Short communication

Effect of humic acid in surface water on the electrochemical performance of bromate detection

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HIGHLIGHTS

- The interference effect of HA could be decreased by the increase of pH value (> 9).
- The addition of $FeCl_3$ could be recovered the proposed BrO_3^- sensor performance.
- The limit of detection for BrO_3^- was 8.9 µg/L in 0.1 mg/L HA solution.
- The proposed BrO_3^- sensor has acceptable stability in the presence of HA condition.

ARTICLE INFO

ABSTRACT

One of the problems of BrO_3^- detection using the electrochemical method, such as a cyclic voltammetry (CV) is that it is impressionable to interferences from Humic acid (HA). The objective of this study was to determine the effect of HA on electrochemical detection of BrO_3^- using metalloporphyrin-based multilayer sensor under different pH conditions in the presence of $FeCl_3$. The effect of HA interference on chemical interaction at the electrode surface in the presence of $FeCl_3$ was determined based on Fourier transform infrared spectrum. CV was used to measure the concentration of BrO_3^- in the solution containing HA with or without different concentrations of $FeCl_3$. Results of CV revealed a dynamic linear concentration range of BrO_3^- from 10 to 100 µg/L in 0.1 to 1 mg/L of HA solution (pH 9). The detection limit for BrO_3^- concentration was 8.9 µg/L in 0.1 mg/L of HA solution.

1. Introduction

The disinfection is one of the most important processes for the production of safe drinking water. Water disinfection is essential to remove or deactivate of pathogenic microorganisms for public health, especially when raw water is supplied from natural waters such as a river, reservoir, groundwater, and seawater [1,2]. The chlorination and ozonation are the most commonly used disinfection processes in the pre-treatment of raw water as well as post-treatment for product water. However, these disinfection processes in water treatment plants can produce undesirable by-products such as bromate (BrO_3^-) which is potentially carcinogenic and neurotoxic to human health problems [3,4]. BrO_3^- has an acceptable maximum contaminant level of 10 µg/L in global drinking water regulations to prevent excessive consumption of BrO_3^- [5–7].

The conventional BrO_3^- monitoring method was intensive labor and lots of time-consuming. Moreover, bulky instruments involved in

ion chromatography (IC) [8], IC with inductively coupled plasma mass spectrometry [9], liquid chromatography-mass spectrometry [10], gas chromatography-mass spectrometry [11], and spectrofluorometry [12] require large volumes of water samples to determine the concentration of BrO_3^-. Also, many pre-treatment procedures such the preparation of high levels of chloride at sample matrix exchange sites [13] are involved with highly expensive tools for maintenance. Therefore, new methods that can provide simple, rapid, and inexpensive determination of BrO_3^- are needed for environmental samples. Electrochemical techniques have been introduced as reasonable, uncomplicated, and fast procedures to detect a wide range of BrO_3^- in water samples [14–18]. These previous studies have focused on finding new sensing platform to analyze refined water samples.

However, components of natural waters are more complicated than water produced by water treatment process. Nature water contains various inorganic ions (metals, salt) and organic compounds (natural organic matter (NOM)). Previous studies on the detection of BrO_3^- in

water samples have provided electrochemical results under different conditions, including the effect of pH, dissolved oxygen, various inorganic ions, and organic compounds on results [14,15,17,18]. However, humic acid (HA), one NOM that is abundant in natural water systems, can seriously interfere with the precise and efficient determination of BrO_3^-, thus limiting the practical application of electrochemical techniques in real natural water samples or under complex conditions. The interference of HA on electrochemical detection of metal ions in waters has already been reported [19–22]. Liu et al. and Gismera et al. demonstrated that Cu(II) can cause significantly decreasing of interfering effects on the electrochemical response of HA [19,20,22]. Gao et al. have reported that the electrochemical behaviour of As(III) using Fe_3O_4 is better than gold to overcome HA interference [21]. However, the previous studies were hard to find a discussion of the interference about HA affects the electrochemical response of BrO_3^-.

Therefore, the objective of this study was to determine the effect of HA on the electrochemical determination of BrO_3^- under different pH conditions. In addition, the effect of HA interference on the concentration of BrO_3^- in the presence of $FeCl_3$ was evaluated using the electrochemical technique, and Fourier transforms infrared (FT-IR) spectrum. Also, one of the significant properties of the proposed BrO_3^- sensor was examined in the presence of HA conditions for the stability verification. The results will offer valuable understandings into the general impacts of natural organic compounds on BrO_3^- determination using electrochemical methods.

2. Material and methods

2.1. Chemicals and reagents

All chemicals and reagents of analytical grade were purchased from Sigma-Aldrich (St. Louis, MO, USA). They were used without further purification. Analytical grade potassium bromate ($KBrO_3$) was also purchased from Sigma-Aldrich. Iron(III) chloride ($FeCl_3$) solution (100 mg/L) was prepared by dissolving $FeCl_3$ in de-ionized (DI) water. A predetermined concentration of bromate (BrO_3^-) solution was completed with supporting electrolyte (0.2 M sodium acetate buffer (SAB), pH 7) for daily preparation. Humic acid (HA) stock solution (1000 mg/L) was prepared by dissolving 100 mg solid HA in 100 mL of DI water. DI water (resistivity > 18 MΩ cm^{-1}) from NANOpure Diamond Ultrapure water system (Barnstead, Newton, MA, USA) was used to prepare all aqueous solutions. It was also used for rinsing. Hydrochloric (HCl) acid solution (0.1 N) and sodium hydroxide (NaOH) were used for pH adjustment.

2.2. Electrochemical measurements

Electrochemical analysis data were obtained using a computer controlled potentiostat (Autolab PGSTAT302N, Netherland) managed by GPES (version 4.9) software for detecting BrO_3^- in water samples. BrO_3^- sensor was connected to the potentiostat using a universal serial bus type cable. For all analyses, the sample volume was 10 mL. 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.

2.3. Fabrication of the bromate sensor

The detailed fabrication procedures for the metalloporphyrin, polyelectrolyte, and oxidized multiwalled carbon nanotubes (OMWCNTs) based layer by layer (LbL) assembled bromate sensor was the same as those in our previous studies [23,24]. As briefly explained, the fabrication process of the sensor for detection bromate as follows: the OMWCNTs modified screen-printed carbon chip (SPCC) was alternately dipped in 2 mM iron(III) porphyrin (Fe(III)P) and 2 mM poly

(sodium 4-styrenesulfonate) (PSS) solution for 30 min each, followed by rinsing with 0.2 M SAB solution (pH 7.0) and drying under N_2 gas. The process was repeated to deposit layers of Fe(III)P with PSS on the OMWCNTs modified SPCC and stored in a dark condition until any electrochemical analysis.

2.4. Instrumentation

Dissolved organic carbon (DOC) was evaluated with a total organic carbon analyzer (TOC-Vcph, Shimadzu, Japan). Before measurements, all samples were filtrated through a polycarbonate filter (pore size, 0.4 μm; Millipore). HA was verified by UV–vis spectrophotometer (DR6000, HACH, USA) with absorbance at 254 nm (Supporting information, Table S1). Fourier transform infrared spectroscopy (FT-IR) analysis was performed with a Tensor 27 IFS-66/S (Bruker Optics, Billerica, MA, USA).

2.5. Preparation for FT-IR analysis

Samples (HA, HA–Fe(III)P, and HA–$FeCl_3$) were prepared in batch experiments. Fe(III)P layer sensor chip was dipped in 0.2 M SAB with 10 mg/L HA solution (pH 7). It was carried out at room temperature for 12 h. To comprehended a whole complex between HA and $FeCl_3$, 30 mg/L $FeCl_3$ solution was added to 10 mg/L HA solution (0.2 M SAB, pH 7) and kept at room temperature for 12 h. The precipitated HA-$FeCl_3$ sample was centrifuged and HA-Fe(III)P samples were washed with DI water several times to remove residual material. These products were dried in an oven at 70 °C for 12 h.

2.6. 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)].

3. Results and discussion

3.1. Effect of pH values in the presence of HA for detecting BrO_3^-

To enhance the detection ability of the BrO_3^- sensor, the experimental parameter was optimized using CV. The effect of pH value with different concentrations of HA was evaluated. Results are shown in
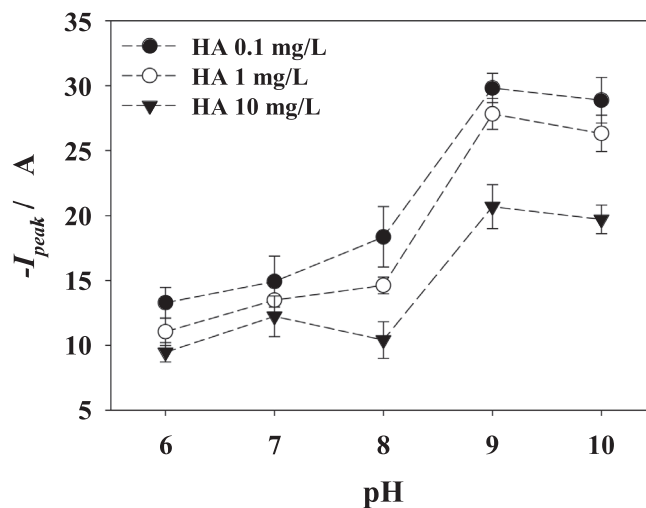

Fig. 1. Effects of pH values in the presence of HA on electrochemical response signal for BrO_3^-.