Efficient electrochemical detection of geosmin in environmental waters

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ABSTRACT

A new electrochemical sensor based on molecular imprinting technology was developed, for rapid and sensitive detection of the odorous substance geosmin (GSM) in water. In this method, the molecularly imprinted membrane was successfully modified on the surface of the glassy carbon electrode (GCE) using the electrochemical deposition method. In the presence of the target analyte (geosmin), the target analyte occupies the detection site and the detection signal will attenuate. As the concentration of the target analyte increases, the attenuation of the electrical signal becomes more pronounced. This sensor can quantitatively detect geosmin at concentrations as low as 5 ng/L, which is currently the lowest limit of detection (LOD) for GSM detection by an electrochemical sensor in reported studies. The modified GCE provided an analytical curve for GSM detection in the range of 5–200 ng/L.

Key words | detection, electrochemical sensor, geosmin, molecular imprinting technique

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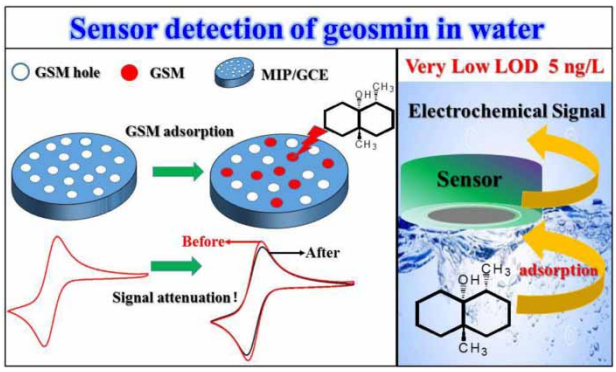
HIGHLIGHTS

- A new electrochemical sensor based on molecular imprinting technology was developed to detect geosmin in water.
- This sensor can detect geosmin at concentrations as low as 5 ng/L.
- The modified GCE provided an analytical curve for geosmin detection in the range of 5–200 ng/L.

GRAPHICAL ABSTRACT



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INTRODUCTION

The quality and safety of water supplies have recently been drawing more attention. Odorous substances present in drinking water are one of the primary complaints of water supply plants (Roccaro *et al.* 2007; Tekerlekopoulou & Vayenas 2008; Eaton & Sandusky 2009). Among the odorous substances, geosmin (GSM) is one of the most common odors present in water supplies and is the culprit behind the majority of customer complaints regarding their drinking water (Izaguirre & Taylor 2004; Li *et al.* 2012). GSM is an odorous substance characterized by a soil odor and a musty taste derived from a few species of fungi and blue-green algae (Zhou *et al.* 2011; Sun *et al.* 2014). GSM is widely found in water environments, and because of its pungent soil odor even at trace levels (<10 ng/L), even small amounts of GSM present in drinking water can result in unpleasant odors (Xue *et al.* 2011). The human odor value of GSM is 1–10 ng/L. The determination of the olfactory threshold is related to specific environmental factors, such as temperature, so the reported values in the literature vary (Yu *et al.* 2007). The smell and odor in drinking water not only affect the potability and the quality of the drinking water, but can also result in losses for the aquaculture industry (Smith *et al.* 2008; Li *et al.* 2010; Morales-Valle *et al.* 2010). The mutagenicity and hepatotoxicity caused by MIB and GSM have been pointed out, but possible health hazards have not yet been reported (Gagné *et al.* 1999; Huang *et al.* 2007). Although such odorous substances are non-toxic, it still results in an overall distrust in the safety of drinking water and doubts regarding its quality (McDowall *et al.* 2009; Xue *et al.* 2016). Therefore, rapid and effective detection of GSM in water is critical for determining the safety and quality of drinking water (Battocchi *et al.* 2010).

Currently, the sensory method is used for preliminary detection of the type of odorous substance present in the water, and if necessary, the quantitative analysis and identification by chemical and instrumental analysis. Sensory analysis mainly includes olfactory threshold detection, olfactory analytic hierarchy, and smell-level description (Ömür-Özbek *et al.* 2007; Vallod *et al.* 2007). The instrumental analysis method mainly uses gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS) (Zhang *et al.* 2018), chemiluminescence, and other methods for analysis. GC-MS is an effective method for the analysis of trace organics (Watson *et al.* 2000; Saito *et al.* 2008; Parinet *et al.* 2011; Cheng *et al.* 2015). This method has a good selectivity and a high sensitivity, and has been widely used all over the world. However, these methods also require the use of expensive instruments, well-trained operators, and have complicated sample pretreatment and testing processes. Therefore, it is crucial to develop a simple and fast method for the detection of GSM (Braga *et al.* 2012). However, the current research on the detection of GSM using electrochemical methods is very limited. Son *et al.* (2015) prepared a bio-electronic nose with human performance for the monitoring of soil odor in water pollution. Human olfactory receptors were used for the specific recognition of GSM. Under optimal experimental conditions, the limit of detection (LOD) for GSM was 10 ng/L. Braga *et al.* (2012) used an electronic tongue system based on the use of polymer sensors, impedance measurements, and multivariate data analysis in order to identify and quantify water samples containing GSM. The analog controller performs data analysis on the capacitance data provided by the electronic tongue to make an optimal linear fit curve. Even at the optimal experimental conditions, the LOD of GSM was 25 ng/L (Braga *et al.* 2012). Kamata *et al.* (2019) electrochemically detected GSM using an embedded platinum nanocarbon film electrode formed by co-sputtering with unbalanced magnetrons, combined with a high-performance liquid chromatography test system. The detection range of GSM was 0.1–1,000 μg/L, and the LOD was 100 ng/L (Kamata *et al.* 2019). Li *et al.* (2019) developed a method for the detection of two algal metabolites, geosmin (GSM) and 2-methylisoborneol (2-MIB) using a competitive displacement technique based on molecular imprinted polymers (MIPs) and fluorescent tags. The LOD of GSM is 69 μg/L at the optimal experimental conditions.

Although the research discussed above has achieved results in the sensor monitoring of GSM, the preparation process of the sensor is relatively complicated, time-consuming, and costly; or the detection limit is relatively high.

Therefore, it is necessary to develop a method for detecting GSM with a sensor that is simple to prepare and operate with a low LOD.

Generally, when the contaminant is adsorbed on the electrode, a redox reaction will happen in the electrochemical system, and there is a direct connection between contaminant concentration and electrical signal. Because it is difficult for GSM to be electrochemically oxidized and the oxidation potential is high, it is difficult for electrodes to obtain such a high electrochemical window. In this study, we first established an electrochemical sensor to quantitatively detect GSM by an indirect method based on molecular imprinting techniques (Vasapollo *et al.* 2011; Lian *et al.* 2015; Wackerlig & Schirhagl 2016). Potassium ferricyanide is often used as a detection probe in general electrochemical experiments because of its high detection activity. When the holes with the shape of GSM molecules are gradually blocked by the target GSM molecules, potassium ferricyanide cannot reach the electrode surface, causing the value of the electrical signal to begin to decrease. The higher the GSM concentration, the more obviously the current signal value decreases (shown in Figure S1, Supplementary Material). Electrochemical impedance (EIS) was used to characterize the electron transfer of the electrodes. The parameters of the sweep speed, eluent, bath time, proportion of template molecules to monomers, and the elution time were all optimized using cyclic voltammetry (CV). We developed a novel sensor that is simple to prepare, with a low detection limit, which can effectively detect GSM in water environments. This provides the foundation for a novel method that can be utilized for the rapid monitoring of GSM in water environments in the future.

EXPERIMENTAL MATERIALS AND METHODS

Chemicals

GSM of standard (purity ≥98%) was purchased from Wako (Japan). Potassium chloride and potassium ferricyanide were both purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All chemicals were of analytical grade and prepared using ultrapure water from a Millipore system with a resistivity of 18.2 MΩ•cm.

Apparatus and procedure

EIS was performed on different electrodes using an Ivium-Vertex electrochemical workstation. EIS was conducted in a 1.0 M potassium chloride (KCl) solution containing 5 mM $K_3[Fe(CN)_6]$. The open circuit voltage was 0.2 V, the frequency range was 1.0×10^6–0.1 Hz, and the amplitude was 5 mV. All electrochemical measurements were performed using a CHI 660E electrochemical analyzer (Shanghai Chenhua Co., Ltd, China). A conventional three-electrode configuration was used. The prepared electrode was used as the working electrode. An Ag/AgCl (3 M NaCl) electrode and a Pt wire were utilized as the reference and auxiliary electrodes, respectively.

Preparation of GCE electrode by molecular imprinting

The GCEs were polished before modification using 1, 0.3, and 0.05 μm Al_2O_3 polishing powders subsequently and then washed by ultrasonic cleaning in secondary distilled water, anhydrous ethanol, and secondary distilled water for 5 min in turn. The GCE was then dried using nitrogen. The dried GCE was placed in an o-phenylenediamine-GSM solution (o-phenylenediamine is a functional monomer commonly used in molecularly imprinted experiments) connected to a three-electrode system, and a molecularly imprinted film was deposited on the electrode surface using the CV method (Wackerlig & Lieberzeit 2015; Tan *et al.* 2016). After the drying process, the electrode was eluted in an eluent (Ji *et al.* 1999). Finally, the prepared molecularly imprinted (MIP) GCEs were sealed and stored until further use.

Detection of GSM

The electrode parameters were optimized using electrodeposition, and then the conditions such as sweep speed, eluent, and bath time were further optimized. KCl was used as an electrolyte solution during GSM detection. Quantitative analysis of GSM was carried out using the CV method under optimal conditions. The potential interval was set as 0–0.8 V, with a time interval of 0.001 s, quiet time of 2 s, scan rate of 0.1 V/s and sensitivity of 1×10^{-5} A/V.

Pretreatment of real water environmental samples

The real water environment samples used for this experiment were tap water samples obtained from the China University of Geosciences (Beijing). All of the samples were filtered through a 0.45 μm polytetrafluoroethylene membrane to remove physical impurities. A specific amount of GSM was then accurately weighed and dissolved in groundwater or tap water to create a GSM stock solution with a final concentration of 10 μg/L. Samples were then diluted to different concentrations and tested for parallel recovery.

RESULTS AND DISCUSSION

Characterization of different modified electrodes

EIS was used to investigate the electronic transfer kinetics of the different electrodes. The impedance spectra of GCE before and after elution are shown in Figure 1. The measurements were performed on a 1 M KCl solution containing 5 mM $K_3[Fe(CN)_6]$. A frequency range of 0.1 Hz–1,000 kHz was used. Changes in the interfacial properties, such as the electron-transfer resistance, of the modified electrodes are illustrated by the obtained impedance spectrum. The Randle's equivalent circuit was used to interpret the electrochemical impedance spectra (Lv *et al.* 2014), as shown in the inset of Figure 1. A solution resistance (*Rs*) in series with a parallel combination of double-layer capacitance (C_{dl}) and a charge transfer resistance (*Rct*) in series with a Warburg impedance (*W*) were observed. The bare GCE has a small semicircular domain (*Rct* ≈ 4,500 Ω), indicating a higher electron-transfer resistance (black curve) for the redox pair $Fe(CN)_6^{3-}$ dissolved in the electrolyte solution. The uneluted molecularly imprinted (NIP) electrode has a larger semicircular diameter (*Rct* ≈ 32,000 Ω) (red curve) as compared with the bare GCE. Compared with the NIP, the eluted MIP has a relatively small semicircular diameter (*Rct* ≈ 6,000 Ω), indicating that the MIP membrane was successfully modified on the electrode surface.

Electrochemical behavior of different modified electrodes

In order to further illustrate the variation of the electron transfer before and after MIP membrane modification, $K_3[Fe(CN)_6]$ was used as a sensitive probe in order to investigate the electrochemical properties before and after electrode modification. The electrochemical behavior of the 5 mM $K_3[Fe(CN)_6]$ probe on a bare GCE, a non-molecularly imprinted membrane electrode (NIP), an MIP/GCE, and an NMIP/GCE is shown in Figure 2. It is clear that the NIP/GCE and the non-eluting molecularly imprinted membrane electrode (NMIP/GCE) completely failed to detect the signal, indicating that a molecularly imprinted membrane modified on GCE was sufficient to achieve an insulation effect. The current value of the MIP/GCE is

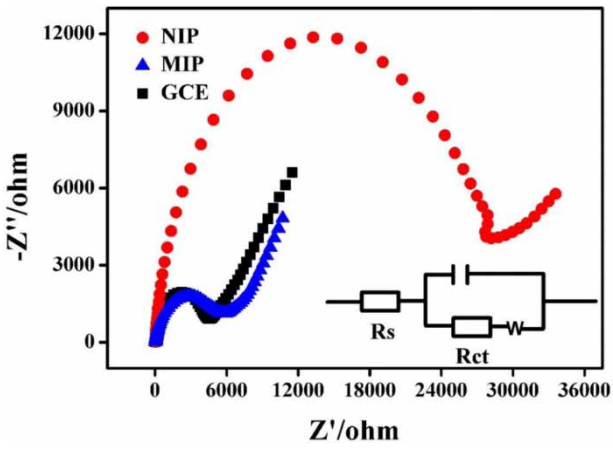

Figure 1 | EIS diagram of different electrodes. The inset shows the equivalent electrical circuit.

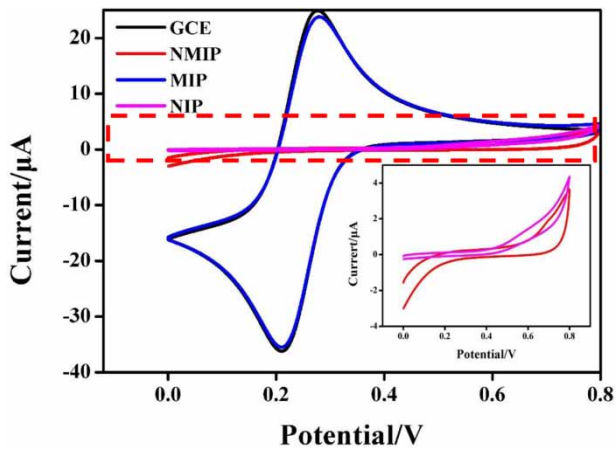

Figure 2 | Detection of GCE, NMIP, MIP and NIP in potassium ferricyanide.

similar to that of the bare electrode, indicating a good elution effect. For the bare GCE, a pair of redox peaks of $Fe(CN)_6^{3-}$ was observed, and the peak separation (ΔEp) was only 65 mV. This indicates that the GCE has good performance.

Optimization of experimental conditions

Effect of scan rate

A series of cyclic voltammograms of 5 mM $K_3[Fe(CN)_6]$ on the MIP/GCE at different sweep rates is shown in Figure 3(a). The peak current shows an increasing trend as the scanning speed increases. The peak current was observed to vary linearly with the scan rates in the range of 10–200 mVs^{-1}, as shown in Figure 3(b). The relationship between the peak current (Ipa/Ipc) and the scan rate can be expressed by the following equations:

$$Ipa\,(\mu A) = 2.72v^{1/2}\,(V^{1/2}s^{-1/2}) - 0.57\,(\mu A)(R^2 = 0.9985) \quad (1)$$

$$Ipc\,(\mu A) = -3.09v^{1/2}\,(V^{1/2}s^{-1/2}) - 2.96\,(\mu A)(R^2 = 0.9996) \quad (2)$$

These equations suggest that the mass transfer phenomenon in the electrodes was primarily diffusion-controlled. Additionally, when the scan rate increased from 10 to 200 mV s^{-1}, the ΔEp of the redox probe remained unchanged for the MIP/GCE.

The effect of the number of laps

The thickness of the molecularly imprinted membrane can be controlled by the number of polymerization cycles used during the process of electropolymerization. The film thickness directly affects the electrochemical performance of the sensor. In this experiment, we compared the elution times and the sensor response sensitivity of the template molecules of a MIP/GCE sensor prepared using 10, 15, 20, 25 and 30 cycles. As the number of scanning turns increased, the response current of the sensor was shown to increase, as shown in Figure 4(a). When the number of polymerization cycles is 20–25 laps, the current growth rate is fastest. When the number of polymerization cycles is greater than 25, more sites for GSM trapping can be obtained, however, the excessively thick blotting membrane results in an increase in membrane resistance, which reduces the overall electrocatalytic activity of the membrane electrode, and which extends the elution time of the template molecule accordingly. However, if the number of polymerization cycles is insufficient, this results in incomplete film formation. Therefore, the number of cycles was chosen to be 25 laps.

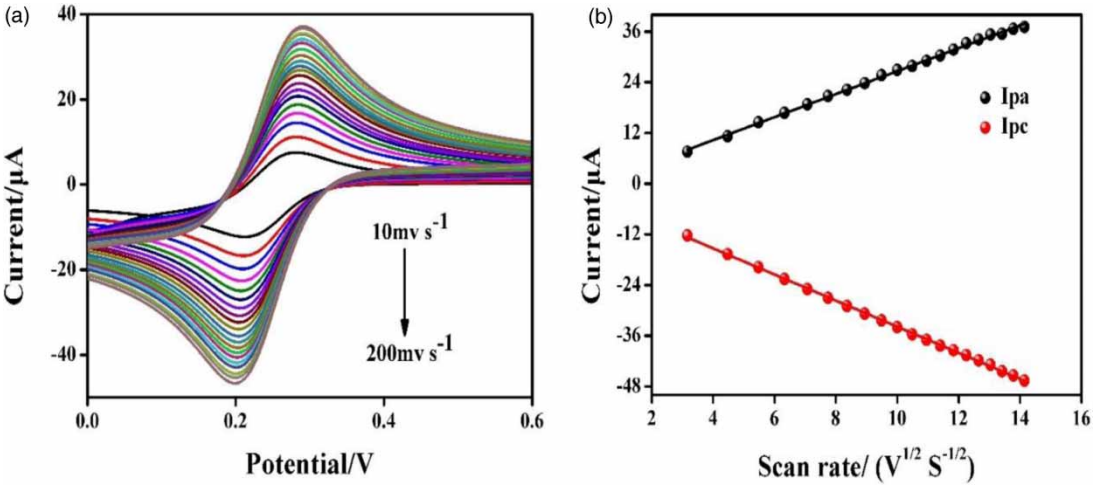

Figure 3 | (a) Effect of scan rate on the MIP/GCE. The scan rates from inner to outer were 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190 and 200 mV s^{-1}. (b) Plots of the peak currents vs the scan rates in (a).

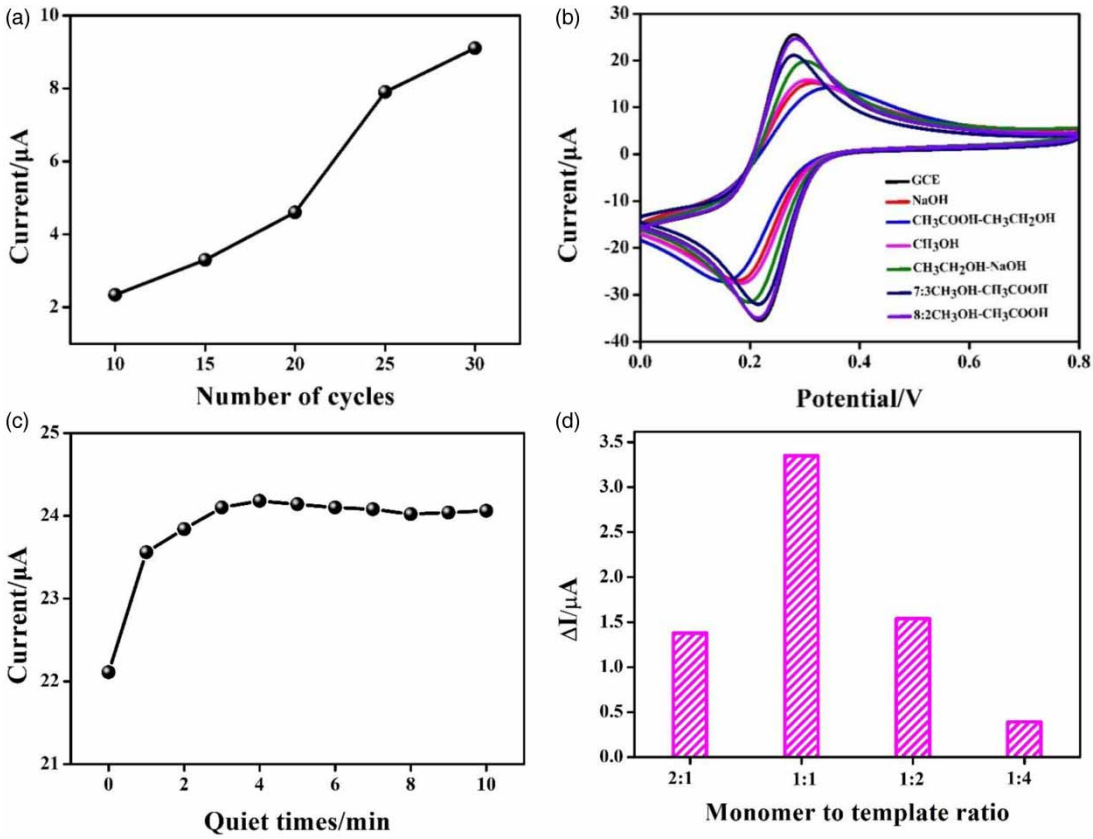

Figure 4 | (a) Effect of the number of scanning turns on the MIP/GCE electrodes at 10, 15, 20, 25 and 30. (b) Effect of different eluents. (c) Effect of warm bath time. (d) Effect of the ratio between template molecules and monomers.

Effect of eluent

According to the solubility properties of the template molecules, the effects of several elution solutions including sodium hydroxide, acetic acid–ethanol, methanol, ethanol–sodium hydroxide, 7:3 methanol–acetic acid, and 8:2 methanol–acetic acid were analyzed (Guo *et al.* 2017; Zhou *et al.* 2017). NMIP/GCE was separately immersed in the above eluents for 15 min, and the resulting elution effect was evaluated by comparing the peak type and peak current value of the MIP/GCE sensor in the $K_3[Fe(CN)_6]$ solution. As shown in Figure 4(b), when the electrode was soaked with sodium hydroxide, acetic acid–ethanol, methanol, and ethanol–sodium hydroxide and was scanned in the $K_3[Fe(CN)_6]$ solution, the peak current value was relatively small, indicating that template molecules cannot be eluted and that these are not suitable for use as eluents. When 8:2 methanol–acetic acid was used as the eluent, an excellent elution effect was observed and an obvious response current value was achieved. Therefore, 8:2 methanol–acetic acid was selected as the elution solution for the template molecule.

Effect of contact time

The relationship between the enrichment time of the MIP/GCE sensor in a 200 ng/L GSM solution and the peak current of $K_3[Fe(CN)_6]$ was studied. As shown in Figure 4(c), an increase in the enrichment time of the MIP/GCE in the GSM solution resulted in an obvious increase in the peak current of $K_3[Fe(CN)_6]$. It is clear that the response current became stable when the enrichment time was larger than 4 min. Therefore, the optimal enrichment time of the imprinted electrode in the GSM solution was determined to be 4 min.

Effect of the ratio between template molecules and monomers

The ratio of template molecules to functional monomers is an important factor in the preparation of molecularly imprinted membranes. If the concentration of the functional monomer is too large, the imprinted film that forms on the surface of the electrode may be uneven and easily fall off; however, if the concentration is too low, the recognition site that forms on the surface of the electrode is small, which affects the imprinting effect. The concentration ratio of the functional monomer and the template molecule prepared in the experiment in the polymerization bottom liquid was 2:1, 1:1, 1:2, 1:4, respectively, and electropolymerization was carried out. As shown in Figure 4(d), a concentration ratio of 1:1 of the template molecule to the functional monomer results in the formation of a non-conductive blotting film, which is easy to elute, and the value of the redox current is the largest after elution. The best polymerization ratio of the experimental selection of template molecules:functional monomer = 1:1 (c/c).

Effect of elution time

As shown in Figure S2 (Supplementary Material), with the elution time increased, the response current value on the MIP/GCE was not shown to significantly change. This indicates that the elution effect of the eluent is good. The template molecules in the polymer film are almost completely dissolved, and the number of specific imprinted pores in the polymeric membrane is increased. Finally, 5 s was selected as the optimal elution time in this experiment.

ANALYTICAL RESULTS

Calibration curves

To obtain a greater sensitivity and response signal, CV measurement was performed in order to detect different concentrations of the GSM standard. The peak current of GSM and the natural logarithm of the GSM concentration were shown to have a good linear relationship in the range of 5–200 ng/L with an LOD of 5 ng/L, as shown in Figure 5. The linear calibration curve can be described with the following equation: $Ip\ (\mu A) = 0.5208 \ln C + 0.1013$ (μA) $(R^2 = 0.991)$. The results obtained using the MIP/GCE sensor in this study were compared with those that have been previously reported in the literature (shown in Table 1). The sensor developed in this study had a comparatively lower LOD in general than that of the previously reported detection methods, which suggests that the MIP/GCE is a promising electrochemical sensor for the *in situ* detection and direct monitoring of GSM. Figure 6 illustrates the specific mechanism of GSM detection on MIP/GCE.

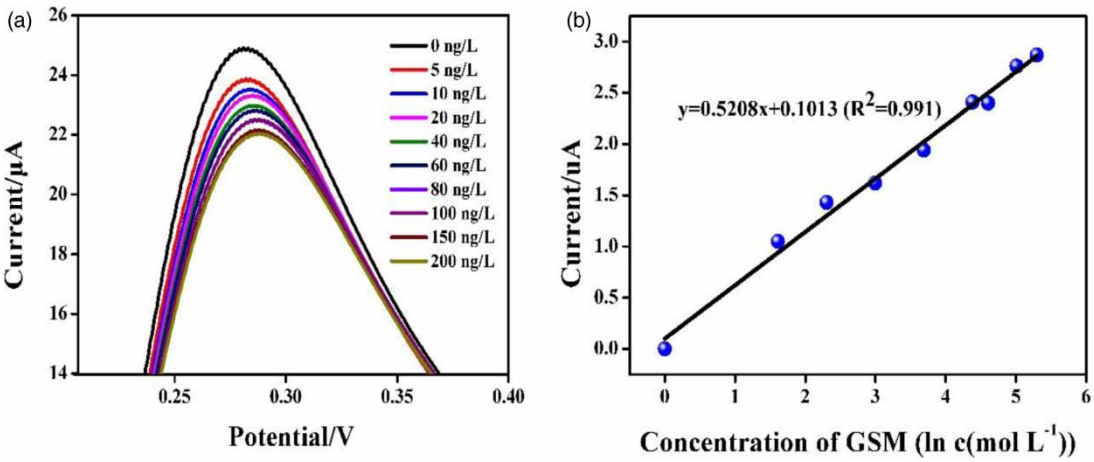

Figure 5 | (a) CV of the MIP/GCE for 0.2 M pH 5.2 HAC/NaAC containing various concentrations of GSM: 0, 5, 10, 20, 40, 60, 80, 100, 150 and 200 ng L^{-1}, respectively. (b) Plots of current versus different GSM concentrations.

Table 1 | Comparison of electrochemical methods of detecting GSM

Method	Linear range (ng L^{-1})	LOD (ng L^{-1})	Reference
GC-MS	5–1,000	1.13	Cheng *et al.* (2015)
PCA-ET	–	25	Braga *et al.* (2012)
swCNT-FET	0.1–100	10	Son *et al.* (2015)
HPLC-ECD with Pt-C	100–106	100	Kamata *et al.* (2019)
MIP-GSMS/MAA/TRIM1	–	69,000	Li *et al.* (2019)
MIP/GCE	5–200	5	This work

GSM detection in the presence of interfering constituents

The influence of different ions known to be present in the water environment on the detection of GSM by MIP/GCE sensors was investigated. According to the water quality standards of groundwater, the chloride concentration in water is $\leq$ 250 mg/L, and the four ions typically present in groundwater, K^+, Na^+, Ca^{2+}, Mg^{2+}, were selected. A GSM solution was prepared with a concentration of 80 ng/L with an ion concentration of 0.25 mg/mL of each of the selected ions. A GSM-alone solution of 80 ng/L was prepared according to the same method to be used as a test control. The electrochemical detection method used was the CV method. As shown in Figure S3 (Supplementary Material), (a) is the peak current difference corresponding to the detection of 80 ng/L GSM by the MIP/GCE modified electrode. The peak current differences of (b)–(e) correspond to the presence of 0.25 mg/mL of K^+, Na^+, Ca^{2+}, and Mg^{2+}, respectively. In the presence of any of the inorganic ions, current changes resulted of 19.4%, 15.8%, 4.2%, 19.4%, and 18.2%, respectively. According to these results, the observed influence of several ions on the MIP/GSM sensor is relatively small.

Detection of GSM in real water environmental samples

The proposed electrochemical method was applied to detect GSM in actual tap water using the optimized conditions. The analytical results are shown in Table 2. The recovery of GSM in actual tap water was between 93.78% and

Table 2 | Recovery during detection of GSM in water environment samples

Sample	Added/ng L^{-1}	Found/ng L^{-1}	RSD (%)	Recovery (%)
Tap water	80	76.48	2.95	95.60
		75.02		93.78
		79.47		99.34
	150.00	158.64	3.36	105.76
		158.63		105.75
		168.04		112

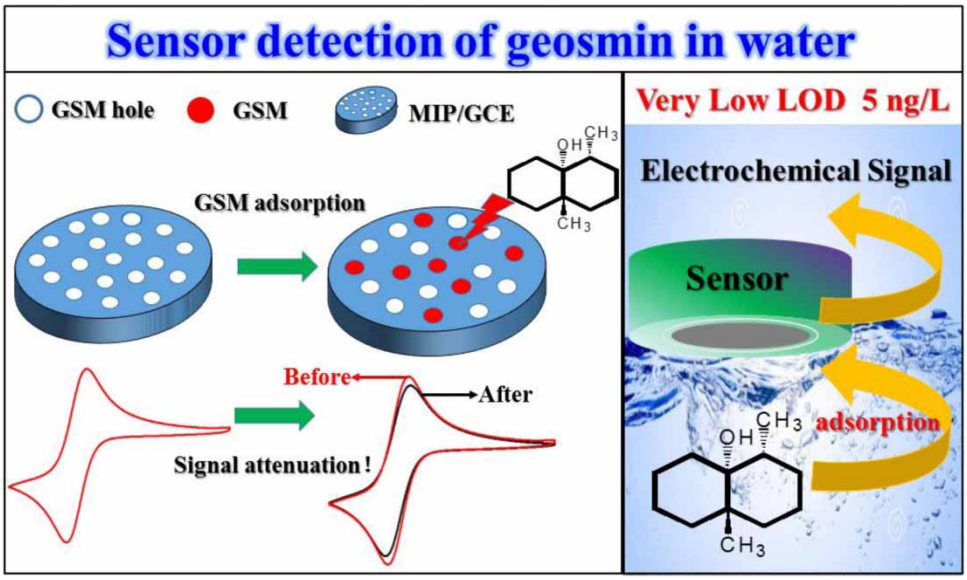

Figure 6 | The mechanism of the sensor detection of GSM in water.

112% with an RSD of less than 3.36%. The good recovery and RSD suggests that the detection of GSM in a real water environment using MIP/GCEs is feasible.

CONCLUSIONS

We have successfully developed a novel MIP/GCE electrochemical sensor by modification of a GC electrode surface through a simple molecular imprinting technique to detect aquatic GSM. This sensor was shown to be simple to prepare with a fast response time. In additions, it exhibits a broad linear response to a GSM concentration range of 5–200 ng/L. Crucially, this sensor was sensitive with a detection limit as low as 5 ng/L. According to our current knowledge, it is the lowest LOD that can be achieved by electrochemical detection. Finally, we employed this sensor to successfully detect GSM in water environment samples.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/ws.2020.119.

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