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Electrochemical sensor based on chlorohemin modified molecularly imprinted microgel for determination of 2,4-dichlorophenol

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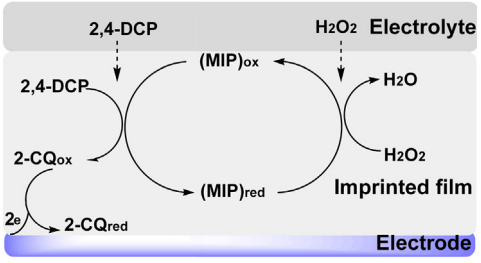
HIGHLIGHTS

- A new molecularly imprinted polymer for 2,4-dichlorophenol is synthesized.
- The polymer can imitate the dehalogenative function of the natural enzyme.
- The polymer modified electrode shows a linear amperometric response to 2,4-dichlorophenol.
- The imprinted sensor exhibits good stability, high specificity and acceptable reproducibility.

GRAPHICAL ABSTRACT



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ABSTRACT

A newly designed molecularly imprinted polymer (MIP) was synthesized and successfully utilized as a recognition element of an amperometric sensor for 2,4-dichlorophenol (2,4-DCP) detection. The MIP with a well-defined structure could imitate the dehalogenative function of the natural enzyme chloroperoxidase for 2,4-DCP. Imprinted sensor was fabricated in situ on a glassy carbon electrode surface by drop-coating the 2,4-DCP imprinted microgel suspension and chitosan/Nafion mixture. Under optimized conditions, the sensor showed a linear response in the range of 5.0–100 μmol L^{-1} with a detection limit of 1.6 μmol L^{-1}. Additionally, the imprinted sensor demonstrated higher affinity to target 2,4-DCP over competitive chlorophenolic compounds than non-imprinted sensor. It also exhibited good stability and acceptable repeatability. The proposed sensor could be used for the determination of 2,4-DCP in water samples with the recoveries of 96.2–111.8%, showing a promising potential in practical application.

1. Introduction

2,4-Dichlorophenol (2,4-DCP) is extensively used as herbicides, fungicides and insecticides in agriculture [1]. It can cause faint, itch, comedo, anemia and has been associated with the occurrence of cancer [2,3]. Methods for 2,4-DCP detection have included UV spectrophotometry [4], gas chromatography [5], high-performance liquid chromatography [6,7] and biosensors [8,9]. Spectrophotometry and chromatography, however, suffer from low selectivity, long analysis time intervals, high cost and possible production of secondary toxic compounds [10]. Meanwhile, the molecular recognition materials in biosensors including microorganisms, enzymes, receptors and antibodies are intrinsic difficult in the practical application due to their instability.

Molecularly imprinted polymers (MIPs), recognized for their versatile adsorption and catalytic properties, are a promising material as the recognition element or modifying agent in the preparation of sensors [11]. As a new kind of enzyme mimics, MIP have a lot of advantages such as moderate cost, ease of preparation and long-time stability comparing to natural antibodies and

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enzymes [12]. So they have been considered as the perfect replacement of biological affinity receptors [13]. More importantly, MIP can be endowed with catalytic activity by incorporating a metalloporphyrin as the catalytic center [14–18]. However, it still needs to overcome the reported difficulties related to the integration of the MIP with the transducer. Hybrid materials prepared with MIP and carbon nanotubes [19,20] have been employed with the same purpose.

This paper used methacrylic acid (MAA) as a functional monomer and chlorohemin as a comonomer to synthesize a molecularly imprinted polymer with catalytic activity for specifically recognizing the template and replacing the natural enzyme chloroperoxidase. Prior to the polymerization the template could act with the carboxyl groups (—COOH) of both the monomer and the comonomer to form relatively strong hydrogen bonds by the chlorine/oxygen atom of 2,4-DCP molecule. Thus chlorohemin could be covalently linked to the polymer network during the polymerization. The incorporation of chlorohemin efficiently introduced chemically active sites into the MIP for catalytic reaction and the anchoring of target molecule, which was able to catalyze the oxidative dehalogenation of the template 2,4-DCP. To overcome the difficulty in transuding the recognition event, biopolymer chitosan (CS) was selected for the immobilization of MIP on electrode surface because of its excellent membrane-forming ability, biocompatibility, high mechanical strength and enjoy preparation and detection in aqueous system with a long period stability [21,22]. Moreover, Nafion was chosen to improve the MIP fixation, based on its chemical, mechanical and thermal stability, as well as cation selectivity and high conductivity [23,24]. The designed sensors showed excellent performance characteristics for the determination of 2,4-DCP.

2. Experimental

2.1. Reagents

Chlorohemin (iron(III)-protoporphyrin IX), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP), zobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EGDMA), and 2-methacrylic acid (MAA) were all purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Chitosan (93.4% deacylated) and Nafion® 1100 (5%) were purchased from Sigma–Aldrich Co. Ultrapure water obtained from a Millipore water purification system (≥18 MΩ, Milli-Q, Millipore) was used in all assays. All other reagents, including H_2O_2 and dimethylsulfoxide (DMSO), were of analytical grade and used as received. Phosphate buffered solution (PBS, pH 7.0) was prepared using 0.2 M Na_2HPO_4 and 0.2 M KH_2PO_4.

2.2. Apparatus

Differential pulse voltammetric (DPV) measurements were performed with a three-electrode system comprising a platinum wire as auxiliary electrode, a saturated calomel electrode (SCE) as reference and an MIP microgel modified glassy carbon electrode as working electrode. These electrodes were connected to a CHI 660D electrochemistry workstation (Shanghai CH Instruments, China). The AC impedance of the MIP film was measured with the Autolab PGSTAT302 electrochemical analyzer (Metrohm, Switzerland). IR spectra were recorded on a Nicolet 6700 Fourier transform-infrared (FT-IR) spectrometer (Madison, USA). Scanning electron microscopic (SEM) images were obtained using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan). The pore parameters and the surface areas of the MIP were measured with an ASAP 2020 accelerated surface area and porosimetry analyzer (Micromeritics, USA). The pH measurements were made with an MP 230 pH meter (Mettler-Toledo, Switzerland).

2.3. Synthesis of 2,4-DCP imprinted microgel

2,4-DCP imprinted microgel was prepared as follows: 0.5 mmol of 2,4-DCP, 4 mmol of MAA and 0.02 mmol of chlorohemin were dissolved in a mixed solvent composed of dimethylsulfoxide (DMSO) and acetonitrile (7:1, v/v) in a small beaker. The mixture was purged with nitrogen for 15 min and sealed with multiple layers of parafilm. Then the beaker containing the solution was placed in a refrigerator for 24 h under 4 °C. Afterwards, 4 mmol of cross-linker (EGDMA) and 113 mg of initiator (AIBN) were quickly added to the solution, and the mixture was purged again for 10 min. Thermal polymerization reaction was then carried out in an oven at 65 °C for 24 h. After being triturated carefully, the resultant polymer was collected on a nylon filter (0.27 μm pore size) and washed with methanol and acetic acid (9:1, v/v) for three times to remove the template, and the 2,4-DCP imprinted microgel (MIP microgel) was obtained. A non-molecularly imprinted polymer (NIP) was also prepared in an identical manner but in the absence of 2,4-DCP.

2.4. Fabrication of 2,4-DCP imprinted sensor

Glassy carbon electrode (GCE, 3 mm in diameter) was polished to a mirror-like finish with 1.0, 0.3, and 0.05 μm alumina slurry (Beuhler), followed by rinsing thoroughly with doubly distilled water. The electrode was successively sonicated in 1:1 nitric acid, acetone and doubly distilled water, and allowed to dry at room temperature. 6 μL mixture of 1% chitosan in 0.8% acetic acid and 0.5% Nafion in acetonitrile in a volume ratio of 6:4 was then coated on the pretreated GCE, which was evaporated at room temperature. 10 μL of 2.0 mg mL^{-1} 2,4-DCP imprinted microgel suspension, obtained by dispersing 20 mg imprinted microgel in 10 mL 0.1 M pH 7.0 PBS, was dropped on the chitosan/Nafion modified GCE and dried in air. Finally, 6 μL of acetonitrile solution of 0.5% Nafion was directly coated at the surface of MIP/chitosan/Nafion modified GCE and stored at 4 °C prior to use. As control, non-imprinted sensor was prepared and treated in the same manner by using the NIP suspension. The entire process of construction was shown in Scheme 1.

3. Results and discussion

3.1. Characterization of 2,4-DCP imprinted microgel

The infrared spectra of the MIP (a), NIP (b) and MIP microgel after 2,4-DCP extraction (c) were shown in Fig. 1, respectively. The

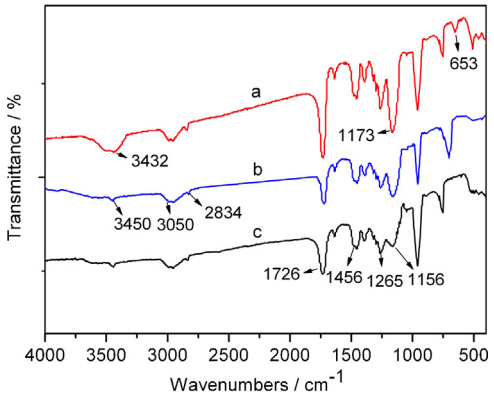
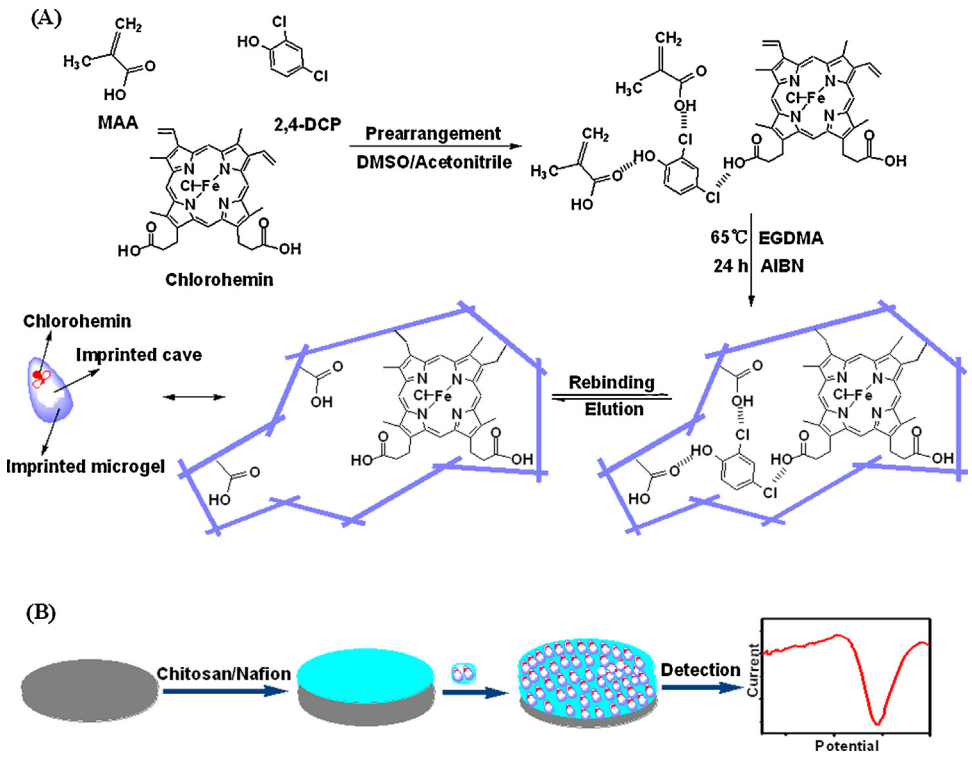


Fig. 1. FT-IR spectra of MIP (a), NIP (b) and MIP microgel after extracting 2,4-DCP (c).



Scheme 1. Schematic representation of (A) preparation of 2,4-DCP imprinted microgel and (B) construction of imprinted sensor.

MIP showed a strong O—H band centered at 3432 cm^{-1} (typical of phenylic acid), a C—O band centered at 1173 cm^{-1} due to the C—O stretching and a weak O—H band centered at 653 cm^{-1} from the O—H panel flexural in the fingerprint region. These characteristic peaks could be evidence of 2,4-DCP linkage in the polymer. A broad band in 3450 cm^{-1} attributed to O—H vibration from backbone of hemin and the adsorbed water was observed in the infrared spectrum of NIP, which also showed a broad band assigned from 3050 to 2834 cm^{-1} due to the C—H stretching of $-CH_2-$ and $-CH_3$ of the polymeric chain and the backbone of hemin. Other bands were common for MAA, hemin and EGDMA, for example, 1726 cm^{-1} corresponded to C=O stretching; 1456 cm^{-1} corresponded to $-CH_2-$ and $-CH_3$ deformation, and 1156 cm^{-1} corresponded to the C—O vibration [25]. After 2,4-DCP was extracted, the characteristic bands attributed to the 2,4-DCP at 653, 1173 and 3432 cm^{-1} disappeared in the spectrum of MIP microgel, demonstrating the efficient removal of the template with the mixture of methanol and acetic acid at 9:1 (v/v).

SEM was employed to capture the detailed morphology of the 2,4-DCP imprinted microgel and NIP. Both the MIP and NIP microgels were uniform microspheres (Fig. 2). Compared with MIP microgel, the surface of NIP microgel was irregular and agglomerate, indicating the ordered cross-linking reaction and imprinting effect of MIP microgel. The specific surface area of the microgel was determined with BET apparatus to obtain the desorption curve, for which 0.5 g of the MIP or NIP microgel was placed in a sample holder and degassed under N_2-gas atmosphere at 80 °C for 10 h. The total pore volume and average pore diameter for the microgel were determined by the multipoint Barrett–Joyner–Halenda (BJH) adsorption model. The specific surface area, total pore volume and average pore diameter of the MIP microgel were 222.104 $m^2\ g^{-1}$, 0.821 $cm^3\ g^{-1}$ and 147.881 Å, respectively. While these parameters in the case of the NIP microgel were 154.7 $m^2\ g^{-1}$, 0.236 $cm^3\ g^{-1}$ and 79.85 Å, respectively, strongly indicating that the MIP microgel was suitable for 2,4-DCP binding.

3.2. Electrochemical behavior of imprinted sensor

DPV assays were performed to evaluate the catalytic activity of the 2,4-DCP imprinted microgel. The testing relied on the reduction current of the oxidative dehalogenation product of 2,4-DCP catalyzed by MIP in the presence of hydrogen peroxide.

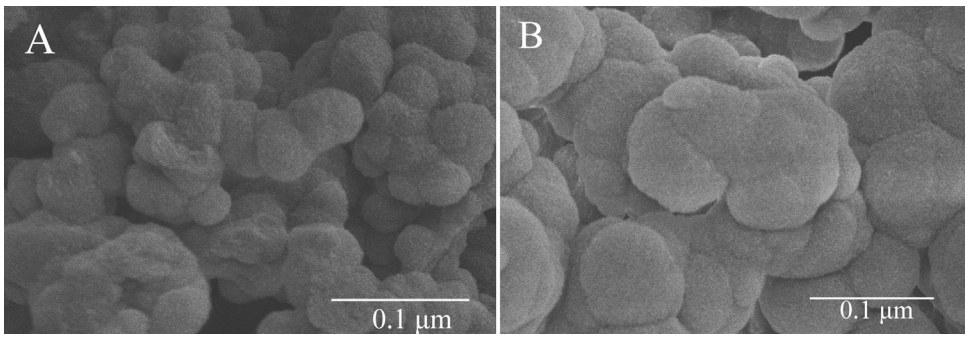


Fig. 2. SEM micrographs of (A) MIP and (B) NIP microgel.

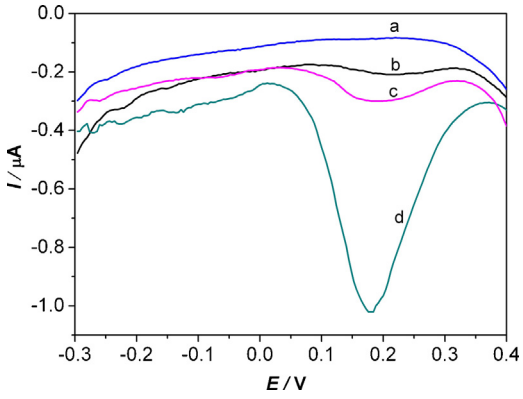


Fig. 3. DPV responses of GCE modified with NIP microgel in (a) absence and (b) presence of 1.0 mmol L^{-1} 2,4-DCP, MIP microgel in (c) absence and (d) presence of 1.0 mmol L^{-1} 2,4-DCP. Electrolyte: 0.1 mol L^{-1} PBS (pH 7.0) containing 100 μmol L^{-1} of H_2O_2. Scan rate: 0.01 V s^{-1}.

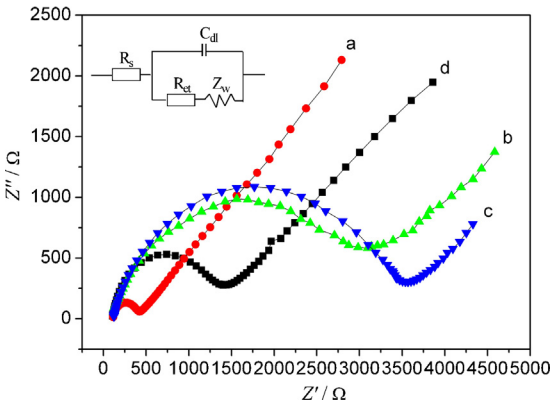
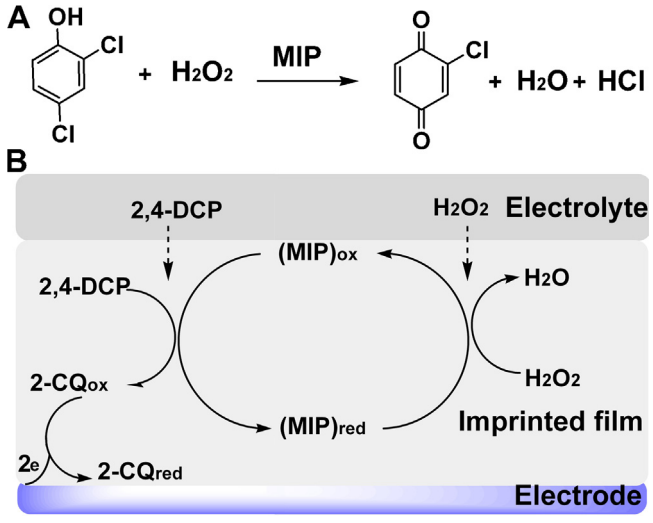


Fig. 4. Electrochemical impedance spectra of bare GCE (a), NIP modified GCE (b), MIP modified GCE before (c) and after (d) extracting 2,4-DCP in 5 mmol L^{-1} $Fe(CN)_6^{4-/3-}$ solution containing 0.1 mol L^{-1} KCl. Inset: equivalent circuit used to model impedance data in the presence of redox couples.

The NIP microgel modified electrode in the absence and presence of 2,4-DCP did not show any response (Fig. 3a and b), since the NIP microgel did not possess the cavities that would provide the selective active sites for 2,4-DCP binding. In the absence of 2,4-DCP, the MIP microgel electrode showed a small response (Fig. 3c), which could be attributed to the residual template molecule. After adding 2,4-DCP to the detection solution, a significant increase of the reduction current was observed (Fig. 3d), suggesting that the 2,4-DCP imprinted microgel acted as both an efficient electrocatalyst with an action similar to that of chloroperoxidase and a recognition element to bind 2,4-DCP. The catalytic principle could be relying on the oxidative dehalogenation of 2,4-DCP in the presence of hydrogen peroxide with the imprinted microgel as catalyst. As shown in Scheme 2, the hemin unit in the immobilized microgel could be oxidized by hydrogen peroxide and then re-reduced by the 2,4-DCP bound in the MIP microgel, and the 2,4-DCP was converted to 2-chloro-1,4-benzoquinone (2-CQ), which is electrochemically active and could be reduced at the electrode surface to produce the DPV response [13,26].

Electrochemical impedance measurement (EIS) is an effective method to probe the interface properties of modified electrodes [27]. In EIS, the semicircle diameter equals to the electron-transfer resistance (R_{et}). Fig. 4 shows the impedance spectra of different



Scheme 2. Schematic representation of (A) oxidative dehalogenation of 2,4-DCP catalyzed by MIP and (B) the proposed mechanism for detection of 2,4-DCP with the imprinted sensor.

modified electrodes in 0.1 M PBS (pH 7.0) including 5 mmol L^{-1} $Fe(CN)_6^{4-/3-}$ as probe, using a 5-mV alternating voltage, a bias potential of 0.250 V and over the frequency range 100 kHz to 100 mHz. A modified Randles equivalent circuit (inset of Fig. 4) was chosen to fit the measured results. The arc at high frequency section of the bare GCE (curve a) shows a value of R_{et} to be 220 Ω. The R_{et} values at NIP (curve b) and MIP (curve c) microgel modified electrodes increase remarkably, demonstrating that the membrane formed a compact structure and acts as a definite kinetic barrier for the electron transfer. However, after the template was removed, the MIP microgel modified electrode showed a great decrease of the interfacial resistance (curve d), which could be attributed to the cavity of the removed 2,4-DCP molecule, forming some channels for probe to arrive at the electrode surface. These appearances could be concluded that the presence of 2,4-DCP during the polymerization led to an imprinted microgel that mimicked the natural chloroperoxidase in the catalysis of the oxidative dehalogenation of 2,4-DCP.

3.3. Optimization of sensor preparation and detection conditions

The amount of MIP microgel for preparation of sensor was firstly optimized by coating 10, 20 and 50 μg of 2,4-DCP imprinted microgel suspension on the working electrode to exam the change of DPV peak current with the increasing reaction time. As shown in Fig. 5A, all these sensors showed the peak current increase in initial 10 min, while the sensor prepared with 20 μg microgel showed quick increase and the maximum reduction current, indicating the most suitable communication between the reaction product 2-CQ and the electrode surface. Lower reduction currents were observed for the sensors prepared with 10 μg or 50 μg of imprinted microgel. This might be attributed to the lack of communication or redundant reaction product that was absorbed into the microgel pores to limit the diffusion. The reaction time of 10 min indicated the recognition kinetic of the imprinted film to the target molecule. As a result, a time of 10 min incubation was taken for all the experiments.

Hydrogen peroxide plays a key role in the catalytic reaction of peroxidases, and can inhibit the catalytic reaction at high concentration [28,29]. Fig. 5B shows the dependence of the sensor response on the H_2O_2 concentration in the range 10–300 μmol L^{-1} at a fixed concentration of 2,4-DCP. With the increasing H_2O_2 concentration the current variation (Δi) increased, and the maximum electrochemical signal was obtained at 100 μmol L^{-1}. This optimum concentration was chosen for subsequent experiments.

The pH of the detection solution affects the degree of ionization and speciation of dichlorophenol, which subsequently leads to a

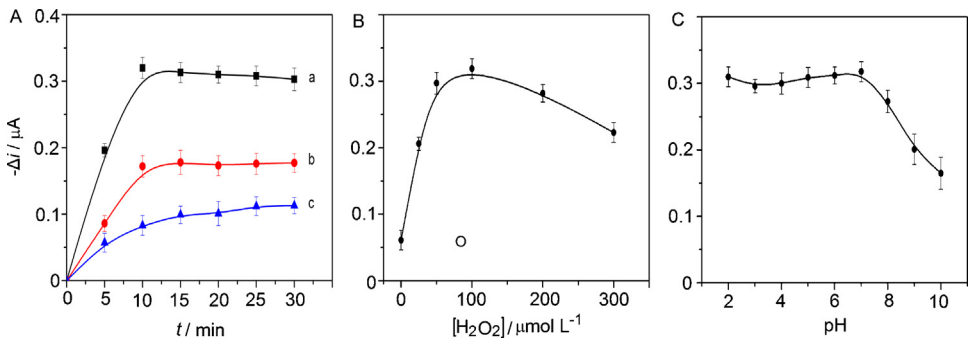


Fig. 5. Effects of (A) time at 20 (a), 10 (b) and 50 μg (c) MIP microgel, (B) H_2O_2 concentration and (C) pH on current variation. Electrolyte: 0.1 mol L^{-1} pH 7.0 PBS containing 100 μmol L^{-1} H_2O_2 at 40 μmol L^{-1} [2,4-DCP].

change in the electrochemical response of the imprinted sensor. Fig. 5C shows the binding of 2,4-DCP to MIP microgel in different pH values from 2.0 to 10.0. The reduction current changed slowly with the increasing pH from 2.0 to 7.0 and reached the maximum value at pH 7.0. An opposite result was obtained with further increase in pH. The high response at pH lower than 7.0 could be explained by the existing form of 2,4-DCP with a pK_a value of 7.98 [30]. When the pH was higher than 8.0, both MIP and 2,4-DCP were negatively charged, which led to their repulsion. Moreover, the stability of the sensor also became worse at high alkalinity. So the detection solution at pH 7.0 was selected.

3.4. Performance of the imprinted sensor

Under optimized conditions, the proposed sensor showed a linear response to [2,4-DCP] in the concentration range of 5.0–100.0 μmol L^{-1}, described by the equation Δi (μA) = −0.0668 + 0.0067 [2,4-DCP] (μmol L^{-1}, r = 0.9951) with a relative standard deviation (RSD) lower than 5% (n = 3) (Fig. 6). The detection limit, estimated as the 2,4-DCP concentration yielding an amperometric signal equal to three times the peak-to-peak noise of the baseline, was 1.6 μmol L^{-1}. Compared with other sensors for 2,4-DCP, the proposed sensor provided similar sensitivity and linear range. Although the biosensor constructed with the natural enzyme showed a lower limit of detection (0.38 μmol L^{-1}) [8], the MIP microgel as recognition element possessed the advantages such as moderate cost, ease of preparation and long-time stability.

The stability and repeatability of the imprinted sensor were estimated by repeating test of 40 μmol L^{-1} 2,4-DCP. It did not showed significant change in the response after 30 measurements. The peak current retained 91.2% of its initial value after 30-day storage at ambient temperature, indicating a satisfactory stability. The relative standard deviations (RSDs) of 4.3% and 4.6% were obtained in 30 measurements with the same sensor and three parallel measurements with five sensors, respectively, indicating acceptable fabrication repeatability.

3.5. Selectivity of the imprinted sensor

Three chlorophenols possessing analogous structures, including 2,6-DCP, 2,4,6-TCP and PCP at the same concentration (40 μmol L^{-1}) were chosen to examine the specific recognition ability of the imprinted sensor (Fig. 7). At 2,4-DCP imprinted sensor, 2,4-DCP showed more than thrice current response than NIP microgel modified GCE. No perceivable difference of current variation between MIP and NIP microgel modified GCE was observed for the analogs, indicating that MIP microgel had the highest specific selectivity toward 2,4-DCP. Meanwhile, competitive experiment was examined at the imprinted sensor in a mixed solution of 40 μmol L^{-1} 2,4-DCP, 2,6-DCP, 2,4,6-TCP and PCP. The result showed that the current response was nearly 93.5% of that obtained individually from 40 μmol L^{-1} 2,4-DCP. The origin of selective recognition was attributed to 2,4-DCP selective binding sites in the polymer microgel created by the imprinting process. Although the same hydrogen bond could form between the structural analogs and MAA, the distinct size, structure and functional groups to the template led to the different recognition effect [31]. Although 2,6-DCP has nearly the same structure as 2,4-DCP, its current response at MIP microgel modified GCE was still much lower than that to 2,4-DCP, suggesting that the memory of specific functional group also played an important role in the conformation memory [32]. The results suggested that the imprinting process significantly improved the specificity and selectivity of the 2,4-DCP imprinted microgel toward template 2,4-DCP.

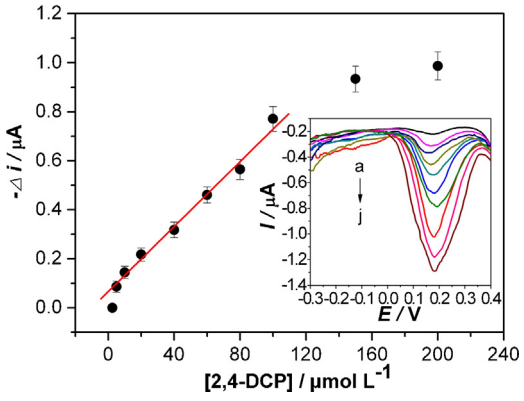


Fig. 6. Plot of current variation vs. 2,4-DCP concentration. Inset: DPV curves for 2,4-DCP detection using the proposed sensor in 0.1 mol L^{-1} pH 7.0 PBS containing 100 μmol L^{-1} H_2O_2 and 2.5, 5.0, 10, 20, 40, 60, 80, 100, 150 and 200 μmol L^{-1} 2,4-DCP (from a to j).

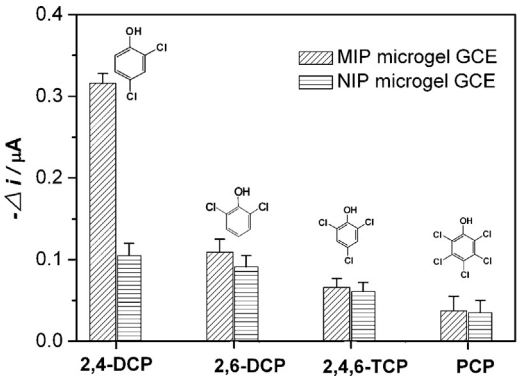


Fig. 7. Competitive binding of MIP and NIP microgel modified GCE with structure analogs.

Table 1
Results for the determination of 2,4-DCP in water samples.

Water samples	Added (μmol L^{-1})	Founded (μmol L^{-1})	Recovery (%, n = 3)
Tap water	20.0	19.24	96.2 (±2.7)
	50.0	48.80	97.6 (±2.3)
River water	20.0	22.36	111.8 (±3.4)
	50.0	51.25	102.5 (±2.6)
Drinking water	20.0	19.28	96.4 (±1.9)
	50.0	50.35	100.7 (±3.0)

The results were expressed as mean values and the ±SD was based on three replicates.

3.6. Preliminary analysis of 2,4-DCP in water samples

The practical applicability of the developed sensor was examined by analyzing the 2,4-DCP from three types of water samples under optimized conditions. Prior to analysis, freshly collected water samples from Nanming River, Guiyang, China, were immediately filtered through a millipore cellulose nitrate membrane (pore size 0.45 μm) to remove suspended particles. The pH of all water samples was adjusted to 7.0 with phosphate buffer solution. The accuracy of the method was evaluated by performing a recovery test after spiking the samples. As seen from Table 1, the recovery was in the range from 96.2% to 111.8% and RSD was from 1.9% to 3.4%, indicating an acceptable result.

4. Conclusions

This work presents a new approach for amperometric detection of 2,4-DCP by using a molecularly imprinted polymer microgel modified electrode. The presence of chlorohemin in the imprinted microgel leads to efficient catalysis of the oxidative dehalogenation of 2,4-DCP. Compared to chloroperoxidase-based biosensors, the proposed sensor possesses better selectivity, repeatability and stability. It shows a great potential in analysis of water samples.

Acknowledgements

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