold microelectrode for *in situ* free chlorine measurement. (a) schematic diagram and (b) microscopic image of the microelectrode tip (tip diameter: 8 μm).

This study developed a highly selective gold microelectrode for free chlorine determination at the micro level according to the depth (μm). In addition to fabricating this novel microelectrode, a detailed evaluation was conducted to characterize its performance by evaluating pH interferences that may occur under drinking water conditions and conducting the optimal pH compensation process to determine the accurate free chlorine concentrations. Free chlorine and pH micro profiles were measured at the same depth and the pH compensation on free chlorine concentrations was conducted for accurate measurements. Other important properties of the electrochemical sensor including detection limit were also evaluated. Finally, the developed gold microelectrode was applied for in situ free chlorine measurement with high spatial resolution from the bulk to the metal surface to determine various kinetic parameters (i.e., reaction rate, flux, and surface concentration).

Materials and Methods

Gold microelectrode fabrication

In this study, a gold wire was used as a sensing material for free chlorine. Gold is known to have less oxygen interference in electrochemical analyses compared to the platinum microelectrode [15,19]. The fabrication procedure of the gold-based free chlorine microelectrode was similar to procedures of a previous platinum based microelectrode [14,16] except using an automatic puller. The gold (Au) wire (0.2 mm diameter, 99.99% purity, Aldrich Chemical Co.) was cut to a section of 4–5 cm in length, and connected to a copper wire using silver conductive epoxy (MG chemicals, 8331-14G). A heat gun (Wagner HT1000) was used to accelerate the curing process. Then the copper wire was inserted into a glass micropipette (Warner Instruments, 640815, O.D.: 1.5 mm, I.D.: 1.1 mm, 10 cm length) with 4 cm of the gold wire left in the open air. The tip of the gold wire was dipped into a 2M KCN solution to sharpen the tip by applying a voltage between the gold wire and a graphite rod (Sigma-Aldrich, 496545-60G, 3mm diameter, 150mm length). A voltage between 1–5V was applied by using AC power (Staco Energy Products Co., Model 3PN 1010B). The etching process consists of two steps: 1) etching the gold wire to reduce the original tip diameter to 20–30 μm and 2) tapering the tip by moving the gold wire up and down for 1–2 minutes for a final diameter of 5–10 μm. Then the etched gold wire was cleaned

by immersing the tip into DI water. A Flaming/Brown micropipette puller (Sutter Instrument Co., Model P-1000) was used to pull the glass micropipette and seal the etched gold wire. The parameters used to program the puller were Heat: 460, Pull: 120, Vel: 100, Delay: 1, Pressure: 500, and Ramp: 445. After pulling the pipette, the sealed area between the glass pipette and the etched gold wire was investigated under a microscope. A good seal is critical to the performance of the micro sensor. Finally, the tip of the microelectrode was beveled using a diamond beveller (Sutter Instrument Co., BV-10) at a 45° angle to expose the gold wire and etched again in the 2 M KCN with applied voltage of 1-2 V for 30 seconds to produce a recess(3–5 μm), which prevents any stirring effect during the profiling. After finishing the fabrication process, the microelectrode was rinsed sequentially with distilled water and acetone, and dried in open air for one hour. The finished microelectrode has a tip size between 10–15 μm with 3–5 μm recess in length (Figure 1).

Calibration and characterization of gold microelectrode

The newly fabricated gold microelectrode was polarized in a 0.83 mM carbonate buffer solution at pH 9.0 and 23 °C with an applied potential of +150 mV vs. Ag/AgCl reference electrode using a micro sensor multimeter (UNISENSE A/S, Denmark) overnight. After stable signals were achieved, the calibration of the free chlorine microelectrode was performed in the same buffer solution with various free chlorine concentrations (0–4 mg Cl_2/L). The applied potential was maintained at +150 mV during the test. The applied potential of +150 mV vs. Ag/AgCl was determined by cyclic voltammetry (CV) test and oxygen interference test (data not shown). The pH was adjusted between 6 and 9 using 1M HCl or 1M NaOH. All the calibration and characterization tests were conducted under a stirred condition at 23 ± 0.5°C. The free chlorine stock solution was prepared by adding a calculated amount of sodium hypochlorite solution and the free chlorine concentration was validated by a colorimetric test kit (Hach-8021) and a spectrophotometer (DR 5000, Hach) during the calibration.

Metal coupons preparation

Ductile iron (F33100, 65-45-12, Metal Samples) was used as a representative pipe material for drinking water distribution systems. Several pieces of ductile iron coupons (1.5 mm thickness × 1.2 cm width × 1.35 cm length) were cleaned using a combination of two American Society for Testing and Materials (ASTM) coupon wash procedures: G31-72 [20] and D2688-83 [21].

Micro profile measurements

Two profiling experiments were conducted in 0.83 mM carbonate buffer solution (BS) at high pH (9.0): without phosphate (experiment 1) and with phosphate of 3 mg P/L (experiment 2). The buffer solution contained 10 mg C/L of Dissolved Inorganic Carbon (DIC) and 4 mg Cl_2/L of free chlorine. Preliminary test showed pH 9.0 compared to pH 7.0 resulted in significant pH changes, over 1 pH unit from the bulk to the ductile iron surface (data not shown).100 mg Cl^-/L and 100 mg SO_4^{2-}/L were added as background ion concentrations. Free chlorine concentration micro profiles were measured using the developed gold microelectrode and pH micro profiles were measured using a commercial pH micro sensor (pH 10, UNISENSE A/S, Denmark). All micro profiles were measured from the bulk to the metal surface in a flow cell under a continuous flow condition
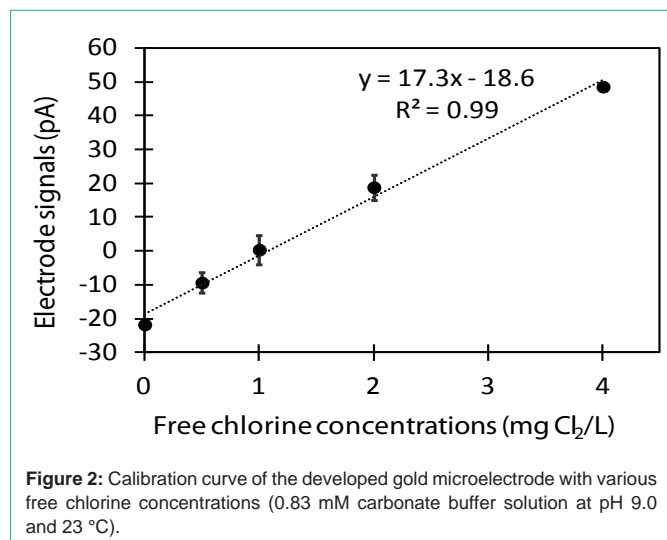
Figure 2: Calibration curve of the developed gold microelectrode with various free chlorine concentrations (0.83 mM carbonate buffer solution at pH 9.0 and 23 °C).

(15 ml/min) [15]. During the experiment, micro profile data of free chlorine concentrations and pH at the same depth were continuously collected with a computer controlled data acquisition and automated profiling set-up program (Unisense A/S, Denmark). Free chlorine concentrations in the flow cell was validated by a colorimetric test kit (Hach-8021) and a spectrophotometer (DR 5000, Hach) during the calibration.

Results and Discussion

Gold microelectrode calibration

A gold microelectrode was successfully fabricated with a tip diameter of 12.5 μm and a recess of 5 μm (Figure 1). Calibrations were conducted at pH 9.0 in 0.83 mM carbonate buffer solution and the y-axis intercept was in the range between 21–22 pA (avg. -21.8). The developed gold based microelectrode showed an excellent sensitivity towards the free chlorine with a slope of 17.3 pA/mg as Cl_2 (Figure 2). The response time was less than5 seconds and the electrode signals were not significantly changed over 30 minutes. The free chlorine concentrations were validated using the colorimetric method and the difference between microelectrode measurement and a spectrometric measurement was less than 0.5 %. The gold microelectrode was shown to have a shelf life of several months (every calibration curve was conducted before and after every profile) unless the tip is broken.

Stirring effect

The stirring effect of free chlorine microelectrode was investigated during the experiment. This reflects the electrode's signal stability and sensitivity when applied to simulated monitoring since the flow rate (and/or velocity) is also an important parameter in metal corrosion [22]. After using several gold microelectrodes to develop calibration curves under a constant stir rate, the results showed that the stirring effect was closely related to the length of the recess of the microelectrode. The decrease of the recess resulted in larger influence on the electrode signals under the stirring condition. 5–6 μm of recess showed the minimum effect on the fluctuation of the electrode signals during the calibration and profiling under the flow condition.

Limit of detection

At an applied potential of +150 mV vs Ag/AgCl, the Limit Of Detection (LOD) was determined using the obtained data and Eq. (1) [23].

$$C_L = Ks_b/b \tag{Eq. 1}$$

Where C_L is the detection limit, k is 3 (a parameter whose value is recommended by the IUPAC [24]), s_b is the standard deviation of the blank signal (current without monochloramine), and b is the slope of the calibration plot. The LOD was found to be 0.08 ± 0.0004 mg Cl_2/L.

pH effect on free chlorine measurements

The previous study on platinum microelectrodes showed highly pH dependent calibration curves during free chlorine measurements [14-16]. A gold microelectrode would have similar pH interference; therefore, several calibration curves were constructed under various pHs (7.0–10.0) in order to quantify and compensate the pH effect on the free chlorine concentration measurements. The results shows that the electrode signals (pA) increased as pH decreased (Figure 3). At lower pH, higher sloped calibrations were obtained (e.g., 57.1 pA/mg as Cl_2 at pH 7.0 vs. 7.7 pA/mg as Cl_2 at pH 10.0). This observation is consistent with the pH influence using a platinum microelectrode [14], indicating that both platinum and gold microelectrodes show a good selectivity to free chlorine; but both electrodes respond to HClO rather than ClO^-. Thus increasing the hydrogen ion concentration (lower pH) will also increase the electrode signal. However, the electrode signals in the absence of free chlorine were constant in all calibration curves at around 22±1 pA, indicating pH independent signals at 0 mg Cl_2/L. The results indicate that the pH gradients should also be measured along with free chlorine concentration measurements for accurate quantification.

Free chlorine reaction at ductile iron coupons

Figure 4 and 5 show the representative free chlorine concentration profiles and pH gradient profiles with two different bulk solutions without (experiment 1) and with phosphate (experiment 2). The metal surface depth was defined as 0 μm with negative distances into the bulk fluid. Figure 4 represented the pH decrease scenario near the ductile iron surface and Figure 5 showed the pH increase scenario near the ductile iron surface as examples for pH compensation during free chlorine measurements. A buffer solution containing 10
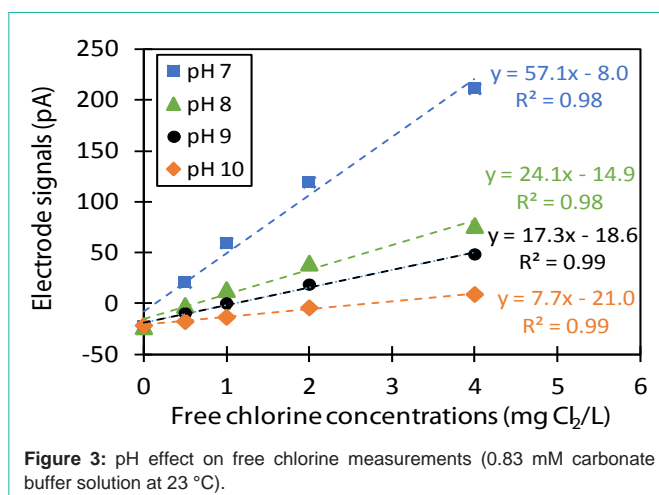

Figure 3: pH effect on free chlorine measurements (0.83 mM carbonate buffer solution at 23 °C).
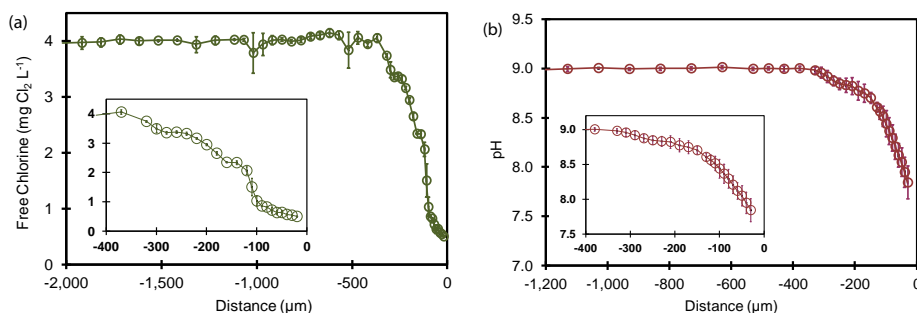
Figure 4: Measured free chlorine concentration and pH micro profiles (experiment 1).
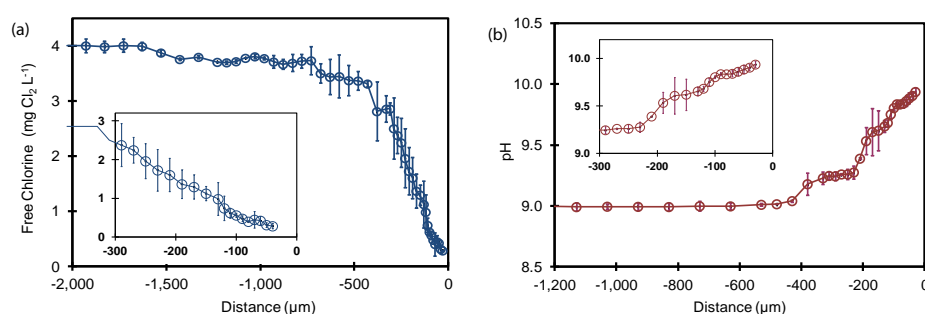

Figure 5: Measured free chlorine concentration and pH micro profiles (experiment 2).

mg C/L of DIC and 4 mg Cl$_2$/L of free chlorine at pH 9.0 showed the free chlorine Diffusion Boundary Layer (DBL) to be 370 μm and a dramatic decrease in free chlorine concentration from 4 mg Cl$_2$/Lafter the DBL to 0.51 mg 0.51 mg Cl$_2$/L at 20 μm above the metal surface (Figure 4). However, the free chlorine concentrations below 120 μm showed a concave shape to the metal surface (Figure 4(a)) indicating a significant reaction for free chlorine consumption. Given that free chlorine electrode signals increase as pH decreases and from the pH micro profiles near the metal surface (Figure 4(b)), the concave shaped free chlorine micro profile (Figure 4(a)) was a result of pH interference on the microelectrode performance, rather than a chlorine reaction with the surface. The increased free chlorine microelectrode signal from the pH changes resulted in an increase of free chlorine concentrations, which is incorrect. The pH micro profile in Figure 4(b) shows that pH significantly dropped from pH 9.0 in the bulk to pH 7.8 at 30 μm above the metal surface, indicating metal oxidation near the surface. The DBL for pH gradients was 330 μm from the metal surface, indicating that the free chlorine concentrations after 330 μm should be under pH compensation. On the other hand, in experiment 2 (buffer solution containing 10 mg C/L of DIC, 4 mg P/L of orthophosphate, and 4 mg Cl$_2$/L of free chlorine at pH 9.0), pH was increased near the metal surface from pH 9.0 in the bulk to pH 10 at 30 μm above the metal surface, indicating phosphate passivation (Figure 5(b)). The increased pH along with the depth to the metal surface means that the electrode signal decreases at a given free chlorine concentration, resulting in the false drop of free chlorine concentration in the profiles (Figure 5(a)). pH was changed from 430 μm above the metal surface, indicating that the pH compensation should be considered from 430 μm. In Figure 5(a), free chlorine concentrations also decreased approaching the metal surface. DBL was around 430 μm and after 130 μm above the metal

surface, the free chlorine concentration was dropped and also showed concave shapes due to the pH effect. The pH changes near the metal surface in Figure 4(b) and 5(b) indicates the electrochemical reactions by free chlorine consumption. The electrochemical reactions with metal as anode may be summarized as follows [25]:

$$M_{(s)} \rightarrow M_{(aq)}^{n+} + ne- \qquad (Eq. 2)$$

$$2H_2O_{(l)} \rightarrow 4H_{(aq)}^+ + O_{2(g)} + 4e- \qquad (Eq. 3)$$

If iron is under the electrochemical reaction which occurs during corrosion (i.e., metal ion release), the reaction will produce hydrogen ions (H+) in the presence of oxygen (i.e., air saturated water), resulting in pH decrease. On the other hand, pH drop at the metal surface indicate that the metal acts as a cathode (e.g., reduction). A rough estimate of the concentration gradient at the metal surface is based on the assumption that the chlorine concentration in the boundary layer changes linearly. Under this assumption, the flux can be calculated from Fick's first law [26]. Figure 6 shows the modified free chlorine concentration profiles after pH compensation and Table 1 compares kinetic parameters between original data and pH compensated micro profiles. The pH compensated free chlorine concentrations were obtained using a series of calibration curves depending on different pHs (Figure 3). Table 1 showed that, even though flux (J) is minimally different, reaction rate (k) and the estimated free chlorine concentration at the metal surface (Cs) were significantly affected by pH changes, indicating that the pH compensation is required for the accurate interpretation of free chlorine consumption.

Conclusion

A gold microelectrode was newly fabricated, characterized, and successfully applied for free chlorine micro profile measurement using ductile iron coupons by simulating water conditions found
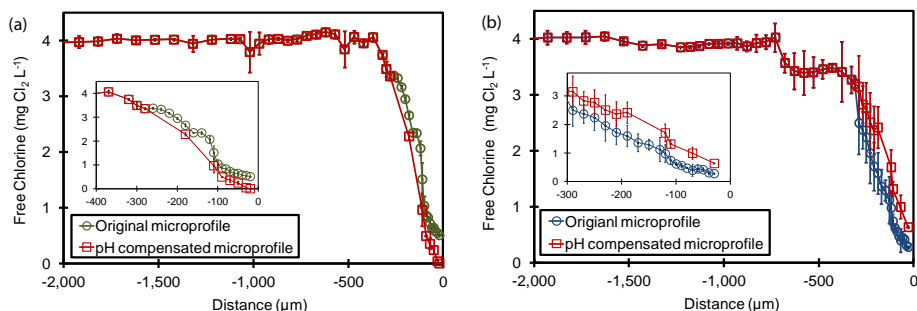
Figure 6: Modified free chlorine concentration profiles after pH compensation: (a) experiment 1 and (b) experiment 2.

Table 1: Comparison of kinetic parameters between before and after pH compensation in free chlorine measurement.

Application		DBL (µm)	J (mg Cl$_2$ cm^{-2} s^{-1})	k (cm s^{-1})	Cs (mg Cl$_2$ L^{-2})
Ex 1	Original profile	370	0.79 × 10^{-6}	2.17 × 10^{-3}	0.37
	Profile after pH compensation	370	0.76 × 10^{-6}	43.20 × 10^{-3}	0.02
Ex 2	Original profile	430	1.23 × 10^{-6}	51.56 × 10^{-3}	0.02
	Profile after pH compensation	430	1.31 × 10^{-6}	3.59 × 10^{-3}	0.37

in drinking water distribution systems. The developed gold microelectrode showed an excellent selectivity toward free chlorine; however, pH was shown to interfere with the gold microelectrode performance amperometrically. Simultaneous pH profiles measurement and consequent pH compensation were required for accurate free chlorine measurements. After pH compensation, important kinetic parameters like flux (J), reaction rate (k), and free chlorine concentration at the metal surface (Cs) were correctly determined. The results demonstrated that the gold microelectrode is a useful experimental tool for evaluating corrosion processes by quantifying free chlorine consumption by metal pipes. Combined with other microelectrodes that can measure oxidation-reduction potential, dissolved oxygen, and phosphate; the developed gold microelectrode will participate in elucidating the mechanism of corrosion and biocorrosion in the drinking water distribution system.

Acknowledgement

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