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A High Sensitive Sensor for Terbuthylazine Determination Based on Molecularly Imprinted Electropolymer of 3-Thiophenemalonic Acid

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A novel sensor for the determination of terbuthylazine (TBA) based on 3-thiophenemalonic acid (3-TMA) as functional monomer was fabricated by molecularly imprinted technology. The polymeric film was obtained on the gold electrode surface by electrocopolymerization of 3-TMA in the presence of the template molecule of TBA, through the use of cyclic voltammetry (CV). Several important parameters controlling the performance of the molecularly imprinted polymer (MIP) modified sensor were investigated in detail such as the monomer concentration, the electropolymerization cycles and pH. The obtained MIP sensor was highly specific towards newly added TBA and the recognition could be quantitatively analyzed by the differential pulse voltammetry (DPV) to verify the changes in oxidation currents of ferricyanide. In the optimal condition, the response of the imprinted sensor to TBA was linearly proportional to its concentration over the range 2.5×10^{-7} mol/L to 1.2×10^{-4} mol/L, with high sensitivity, good stability and reproducibility (RSD, 2.05%). The method has been successfully applied to the determination of TBA in real samples, with a recovery ranging from 71.2% to 84.9% and a detection limit of 2.0×10^{-8} mol/L (S/N=3).

Keywords: Terbuthylazine (TBA); Molecularly imprinted polymer (MIP); 3-Thiophenemalonic acid (3-TMA); Sensor; Electropolymerization

1. INTRODUCTION

Terbuthylazine (TBA), as a selective herbicide of triazine family, is widely used for pre-emergence or post-emergence control of many grass and broadleaf weeds in agricultural fields. The residue of TBA in agricultural products and natural environments is extremely harmful to human health and zoology [1]. Many methods have already been developed to detect it by use of complicated analytical instruments such as gas chromatography (GC) [2], high performance liquid chromatography (HPLC) [3], capillary electrophoresis [4] and related technologies [5-7]. Although chromatographic approaches are well established methods with a low detection limit, the tedious sample pretreatment and expensive apparatus still hinder their practical applications. Electrochemical sensors based on molecularly imprinted technology were undoubtedly another important choice for this aim [8-11]. They can be prepared by several methods including in situ polymerization [12], sol-gel [13], self-assembly [14] and electrochemical polymerization [15]. Molecularly imprinted polymers (MIPs) have been elucidated to work as artificial receptors. Recently, numerous attempts have been made by construction MIP sensors for the detection of triazine pesticides [16, 17]. These sensors were generally prepared by directly depositing an MIP film onto an electrode surface from a functional monomer solution in a porogenic solvent, in the presence of a template molecule. This film should adhere well to a (roughened) electrode surface and the film thickness can be governed by the amount of charge transferred during electropolymerization. Shoji and et al. reported an atrazine sensor fabricated by directly polymerizing the atrazine-imprinted polymer composed from methacrylic acid and ethylene glycol dimethacrylate onto the surface of a gold electrode. The sensor exhibited a selective response to atrazine. A nonimprinted polymer-modified electrode did not show selective response to atrazine, thus implying that the imprinted polymer acts as recognition element of atrazine sensor [18]. Similar researches based on electrochemical sensor for detection of atrazin were carried out by Pardieu and et al. Poly(3,4-ethylenedioxythiophene-co-thiophene-acetic acid), was electrochemically synthesized onto a platinum electrode following two steps: (i) polymerization of comonomers in the presence of atrazine, already associated to the acetic acid substituent through hydrogen bonding, and (ii) removal of atrazine from the resulting polymer, which leaves the acetic acid substituents open for association with atrazine [19]. Another paper used for the electrochemical detection of atrazine was reported recently. The sensitive layers based on conducting homopolymer [poly(3,4-ethylenedioxythiophene), denoted PEDOT] and copolymers [molecularly imprinted and non-imprinted poly(EDOT-co-3-thiophene acetic acid), denoted MICP and NICP, respectively] were electrosynthesized on gold substrates [20]. Influence of the chemical functionalities of a molecularly imprinted conducting polymer on its sensing properties was ever investigated by Lattach and et al. Differently functionalized molecularly imprinted conducting polymers (FM-MICP) were electrosynthesized and then washed and used as sensitive layers for atrazine recognition. A strong correlation was found between FM-MICP sensitivity and the amount of thiophene-based functional monomers/atrazine prepolymerization complexes [21]. In addition, an electrochemical sensing chip modified by simazine MIP was developed on its reductive current measured by cyclic voltammetry. The prepared simazine-MIP sensor possessed a high selectivity and sensitivity with a detection limit of 0.4 mmol/L [22].

In this work, a new type of polymeric films containing molecular recognition sites for TBA was prepared on the gold electrode using the molecular imprinting approach. To the best of our knowledge, no report using 3-TMA as a single functional monomer for electropolymerization in the presence of the template molecule (TBA) was published. The MIP-modified sensor exhibited more sensitive response to TBA, compared with its analogues, but A NIP-modified electrode did not show selective response to TBA and its analogues, suggesting that the imprinted polymer effectively acted as recognition element of TBA sensor.

2. EXPERIMENTAL

2.1. Reagents and apparatus

TBA (97.0%), atrazine (97.0%), cyromazine (97.0%), melamine (99.5%), ametryn(80.0%) were kindly provided by Graduate of Life Science, Hunan Agricultural University; 3-TMA (98%，Jiangsu Pingguang Pharmacy Co., Ltd.); LiCl (97.0%, Sinopharm Chemial Reagent Co., Ltd.). All other chemicals were of analytical grade, and doubly distilled water was used throughout.

All electrochemical measurements were performed on a CHI 760C electrochemical workstation (Shanghai Chenhua Instrument Company, Shanghai, China) with a standard three electrode configuration, controlled by an HP-compatible computer. A gold electrode modified with MIP, a platinum wire and a Ag/AgCl electrode were used as the working, the counter and reference electrodes, respectively. A magnetic stirrer (Model 79-1, Shanghai Hexin Technique and Education Equipment Co., Shanghai, China) was employed to stir the test solution during measurements. All measurements were carried out in 50 mL glass cells at room temperature.

2.2. Preparation of MIP-modified electrode

A gold disk electrode (2.0 mm in diameter, CH Instruments, Inc., Austin, TX, USA) was used as a working electrode throughout the experiment. Prior to use, the surface of the gold electrode was polished carefully with 0.3 and 0.05μm alumina slurry on a 1,200 grit Carbimet disk until a shiny mirrored surface was obtained, and then sonicated sequentially in ethanol and doubly distilled water for 3 min, respectively, in order to remove trace alumina and possible contamination. To ensure a clean surface, the polished electrode was subjected to cyclic potential sweeping between 0.0 and 1.5 V in 0.5 mol/L sulfuric acid until a stable cyclic voltammogram was obtained.

The MIP was constructed by electropolymerization of TBA and 3-TMA on the surface of the gold electrode, using CV in the potential range between −0.50 and +1.50 V, scan rate (V/s) =0.1. Twenty cycles in a solution of 0.5 mmol/L TBA and 2 mmol/L 3-TMA were dissolved in 5 mL C_3H_5OH /H_2O (*v*:*v* =1:1) in the presence of 5 mmol/L LiCl as supporting electrolyte. A time of 30 min was used for the association, through hydrogenbonds between two molecules of 3-TMA and one of TBA. A NIP electrode was also prepared under the same experimental conditions in absence of TBA. The schematic representation of imprinting and removal of TBA from imprinted poly-(3-TMA) modified gold electrode was shown in Figure 1. The hydrogen atom in the N-H group of the TBA molecule forms a hydrogen bond with the oxygen atom in the C=O group of the 3-TMA units. Hydrogen bonding could occur between the nitrogen atom in the secondary amine group of TBA structure and the hydroxyl of the carboxyl group of 3-TMA units, too. Chain branching and cross linking in poly-(3-TMA) generated a three-dimensional matrix with niches containing the template TBA. This imprinting process created a microenvironment for the recognition of TBA molecule based on shape selection and positioning of the functional groups.

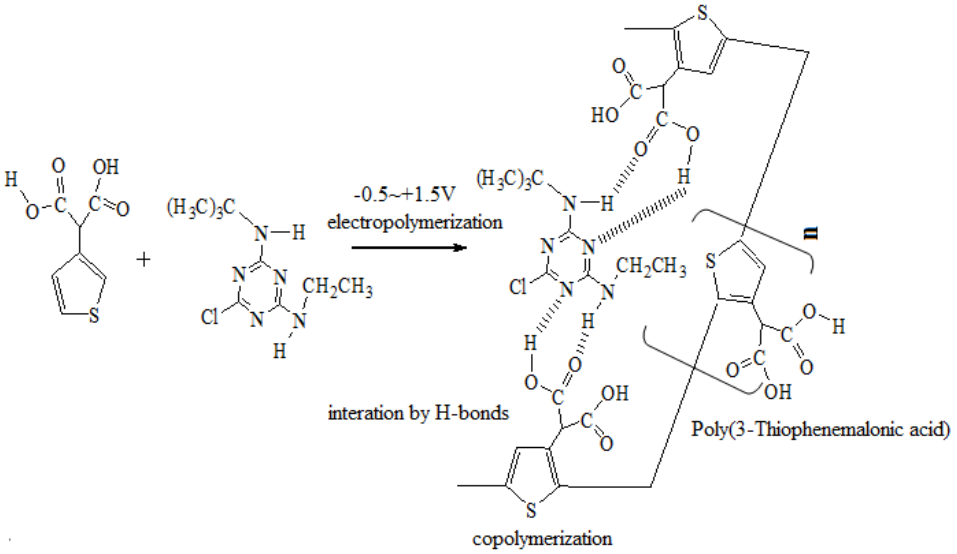

Figure 1. Schematic representation of poly (3-TMA) copolymerization after the establishment of H-bonds between TBA and 3-TMA in a prepolymerization complex.

2.3. Electroanalytical measurements

The gold electrodes were modified through electropolymerization in the presence of TBA, and in the absence of TBA, respectively. After that, the MIP and NIP electrodes was removed by ultrasonically extraction using a two step procedure as follows: the mixture solution of acetic acid and methanol (1:9, *v*/*v*) was firstly used for washing about 20 min to remove the imprinting molecules, followed by acetone for 10 min as a second step. This procedure was repeated for several times until a stable response value in 0.01mol/L $K_3[Fe(CN)_6]$ solution could be obtained for the eluted MIP electrode by CV scan. The TBA molecules could escape from the stereo-cavity of the molecular imprinting membranes due to the destruction of the hydrogen bonds between TBA and the molecular imprinting membranes. In order to achieve a high sensitive sensor, the selection of a proper electrochemical technique is of great importance. DPV and square wave voltammetry (SWV) were compared in our experiments. The response obtained by DPV was better than that obtained by SWV for TBA in the same conditions of extraction and determination, so DPV was selected for our next experiments. DPV measurements were carried out in a three-electrode cell, 0.01 mol/L $K_3[Fe\ (CN)_6]$ was taken as the probe and LiCl (5 mmol/L) as supporting electrolyte. Before the measurements, electrolytic solutions were purged with nitrogen for 5 min. Current measurements were performed using DPV, the following instrumental parameters were used: init E (V)=-0.1, final E(V)=0.6, amplitude (V)=0.05, pulse width (s)=0.2, pulse period (s)=0.5.

2.4. Sample preparation

Tomato samples (500g) purchased from local market were chopped, triturated and homogenized in a blender and a portion of 50 g blank sample and spiked samples with a final TBA concentration of 2, 4 and 6×10^{-5} M, respectively, was subsequently shaken for 5 min in a vortex mixer at high speed. After filtration through a Buchner funnel and 0.45μm filter, the sample was submitted to clean-up procedure by the C_{18} SPE cartridge. The C_{18} SPE cartridge was pre-conditioned with 10 mL ethanol, 20 mL pure water and 10 mL 80% (v/v) methanol. After the sample solution was passed through the pre-conditioned C_{18} column, the column was then rinsed with 6 mL 80% (*v*/*v*) methanol. The elution of the sample solution and rinsed solution was collected together, dried with nitrogen, and re-dissolved in 100 μL of C_3H_5OH and H_2O (*v*:*v* =1:1) . The dried soil samples from the campus of Henan Institute of Science and Technology were ground and sieved with a 100 mesh screen. After samples were weighed in a small tube and spiked with different volumes of TBA standard solution, they were vibrated with a reciprocating shaking-table about 4h at room temperature. Samples were then extracted with 20mL of acetonitrile by ultrasonic agitation for 30 min, followed by centrifugation at 3800 rpm for 10 min. The supernatant was collected, dried with nitrogen, and re-dissolved with 5mL of acetonitrile, then subjected to the extraction procedure by clean-up procedure by the C_{18} SPE cartridge following the same procedure as tomatoes. Prior to electrochemical detection, both tomato and soil samples were filtered through a sterile Millipore membrane (0.22 mm) and adjusted using 0.1 mol/L NaOH with a final pH value of 7.0.

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of molecularly imprinted film between TBA and 3-TMA

Figure 2 showed a typical CV for the deposition of pure poly-(3-TMA) film in the absence and in the presence of TBA, respectively.

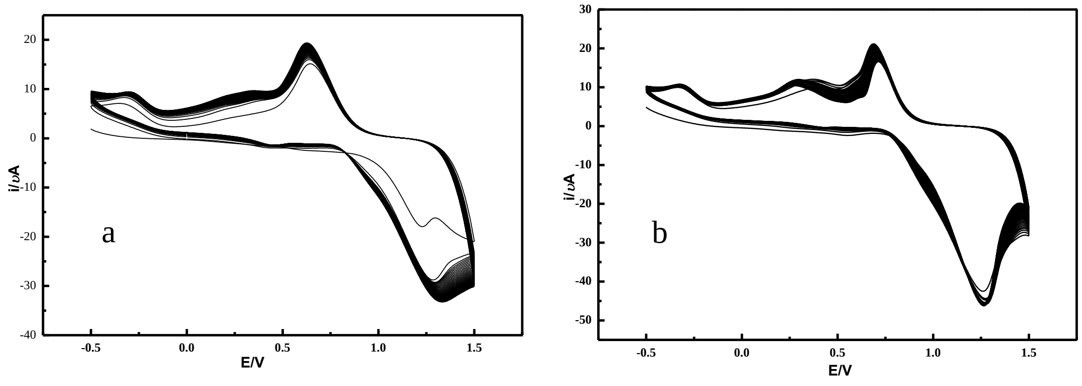

Figure 2. Cyclic voltammograms of the imprinted and non-imprinted copolymer films: (a) 2 mmol/L 3-TMA were dissolved in 5mL C_3H_5OH/H_2O (*v*:*v* =1:1), (b) 0.5 mmol/L TBA and 2 mmol/L 3-TMA were dissolved in 5mL C_3H_5OH/H_2O (*v* :*v* =1:1) .Potential cycling from -0.5 to +1.5 V at a scan rate(V/s) =0.1 for 20 cycles with 5 mmol/L of LiCl as supporting electrolyte.

For both NIP (a) and MIP (b) films, the oxidation wave appeared completely irreversibly. In the first cycle, 3-TMA oxidation was visible at 1.26 V, and the peak current dropped significantly with each scan. The peak current decreased as the polymer layer became thicker and thus the property of dielectric would change with the recycling. In the initial cycles, the current change was very obvious. It was found that the current reached a final value after 20 cycles, which was attributed to a stabilized layer of polymeric film on the gold electrode. Although the current change and the position of oxidation were no significant difference for two films, another redox peak current at 0.28 V of TBA was observed for MIP film in the same polymerization conditions, which was attributed to the introduction of electroactive TBA.

3.2. Effect of the monomer concentration

The ratio of TBA to 3-TMA has a significant effect on the sensor response because the ability of binding the template molecules, mainly depends on the number of cavities within the coating film, which are complementary to the molecular structure of template in shape. A series of modified electrodes were prepared with different ratios of TBA/3-TMA (2:1, 3:1, 4:1 and 5:1) according to the previously mentioned methods. As evident from Figure 3, the maximum current was achieved with the molar ratio (TBA/3-TMA) of 4:1 through the MIP electrode after TBA molecules were removed from the MIP modified electrode. Moreover, the cavity amounts of the MIP would increase with different molar ratios of 2:1, 3:1 and 4:1 accordingly, it resulted from that more template molecules were involved in the polymerization reaction with the increase of the functional monomer. If the TBA template is successfully incorporated into the surface of the polymer matrix during its formation and subsequently extracted, it should leave an imprinted polymeric surface architecture complimentary to itself formed in the polymer film. The formed MIP films on the surface of electrode were denser and hard to be washed when the molar ratio (TBA/3-TMA) was 5:1, and then it hindered ferricyanide probe access to the electrode surface. This was supported from earlier concept of ‘stoichiometric noncovalent interactions’ where the interaction during the polymerization was reportedly stoichiometric in nature [23].

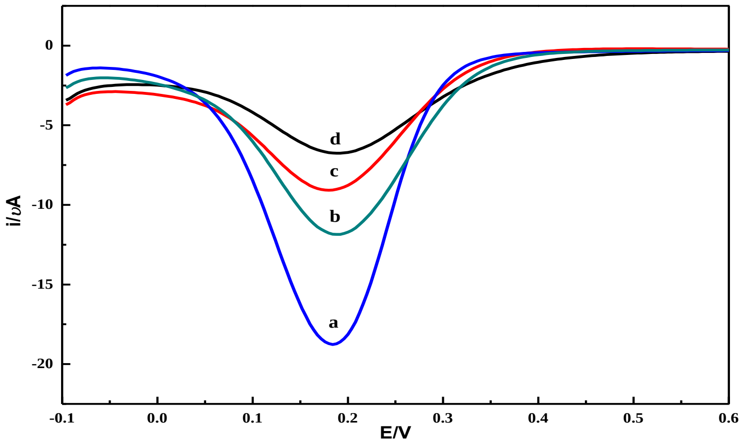

Figure 3. DPV graph of the different molar ratio of monomers to template prepared MIP electrodes in 0.01mol/L $K_3[Fe(CN)_6]$ solutions containing 0.05mM LiCl.

Symbol a, b, c and d stand for a molar ratio (TBA/3-TMA) of 4:1, 5:1, 3:1 and 2:1, respectively.

3.3. Electrochemical behaviour of MIP and NIP films

Figure 4 compared the obtained DPV of four kinds of gold electrodes in 0.01mol/L $K_3[Fe(CN)_6]$ solutions containing 0.05mM LiCl. There were obvious changes of current response for bare gold electrode (a), MIP-modified gold electrode after removal of the imprinted molecules of TBA (b), MIP modified gold electrode before the removal of the imprinted molecules of TBA (c), and NIP modified gold electrode (d), respectively. It was easily understood that the current decrease was caused by the formed films on the surface of gold electrode. The peak current of the “a” curve is higher than that of the “b” curve, but the weakest peaks were obtained for both “c” and “d” curves. This behavior was attributed to the presence of cavities that enabled ferricyanide diffusion through polymer film towards the gold electrode. If those cavities would not present (like in NIP modified gold electrode), almost no electrochemical response could occur. This was likely because electron transfer was blocked by the non-conducting poly–(3-TMA) membranes covering the electrode. From the “b” curves, it suggested that the MIP membrane allowed electron transfer once TBA had been removed.

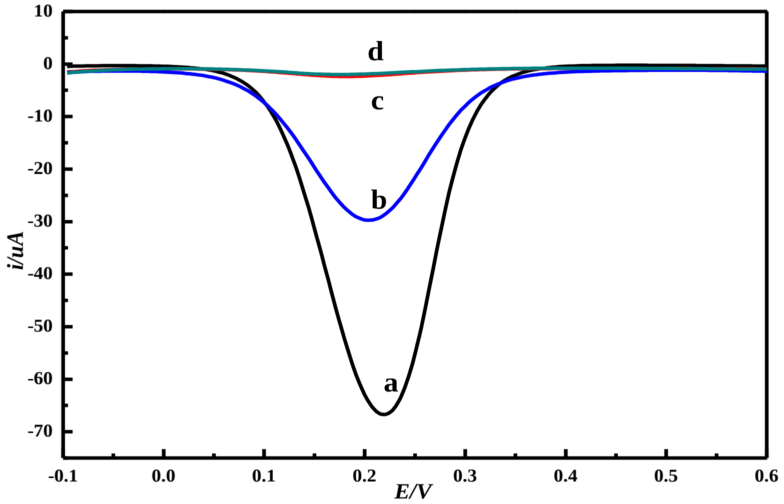

Figure 4. DPV graph of four kinds of gold electrodes. a) bare gold electrode, b) MIP-modified gold electrode after removal of the imprinted molecules of TBA, c) MIP modified gold electrode before the removal of the imprinted molecules of TBA, d) NIP modified gold electrode. Instrumental parameters: init E (V)=-0.1, final E (V)=0.6, amplitude (V)=0.05, Pulse Width (s)=0.2, Pulse Period (s)=0.5.

3.4. Characterization of the surface morphology of the MIP sensor

Scanning electron microscopy was utilized to examine the surface morphology of both the MIP electrode and NIP electrode at 20 kV accelerating voltage and 80A current beam at pressure of 7 Pa.

As shown in Figure 5, the modified electrodes with NIP and MIP films were covered with a layer of uniform and dense film, respectively. After being extracted, the MIP film (Fig. 5a, 5b) on the surface of gold electrode had a different morphology, compared with that of the NIP film (Fig. 5c). It resulted from a change in the polymeric structure as a function of imprinting. The MIP electrode was covered with porous reticulations with obvious pinhole structure. The template removal from MIP electrode delivered porous cavities within each bristle of MIP brush and the appearance of pores channelized from the top to bottom between MIP-bristles. This change was likely due to steric hindrance caused by the hydrogen bonding between the amino hydrogen of the TBA and the carboxyl group in the 3-TMA. This hydrogen bonding was likely responsible for the formation of the imprint–monomer complex that led to the formation of the recognition site. The porous reticulations with obvious pinhole structure caused by elution of TBA could be observed clearly. These cavities could selectively bind with the object molecular, TBA and its analogues, and allowed them to penetrate freely. The results were proved by the subsequent test of the affinity and selectivity of the imprinted film towards TBA.

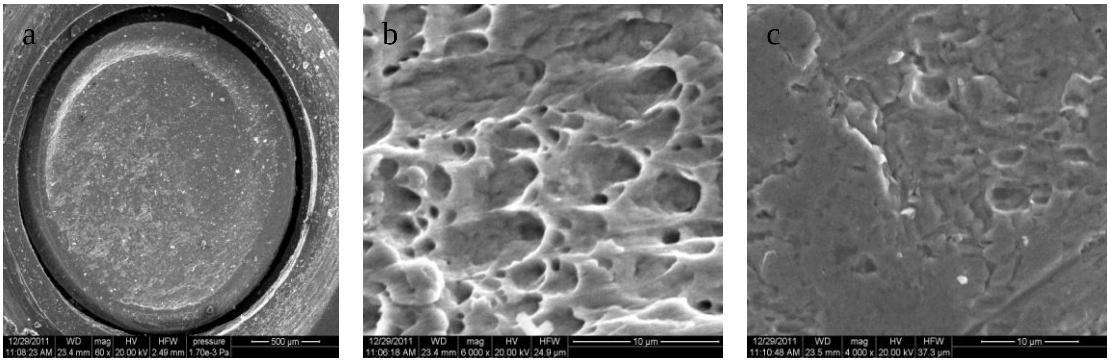

Figure 5. SEM images of (a) molecularly imprinted gold electrode surface (magnification 60×), (b) MIP electrode (magnification 6000×), (c) NIP electrode (magnification 4000×).

3.5. Effect of pH

The pH value of the solution has a significant influence on the current response of the polymeric film in $K_3[Fe\ (CN)\ _6]$ solution. The effect of pH on the current response was investigated in the pH range of 3.0-9.0 at different TBA concentration (form 0.02 to 0.10 mmol/L). The pH value of the sample solution was adjusted to the given value by 0.01mmol/L HCl or by 0.01mmol/L NaOH solution. The obtained results were illustrated by DPV in Figure 6. Through the experiments, we found if the pH was higher (pH=9) or too lower (pH=3), the current signal would be smaller. For example, the current response values were -15.58 μA, -12.37μA, -11.20 μA and -10.93 μA at a TBA concentration of 0.04 mmol/L, corresponding to different pH of 7.0, 5.0, 9.0 and 3.0, respectively. It could be explained as follows: when pH was greater than 9, there were more abounding –COOH would change to $–COO^-$ due to the elution of imprinted molecule. It would cause strong anion effect in the center of cavities and impede $[Fe(CN)_6]^{4-}$ to approach the surface of gold electrode. In contrast, when pH was less than 3, TBA would be positive-charged and improved the rapid combination between TBA and –COOH. A strong absorption of TBA would occur at the cavity surfaces and dynamic absorption-desorption states were hard to form, thus impeded $[Fe(CN)_6]^{4-}$ to approach the surface of gold electrode. For other TBA concentration, similar trend could be obtained at different pH. In order to obtain the optimal current response, pH=7.0 was selected throughout the experiment.

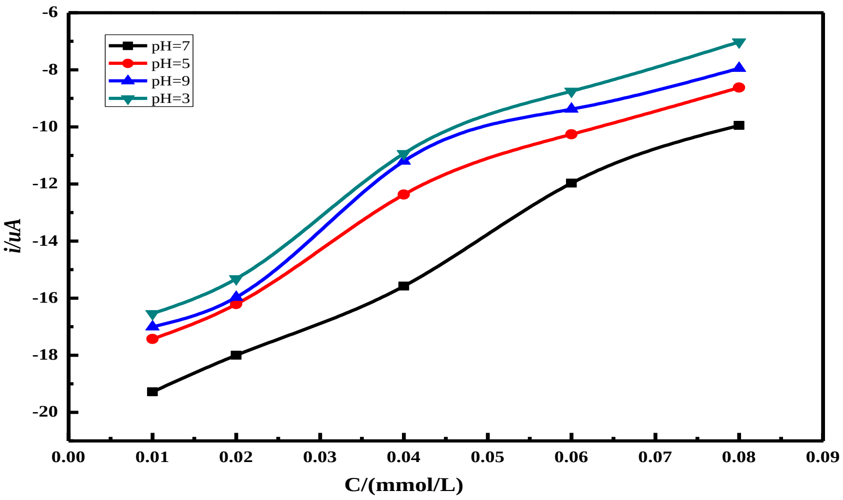

Figure 6. The effect of different PH value on oxidation peak current

3.6. Affinity and selectivity of MIP sensor

In order to verify the specificity of the MIP sensor for TBA, some TBA structural analogues (see Fig. 7) including melamine, atrazine, cyromazine and ametryne were selected for the comparative experiments. The MIP electrode were immersed in C_3H_5OH/H_2O (v:v =1:1) solutions containing 0.01mol/L $K_3[Fe(CN)_6]$, 5 mmol/L LiCl and TBA or their structural analogues with different concentration, respectively.

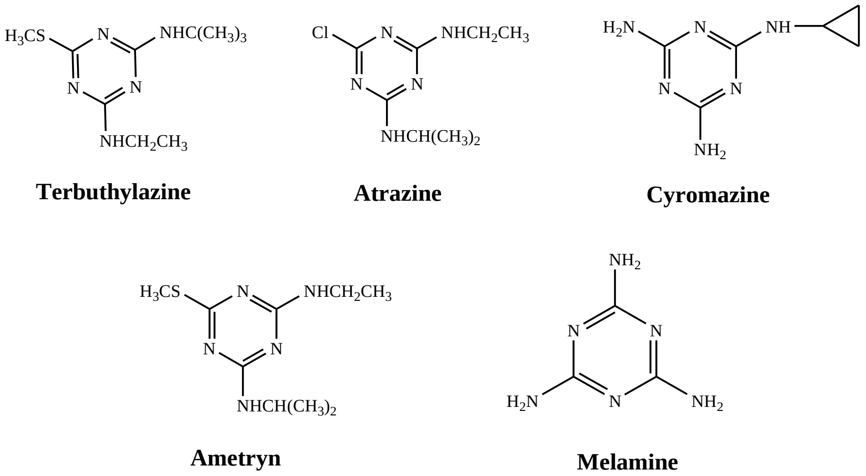

Figure 7. Molecular structure of five analytes for the specificity study

The response current of DPV was used to quantify the detection of these compounds in their respective concentration range of 0.01-0.10 mM. The relative currents deduced from the DPV for TBA analogues were generally lower than that of TBA itself at the same concentration in Figure 8.

The weaker recognition could be understood that although there were similar structure in terms of molecular size and side-chain radical, they still mismatched the imprinting sites of TBA. The MIP sensor was able to detect a large range of TBA owing to the presence of pre-shaped functionalized cavities present into the MIP backbone. Although, these TBA analogues were different from TBA in molecular size and they also had some chances of approaching the imprinting sites. From the comparable results, it was easily understood that the developed electrochemical sensor possessed a selective recognition towards triazinic family. Moreover, the shape, the size and the spatial disposition of the functional cavities of the MIP formed during the electropolymerization enabled the more specific detection of TBA.

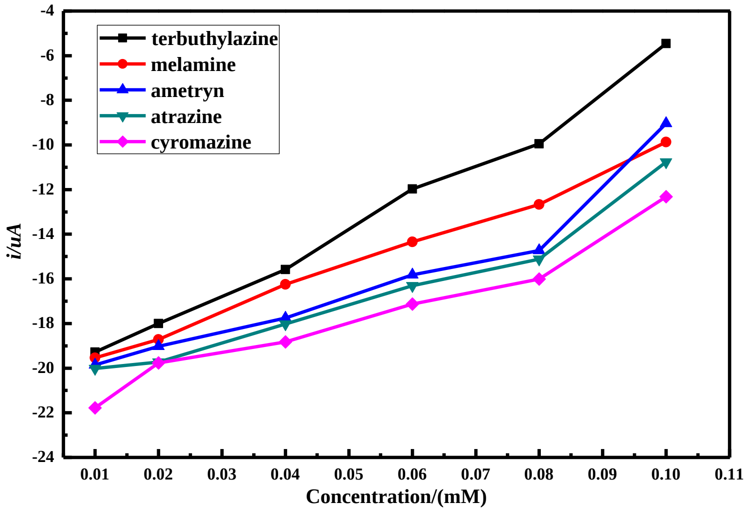

Figure 8. Response current of DPV with the MIP modified sensor for structural analogues different compounds. Each value represents the average of three independent measurements.

3.7. Electrochemical response characteristics

DPV were performed after the MIP electrode was incubated in 0.01 mol/L $K_3[Fe(CN)_6]$ solution with the addition of different concentration of TBA in the range of 1.25×10^{-4} mmol/L to 0.24 mmol/L. Figure 9 showed the dependence of the reduction current on the concentration of TBA (2.5×10^{-4} mmol/L to 0.12 mmol/L). As it was clearly, the peak current gradually decreased with the addition of TBA. The increasing number of the binding sites in the film were occupied by TBA molecules, so that it was more difficult for ferricyanide diffusion to reach the electrode surface through MIP cavities. The calibration curve between the relative reduction peak current (y) and the TBA concentration (C, mM) was exhibited in the inset of Figure 9. As could be seen, at the high concentration range, the current change tended to be stable, which indicated that the imprinting sites were gradually occupied by TBA molecules. The linear range was calculated to be 2.5×10^{-7} mol/L

~1.2×10^{-4} mol/L with a detection limit (LOD) of 2.0×10^{-8} mol/L based on a signal-to-noise ratio (S/N) of 3. The linear equation was given as follows: $y=-2.07\times10^{-5}+1.41\times10^{-4}$ C, and the correlation coefficient (*r*) was 0.9917. Although this dynamic range was at present not large, the formed films did not show loss of sensitivity for at least 1 month.

The current responses for TBA were stable upon repeated injection of TBA. Moreover, the modified Au electrode responded rapidly, the current response reached 96% of the steady-state current within 40s, which allowed convenient quantification of TBA. The improvement in response time was probably due to the rapid equilibrium that could be established by the MIP sensor.

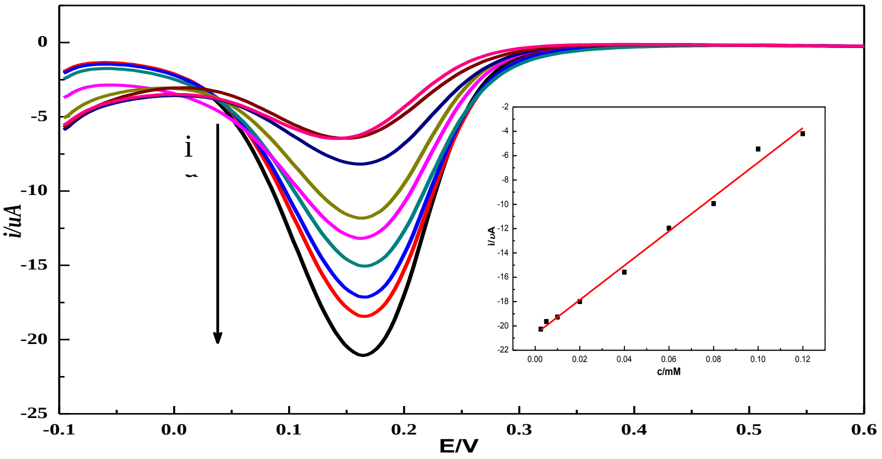

Figure 9. DPV graph of TBA at a concentration range of 2.50×10^{-4}mmol/L~0.12 mmol/L (a-i) on the surface of the MIP-modified electrode. Inset figure is a calibration curve.

Instrumental parameters: init E (V)=-0.1, final E (V)=0.6, amplitude (V)=0.05, Pulse Width (s)=0.2, Pulse Period (s)=0.5.

3.8. Reproducibility and stability

Five sensors were fabricated under the same experimental conditions to test the reproducibility of sensor preparation. Repeated use of 0.04 mmol/L TBA showed a relative standard deviation (RSD) of 2.05% (n=8) under continuous DPV determinations, indicating good electrode-to-electrode reproducibility of the fabrication method. It suggested that the amount of coating film could be accurately controlled by using the proposed technique. Generally, after the first electrochemical determination of TBA, the electrode was immersed in methanol/acetic acid to remove TBA and other impurities left in the polymer, followed by immersing in LiCl for 1 h prior to the next measurement. Furthermore, no obvious change of the TBA response at the imprinted electrode was achieved after it was used at least 10 or 15 times with subsequent washing and measuring operations. After each use, the electrode was stored at 4℃. No apparent decrease in response to 0.04mM TBA was observed after 1 week. Over the next week, the current response decreased by about 7.2%, and about 13.5% after 1 month, compared to its initial response. It demonstrated that the fabricated sensor possessed a good stability.

3.9. Sample analysis

In order to ascertain its potential application, the sensor was used to determine TBA in real samples according to the recommended method. The results were represented in Table 1. These two samples were spiked with certain levels of TBA and analyzed. The recoveries of TBA in these spiked samples ranged from 71.2% to 84.9% with the largest relative standard deviation (RSD) less than 10.1%.

Table 1. Recoveries and RSD of TBA for spiked tomato and soil samples (n = 6).

samples	Added concentration ($\times 10^{-5}$mol/L)	Found concentration ($\times 10^{-5}$mol/L)	Recovery (%)	RSD (%)
tomato	2	1.53	76.5	4.2
	4	3.29	82.3	7.2
	6	4.84	80.7	6.7
soil	2	1.70	84.9	6.5
	4	3.35	83.8	10.1
	6	4.27	71.2	9.4

4. CONCLUSIONS

In this work, the MIP membranes modified gold electrode was successfully prepared by electrochemical polymerization of 3-TMA, and has been successfully used as a sensor for fast, selective recognition and accurate determination of TBA in tomato and soil samples. The MIPs sensor showed excellent precision and accuracy, wide linear range, low detection limit, high selectivity and good reusability. The advantages of very simple instrumentation and easy preparation of the proposed sensor make the system useful in constructing simple devices for determination of TBA.

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