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Application of sensitive electrochemical sensing system for detecting bromate from disinfection process in desalination plant

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ABSTRACT

Chlorination is the most commonly used in disinfection to prevent from the bacterial growth in both intake and distribution pipelines or storage tanks. However, the disinfection treatment can result in an undesirable by-product, such a bromate (BrO_3^-), which is a suspected human carcinogen. Seawater has a high potential of BrO_3^- formation because of high bromide (Br^-) concentration (around 65 mg/L) which can be transformed by chlorination in disinfection process. Therefore, the measurement or monitoring of BrO_3^- formation is necessary. This study aims to apply the sensitive amperometric sensing system for detecting BrO_3^- in free chlorine condition. A linear dynamic ranged from 60 to 200 nM of BrO_3^- even in 28 μM free chlorine solution with a sensitivity of 108.8 μA/μM. The detection limit level of BrO_3^- was 38.6 nM and the limit of quantification value of BrO_3^- was 113.7 nM (at pH 7). This detection limit value was half of global guideline value for drinking water. The proposed technique had no noticeable interference to the sensing of BrO_3^- over various potentially interfering agents and other chlorinated disinfection by-products. The data measured by multilayered sensor system was in a good agreement for detecting BrO_3^- with validated data measured by using a conventional UV–vis spectroscopic method. As a final demonstration, the proposed amperometric sensing system would significantly contribute to the on-site detection of BrO_3^- concentration from chlorinating disinfection process within drinking water treatment plants, including desalination, and water quality monitoring applications.

1. Introduction

The global population growth and industrial expansion have provoked increasing water stress and lack of fresh water resources. These problems have led to greater consideration for alternative potable water and freshwater sources such as brackish water and seawater desalination [1,2]. Salt water desalination is no longer a limited or additional water resource in some Middle East countries such as Saudi Arabia and the United Arab Emirates and has become the main type of water treatment [3].

In desalination plants, disinfectants are applied during the pre-treatment process to prevent the growth of marine microorganisms and biofouling in the membrane process [4]. Then, during the post-treatment process of permeate water before the final water distribution system, disinfectants are applied to eliminate pathogens and to improve the desalinated water quality. Chlorination using $HOCl/OCl^-$ is the most commonly used disinfectant method for the pre-treatment of the feed water as well as post-treatment of the permeate water produced by the desalination system. In particular, the electro-chlorination process is a simple and new effective disinfection method for the desalination system, in which sodium hypochlorite (NaOCl) is generated on-site by the electrolysis of salt water [5]. However, this electrochemical disinfection process in the desalination system creates the undesirable by-products such as bromate (BrO_3^-), which presents a potential problem to human health [6].

BrO_3^- has been classified as a group B2 carcinogen and has an acceptable maximum contaminant level of 79 nM (10 μg/L) for BrO_3^- in global drinking water regulations to prevent the consumption of excess BrO_3^- [7–9]. BrO_3^- is a bromine-based oxyhalide formed as a disinfection byproduct during chlorination and has a high concentration in seawater (Br^-, average concentration 65 mg/L) [10]. The previous studies have demonstrated that on-site generation of chlorine using seawater for disinfection in desalination plant may occur the high concentration of BrO_3^-. Oh et al. observed the conversion rate of Br^- to BrO_3^- of 72% during the electrolysis of seawater for disinfection in the desalination process [11], and Bergmann et al. reported that the electrolysis of synthetic drinking waters containing Br^- results in BrO_3^- formation on boron-doped diamond anodes with yields of

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approximately 100% [12]. Therefore, the monitoring of BrO_3^- in produced water from water treatment plants involving seawater desalination plant is a critical point for public human health.

Several studies have been carried out in various countries to determine the concentration of BrO_3^- in seawater samples using ion chromatography (IC), IC with inductively coupled plasma mass spectrometry (IC-ICP/MS) [13,14], and spectrofluorometry [15]. Although these analytical methods are useful for determining BrO_3^-, they require many pre-treatment procedures. Because salt water contains high levels of chloride (Cl^-), it may be difficult to distinguish between Cl^- and BrO_3^- in the sample matrix [13]; in addition, these methods require complicated, expensive instruments, and are too much dilution for measurement and interference in the presence of salts. Therefore, the development of new, simple, rapid, and inexpensive methods for determining BrO_3^- is required for salt water and desalinated water samples. Hence, electrochemical determination techniques have been introduced that involve reasonable, uncomplicated, and fast procedures for detecting BrO_3^- in water samples [16–18].

In a previous study, a highly selective electrochemical sensor was developed for detecting BrO_3^- in water samples, using a layer by layer (LbL) technique with metalloporphyrin and polyelectrolyte [18]. The results using the sensor showed a wide concentration range of BrO_3^- in sodium acetate buffer solution of from 100 nM to 2.5 mM, with a sensitivity of 115.2 μA/mM, while a detection limit of 43 nM was achieved with good selectivity. In addition, the developed BrO_3^- sensors showed acceptable performance for detecting BrO_3^- in real water samples (tap water and bottled water). However, no reports have been presented on the detection of BrO_3^- using the electrochemical sensor in a seawater desalination system for water samples from raw water to produced water, involving the chlorination disinfection process.

The objective of this study is to evaluate the possibility of applying the highly selective electrochemical sensor design based on the multilayers sensor for detecting BrO_3^- in chlorinated water, assuming the desalination system involves a chlorination disinfection process. Especially, the pH value of product water for drinking after chlorination disinfection process was between 7 and 8. This pH range is also optimal BrO_3^- formation. Liu et al. [19] have demonstrated that they observed the highest BrO_3^- formation for pH range from 7 to 8 [19]. Thus, we determined the BrO_3^- using the proposed sensor at neutral pH condition. Therefore, the performance of the novel monitoring method for detecting BrO_3^-, including the sensitivity, selectivity, and stability of the method, was evaluated using the electrochemical sensing system.

2. Experimental

2.1. Microfabrication of amperometric BrO_3^- sensor

The microfabrication procedures for the metalloporphyrin, polyelectrolyte, and oxidized carbon nanotubes based layer by layer (LbL) assembled sensor were the same as those in our previous study [18].

2.2. Apparatus

The electrochemical analysis data were obtained using a computer controlled potentiostat (Autolab PGSTAT302N, Netherland), managed by the General Purpose Electrochemical System (GPES) (version 4.9) software for detecting BrO_3^- in water samples. An amperometric sensor was connected to the potentiostat using a USB type cable (Fig. 1). For all the analyses, we used 10 mL as the sample volume. Cyclic voltammetry (CV) with a scan rate of 100 mV/s was employed, unless otherwise specified. All electrochemical measurements for BrO_3^- were performed at room temperature. The morphological structure changes of the modified electrodes in the presence of free chlorine was characterized by field emission scanning electron microscopy (FE-SEM), and the energy dispersive X-ray spectrometric (EDS) microanalyses were carried out on a representative multilayers sensor surface area (FESEM/EDS, JSM-7600F, JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCALAB 250 spectrometer with a Mg Kα X-ray source (Thermo Scientific, MA. USA).

2.3. Chemicals and analytical methods

All chemicals and solvents used were of analytical reagents grade without further purification and were purchased from Sigma-Aldrich (St. Louis, MO, USA). The supporting electrolyte, sodium acetate buffer (pH 7.0), was purchased from Sigma-Aldrich (S2404, St. Louis, MO, USA). De-ionized (DI) water (resistivity $> 18\ M\Omega\ cm^{-1}$) produced by the NANOpure Diamond Ultrapure water system (Barnstead, Newton, MA, USA) was used for preparing all aqueous solutions and for rinsing. Hydrochloric (HCl) acid and sodium hydroxide (NaOH) were used for pH adjustment.

The analysis of disinfection by-products (DBPs) effects, such as trihalomethanes (THMs) and haloacetic acid (HAA), for selectivity of the amperometric BrO_3^- sensors was performed according to the EPA Method 501.1 and 552.2 with dibromochloromethane (DBCM), bromodichloromethane (BDCM), bromoform, and bromoacetic acid (BAA) in permeate water or salt water. THMs and HAA were analyzed using gas chromatography–mass spectrometry (GC–MS) coupled with purge and trap technology (Agilent Technologies, Santa Clara, CA, USA).

The proposed amperometric sensors as a novel monitoring method were employed to analyze the BrO_3^- concentrations in the permeate water samples, and the result was validated by taking simultaneous measurements with an Ultraviolet-visible (UV–vis) spectrophotometer (DR6000, HACH, USA) [20]. Various concentrations (60 nM – 1 μM) of BrO_3^- solution (20 mL) were prepared by dissolving potassium bromate ($KBrO_3$) in DI water. After producing a 5 mL volume of BrO_3^-, the solution was decanted from a 15 mL volume test tube. A 5 mL quantity of freshly prepared 0.5% potassium iodide (KI) solution in 0.1 N HCl was added to the BrO_3^- solution. Any color change was noted. The presence of BrO_3^- was verified by a shift in color from light yellow (low concentration of BrO_3^-) to purple (high concentration of BrO_3^-). The absorbance of the samples was taken at a wavelength of 352 nm using a UV–vis spectrophotometer.

2.4. Analytical quality control

All the samples were detected in triplicate, and the mean was calculated to indicate the result. The instrument detection limit of the BrO_3^- concentration was calculated as [(3 × the standard deviation of the blank response) divided by (the corresponding slope of the calibration curve)]. The limit of quantification (LOQ) value for the proposed BrO_3^- sensor was calculated as [(10 × the standard deviation of the blank response) divided by (the corresponding slope of the calibration curve)] [21].

3. Results and discussion

3.1. Effect of supporting electrolyte pH and the presence of free residual chlorine

The pH value of the supporting electrolyte solution is a major factor for the electrochemical sensor [18,22]. The pH value can influence the amperometric response of the multilayer BrO_3^- sensors. As shown in Fig. 2, the multilayers sensors were measured between pH 6 and pH 10 in the 0.2 M sodium acetate buffer (SAB) in the presence of 200 nM BrO_3^-. The maximum response and constant stability were obtained in a neutral condition (pH 7) without free residual chlorine. Thus, the neutral condition might be acceptable for detecting BrO_3^- using the proposed multilayers sensor. Furthermore, the pH value may affect in the presence of free residual chlorine in supporting electrolyte solution [23]. Free residual chlorine is common as a hypochlorite anion (ClO^-)