

Electrochemical oxidation behavior of bisphenol A at surfactant/layered double hydroxide modified glassy carbon electrode and its determination

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Abstract Electrochemical behavior of bisphenol A (BPA) at glassy carbon electrode-modified with layered double hydroxide (LDH) and anionic surfactant (sodium dodecyl sulfate) is investigated by electrochemical techniques. Compared with the bare electrode and LDH-modified electrode, the oxidation peak potential of BPA shifted negatively and the peak current increased significantly due to the enhanced accumulation of BPA via electrostatic interaction with LDH at the hydrophobic electrode surface. Some determination conditions such as LDH loading, pH, scan rate, accumulation potential, and accumulation time on the oxidation of BPA were optimized. And some kinetic parameters were investigated. Under the optimized conditions, the oxidation current was proportional to BPA concentration in the range of 8×10^{-9} to 2.808×10^{-6} M with the detection limit of 2.0×10^{-9} M by amperometry. The fabricated electrode showed good reproducibility, stability, and anti-interference. The proposed method was successfully applied to determine BPA in water samples, and the results were satisfactory.

Keywords Bisphenol A · Layered double hydroxide · Electrochemistry · Anionic surfactant · Determination

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Introduction

Endocrine-disrupting chemicals (EDCs) are substances that mimic natural hormones in the endocrine system, thus causing adverse effects on human and wildlife [1]. Bisphenol A (2,2-bis (4-hydroxyphenyl) propane, BPA, CAS no. 80-05-7) is a typical EDC, which shows estrogenic activity even at concentrations as low as the 10–25 nM level [2–4]. It could potentially interfere with the endocrine system of both the wildlife and human, cause cancer, decrease semen quality, reduce immune function, and impair reproduction [5, 6]. However, BPA is heavily used as a monomer in synthesis of epoxy resins, polystyrene resins, polycarbonate plastics, flame retardants, and other specialty products, which are widely used for inner coating of food cans, dental composites, and drug delivery systems [7]. There are several potential routes of BPA entry into the environment. At manufacturing and processing facilities, low levels of BPA are directly released to surface waters. Additionally, BPA could be released from various products that contain small amounts of unreacted BPA, for example, nursing bottle, food can linings, and beverage container [7–9]. Therefore, an efficient determination method is required for monitoring the levels of BPA.

The reported analytical methods for the determination of BPA in environment involve mainly high-performance liquid chromatography [10] and gas chromatography [11]. The satisfactory results were obtained with high sensitivity, excellent selectivity, and lower detection limit. However, these techniques also require skilled operators, complicated and expensive instrumentations, large sample volumes, and time-consuming detection process. So, they are unsuitable for online or field monitoring. It is well known that electrochemical method has the advantages of fast response speed, cheap instrument, inexpensiveness, simple opera-

tion, timesaving, high sensitivity, excellent selectivity, and real-time detection in situ condition as an analytical technique. But direct detection of BPA using traditional electrochemical sensor is rare because the response of BPA is poor. Therefore, the development of modified electrochemical sensor is necessary. For example, Sánchez-Acevedo et al. fabricated a biosensor for fast picomolar selective detection of BPA in water based on a carbon nanotube field effect transistor functionalized with estrogen receptor α [12]. Though the detection concentration in that work is very low, it is still a challenge to investigate novel electrochemical sensor based on new sensing material with high sensitivity and selectivity.

Layered double hydroxides (LDH), which are referred to as hydrotalcite-like compounds (HT), are an important class of ionic lamellar solids [13]. Structurally, LDH consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. The general chemical formula of these lamellar solids can be expressed as $[M^{II}_{1-x}M^{III}_x(OH)_2(A^{n-})_{x/n}] \cdot yH_2O$, where M^{II} and M^{III} represent divalent and trivalent metal ions within the brucite-like layers and A^{n-} is an interlayer organic or inorganic anion. One of the most important properties of LDH is the anionic exchange capacity. The anions and water molecules intercalated into LDH interlayers can be replaced with other organic anions and polar molecules [14]. Therefore, positively charged LDH structures can adsorb organic compounds. However, the adsorption affinity of inorganic LDH to nonionic organic compounds was weak in water due to the hydrophilicity of LDH. The positively charged hydrotalcite layers have strong affinity to the negative head of surfactants (such as sodium dodecylbenzenesulfonate, octylphenoxypolyethoxyethanol, sodium octyl sulfate, sodium dodecyl sulfate (SDS)), and the inorganic anions in LDH interlayers can be replaced with long-chain surfactants, yielding modified LDH with hydrophobic surface property, resulting in high adsorptive capacity of modified LDH to nonionic organic compounds, such as phenol [15, 16], 2,4-dichlorophenol [17], 2,4,6-trinitrophenol, and dodecylbenzylsulfonate [18]. Another important property of LDH is the catalytic activity, which could electrocatalyze oxidation of phenol [15, 16], ascorbic acid [19], uric acid [19], fructose [20], and hydrogen peroxide [21]. Our previous work also demonstrated the excellent electrocatalytic activity of LDH towards BPA oxidation [22].

Integrating the good performance of LDH and SDS, we think that LDH modified with SDS (Mg-Al-SDS) would be a more attractive material than LDH only in electrode surface modification for electrochemical determination of BPA. To prove it, in this work, the Mg-Al-SDS-modified glassy carbon electrode (Mg-Al-SDS/GCE) was fabricated, and the electrochemical determination of BPA was carried

out using this modified electrode. Additionally, the proposed method was applied to determine trace amounts of BPA in water samples.

Experiments

Reagents and apparatus

BPA was purchased from Aldrich Chemical Co. (USA). A 0.1 M BPA stock solution was prepared with anhydrous ethanol and kept in darkness at 4°C. Working solutions were freshly prepared before use by diluting the stock solution. SDS was purchased from Aladdin (China). Phosphate buffer solution (PBS) was prepared by mixing the stock solutions of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 and adjusting the pH with HCl or NaOH. $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 2H_2O$, NaOH, Na_2CO_3 , and all other reagents were of analytical reagent grade and used as received without further purification. All the solutions were prepared with redistilled deionized water from quartz.

Electrochemical experiments were performed with CHI660C electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. A bare GCE (CHI104, CH instruments, Inc., USA) or modified GCE was used as working electrode. A saturated calomel electrode and a platinum wire were used as reference electrode and auxiliary electrode, respectively. The pH measurements were carried out on PHS-3C exact digital pH meter (Shanghai KangYi Co. Ltd., China). All the measurements were carried out at room temperature.

Preparation of Mg-Al- CO_3 LDH

Mg-Al- CO_3 LDH was prepared according to a method described elsewhere [23] with minor modification. In brief, a 25-mL solution containing 0.06 M $Mg(NO_3)_2$ and 0.02 M $Al(NO_3)_3$ was titrated with 25 mL of mixture solution of 0.2 M NaOH and 0.02 M Na_2CO_3 under vigorous stirring. The titration rate was 2 mL min^{-1} . During the synthesis, the temperature was maintained at 25°C. The resulting suspension was then aged at 65°C in a thermostatic bath for 1 h with stirring. The obtained product was filtered, washed thoroughly with redistilled deionized water until the filtrate showed no free radicals of OH^- , CO_3^{2-} , and NO_3^- , subsequently dried at 90°C for 24 h in air, and ground to a fine powder form.

Preparation of Mg-Al-SDS LDH

Mg-Al-SDS LDH was synthesized according to [15]. In brief, the synthesized Mg-Al- CO_3 LDH was added to SDS water solution (0.1 M), with a solid/solution ratio of 1:50(g/mL).

The suspension was sonicated for 30 min to homogenize the particles and stirred at 40°C for 2 h, and then the supernatant solution was decanted. The solid material was filtered, washed three times using redistilled deionized water, and oven-dried at 70°C for 1 h.

Preparation of Mg-Al-SDS/GCE

Before modification, the bare GCE (3 mm in diameter) was polished to a mirror-like finished with 0.3 and 0.05 μm alumina slurry on micro-cloth pads, rinsed thoroughly with redistilled deionized water between each polishing step, then washed successively with redistilled deionized water, anhydrous alcohol, and redistilled deionized water in an ultrasonic bath, and dried in air before use.

For preparation of the modified electrode, 1 mg mL⁻¹ Mg-Al-SDS LDH solution was first prepared with redistilled deionized water, followed by ultrasonication for 30 min. With a microinjector, 5 μL of Mg-Al-SDS LDH solution was deposited on the freshly prepared GCE surface. After the solvent was evaporated, the electrode surface was thoroughly rinsed with redistilled deionized water and dried under ambient condition. The obtained electrode was noted as Mg-Al-SDS/GCE. The modified electrode was stored at 4°C in a refrigerator before use.

Results and discussion

Cyclic voltammetric behavior of BPA

The electrochemical behaviors of 0.1 mM BPA at GCE and Mg-Al-SDS/GCE were investigated in 0.1 M pH 9.0 PBS by cyclic voltammetry (CV). As can be seen in Fig. 1, only low background current was observed at Mg-Al-SDS/GCE in the absence of BPA (curve d), indicating that Mg-Al-SDS was

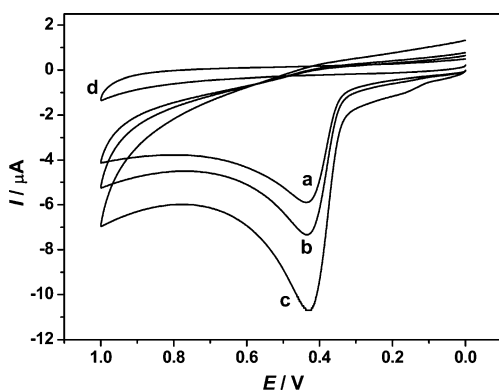


Fig. 1 Cyclic voltammograms of 0.1 mM BPA in 0.1 M pH 9.0 PBS at GCE (a), Mg-Al-LDH/GCE (b), and Mg-Al-SDS/GCE (c). Scan rate 100 mV s⁻¹; accumulation time 150 s; accumulation potential 0.1 V. (d) Cyclic voltammogram of Mg-Al-SDS/GCE in blank PBS

electro-inactive in the selected potential region. Upon addition of BPA to the buffer solution, an irreversible oxidation peak was observed during the sweep from 0.00 to 1.00 V with the oxidation peak potential of 0.437, 0.435, and 0.429 V at GCE (curve a), Mg-Al-LDH/GCE (curve b), and Mg-Al-SDS/GCE (curve c), respectively. It suggested that the electrode response of BPA was typical of totally irreversible electrode reaction in accordance with other reports [24–29].

From the comparison of curves (a)–(c) in Fig. 1, it was very clear that Mg-Al-SDS LDH not only significantly enhanced the oxidation peak current of BPA but also decreased its oxidation peak potential from 0.437 to 0.429 V, suggesting that the electrochemical oxidation of BPA was facilitated by GCE modified with Mg-Al-SDS after accumulation. The reason might be attributed to the fact that the molecular film of surfactant was intercalated between LDH layers, yielding a hydrophobic clay, which could preconcentrate more BPA to the electrode surface [15].

In addition, the oxidation peak current of BPA disappeared completely during the second cyclic potential sweep at Mg-Al-SDS/GCE. This phenomenon can be attributed to the electrode contamination, resulting from the oxidative product of BPA to form dimer or polymer deposited on the electrode surface, which blocks BPA from further access to the electrode [28]. Similar behavior has also been observed in previous reports for anodic oxidation of BPA [22, 24–28, 30]. Thus, the oxidation peak current in the first anodic sweep is recorded for BPA analysis in the following studies.

Condition optimization

The effect of Mg-Al-SDS loading ranging from 0 to 3 mg mL⁻¹, on the CV of 0.1 mM BPA in 0.1 M pH 9.0 PBS, was studied. The current response increased with increasing concentration of Mg-Al-SDS from 0 to 1 mg mL⁻¹ and then decreased with further increasing Mg-Al-SDS concentration. The reason for current increase could be attributed to the fact that the sites for catalysis and adsorption increased with increasing Mg-Al-SDS loading on the electrode surface while the excess of Mg-Al-SDS surrounding the electrode surface will decrease the efficient area of electrode and increase film thickness. Hence, a loading of 1 mg mL⁻¹ Mg-Al-SDS-modified glassy carbon electrode was used throughout this work.

The effect of accumulation time, ranging from 0 to 240 s on the oxidation peak current of BPA with a fixed accumulation potential of 0.10 V, was investigated. The oxidation peak current increased linearly with the accumulation time of up to 150 s. The longer the accumulation time, the more BPA is adsorbed onto the electrode surface.

Afterwards, the peak current tended to be stable, with accumulation time further extending beyond 150 s. This phenomenon may be caused by the saturated adsorption of BPA at the electrode surface. Considering both sensitivity and work efficiency, the optimal accumulation time of 150 s was employed in further experiment. The influence of accumulation potential on the oxidation peak current of BPA was investigated at different potentials from -0.40 to 0.30 V at a potential interval of 0.10 V and a fixed accumulation time of 150 s. When the accumulation potential shifted from -0.40 to 0.10 V, the oxidation peak current increased gradually. Then, a great decrease in the oxidation peak current was observed when the accumulation potential shifted more positively. Therefore, 0.10 V was chosen as the optimal accumulation potential.

The effect of pH on the oxidation of 0.1 mM BPA at Mg-Al-SDS/GCE was investigated with CV in the pH range of 5.0 to 10.0, and the results were shown in Fig. 2a,

b. The oxidation peak current of BPA increased gradually with increasing pH from 5.0 to 9.0, and the maximum current was achieved at pH 9.0. With the further improving pH value, a great decrease of the oxidation peak current was observed. This phenomenon could be attributed to the higher concentration of hydroxyl anion, which may replace BPA molecule on the adsorption sites of the Mg-Al-SDS surface [16]. As is well known, the pK_a of BPA is about 9.7 [31], and the maximum current response to pH value is lower than the pK_a of BPA, suggesting that nondissociated BPA can adsorb better than the dissociated BPA on the Mg-Al-SDS/GCE surface. The similar phenomenon was obtained with the studies of electrocatalytic oxidation of phenol at SDS-Co-Al-HT clay-modified glassy carbon electrode [15]. Considering the sensitivity of the determination of BPA, a pH of 9.0 was chosen for the subsequent analytical experiments

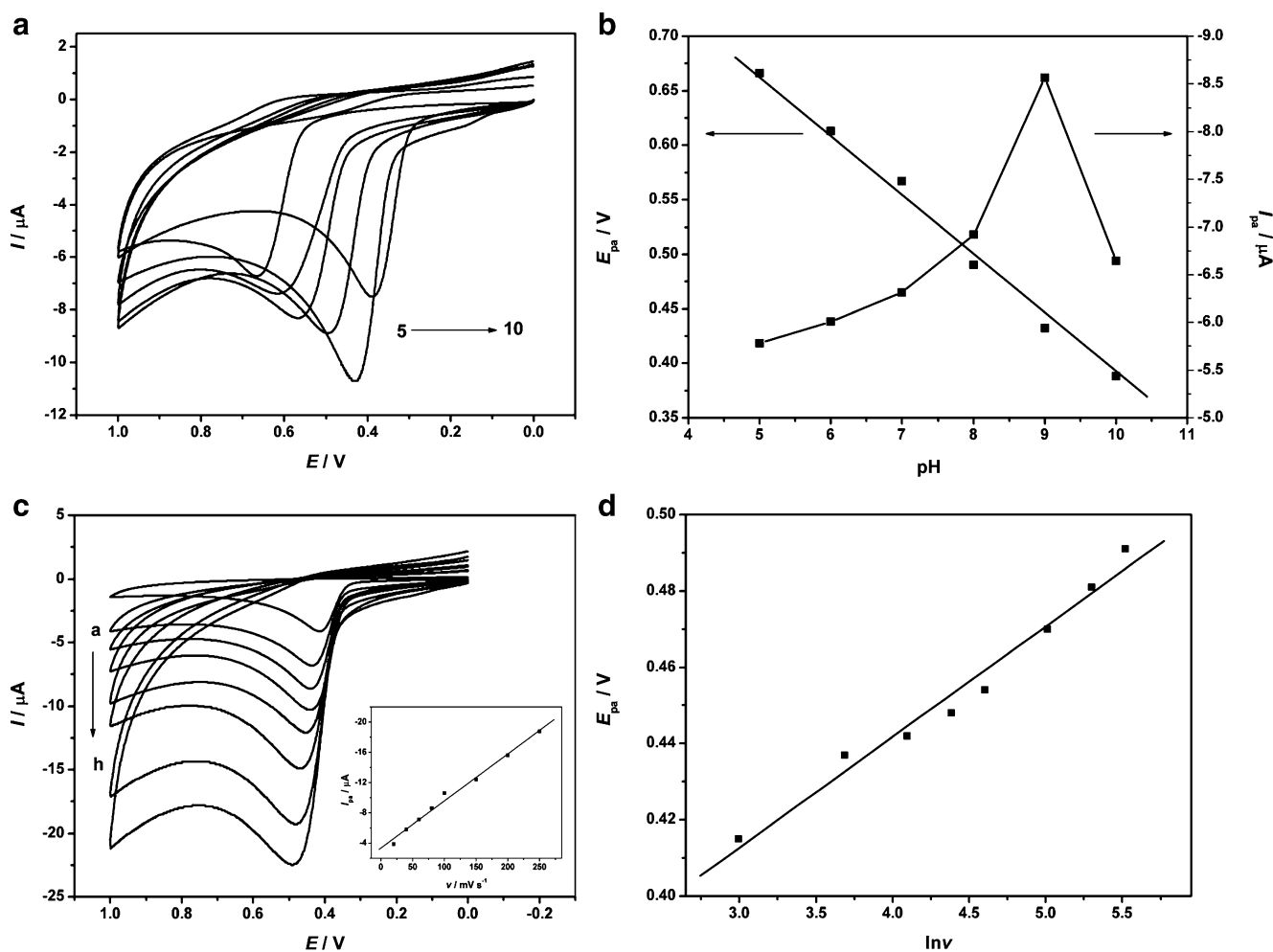


Fig. 2 a Cyclic voltammograms of 0.1 mM BPA at Mg-Al-SDS/GCE under different pH of 5, 6, 7, 8, 9, and 10. b Plots of E_{pa} vs. pH and I_{pa} vs. pH. c Cyclic voltammograms of 0.25 mM BPA at Mg-Al-SDS/GCE with different scan rates. Curves a–k are obtained at 20, 40, 60,

80, 100, 150, 200, 250 $mV s^{-1}$, respectively. *Insert:* Dependence of the oxidation peak current on the scan rate. d The relationship between E_{pa} and $\ln v$. Other conditions are the same as Fig. 1

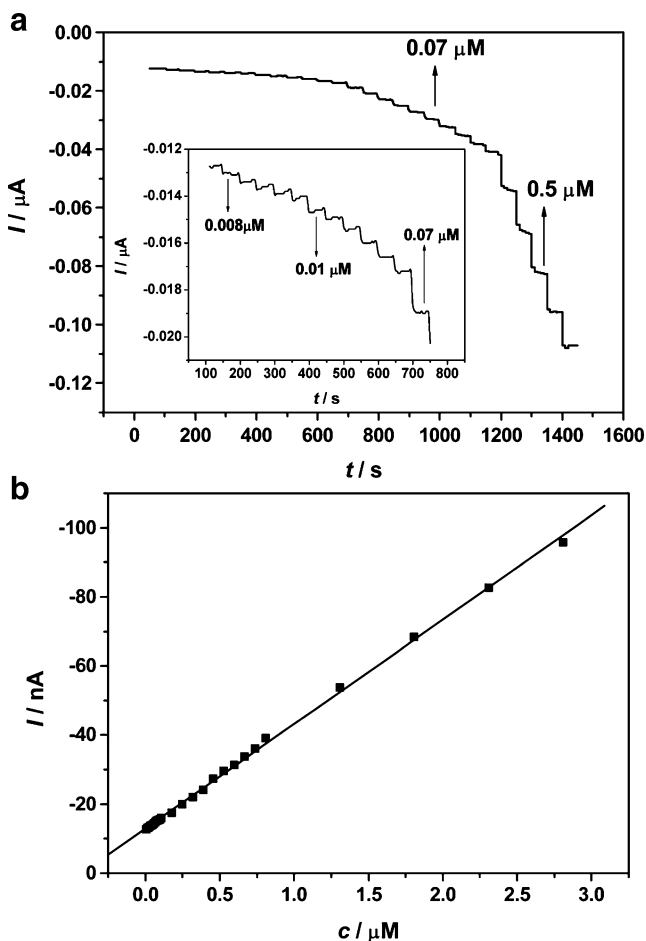


Fig. 3 **a** Current–time recording obtained at Mg-Al-SDS/GCE for successive additions of 0.008, 0.01, 0.07, and 0.5 μM of BPA in pH 7.0 PBS. Applied potential of 0.44 V. *Insert*: The magnified curve from 100 to 750 s. **b** Calibration curve

As shown in Fig. 2b, a linear shift of the oxidation peak potential (E_{pa}) towards negative potential with an increase in pH indicated that protons were directly involved in the oxidation of BPA, and it obeyed the following equation: E_{pa} (V) = $-0.057 \text{ pH} + 0.957$ ($R=0.9973$). A slope of 0.057 VpH^{-1} suggested that the proton transfer number (m) was equal to the electron transfer number (n) [32].

Figure 2c showed cyclic voltammograms of 0.25 mM BPA at Mg-Al-SDS/GCE with different scan rate. It can be seen in the insert of Fig. 2c that the peak current increased linearly with scan rate in the range of 20 to 250 mV s^{-1} , suggesting a typical adsorption-controlled process.

Figure 2d showed the relationship between the peak potential (E_p) and the natural logarithm of scan rate ($\ln v$). It is clear that E_{pa} changed linearly versus $\ln v$ with a linear regression equation of $E_{pa} = 0.028 \ln v + 0.3258$ (V, mV/s, $R=0.9871$) in the range of 20 to 250 mV s^{-1} . For a totally irreversible electrode process, the relationship between the potential (E_p) and scan rate (v) is expressed as follows by Laviron [33]:

$$E_{pa} = E^o + (RT/\alpha nF) \ln(RTk^0/\alpha nF) + (RT/\alpha nF) \ln v \tag{2}$$

where α is cathodic electron transfer coefficient, n is electron transfer number, and R , T , and F have their usual meanings. According to the slope of the plot of E_{pa} versus $\ln v$, αn was calculated to be 0.92. Generally, α is assumed to be 0.5 in totally irreversible electrode process. So the electron transfer number (n) in electrooxidation of BPA is 2. The pH effect on E_{pa} demonstrated that the number of electrons and protons involved in BPA oxidation is equal. Therefore, the electrooxidation of BPA at Mg-Al-SDS/GCE is a two-electron and two-proton process.

Calibration curve

Figure 3a showed a typical current–time plot of Mg-Al-SDS/GCE obtained for successive additions of 0.008, 0.01, 0.07, and 0.5 μM BPA under optimal experimental conditions with stirring. With the increase of BPA concentration, the modified electrode responded rapidly and 95% steady-state current was reached within 4 s. As can be seen in Fig. 3b, the response current increased linearly with BPA concentration in the range of 8×10^{-9} to 2.808×10^{-6} M with the linear regression equation of I (nA) = $-30.25c$ (μM) -12.9 ($R=0.9994$). The detection limit was estimated to be 2.0×10^{-9} M at a signal to noise of 3, which was lower than those reported previously, such as 23 μM (tyrosinase/poly(thionine)/GCE) [34], 1 μM (tyrosinase/boron-doped diamond electrode and tyrosinase–MWCN paste electrode) [35, 36], 0.15 μM (tyrosinase–CPE) [37], 0.1 μM (tyrosinase CPE) [35], 0.038 μM (MCM-41/CPE) [38], 0.03 μM (tyrosinase–SF–MWNTs–CoPc/GCE) [29], 0.02 μM (tyrosinase–SWCN paste electrode) [35], 0.01 μM (CoPc–CPE) [26], 0.0075 μM (CPE) [39], 0.005 μM (LDH/GCE) [22], and 0.00386 μM (NiTAPc/Au) [40], and a little higher than that

Table 1 Determination of BPA in water samples

Samples	Measured ^a (μM)	Added (μM)	Found ^b (μM)	RSD (%)	Recovery (%)
Lake water	0.115	0.500	0.593	2.12	96.42
River water	–	0.500	0.496	3.46	99.20
Tap water	–	0.500	0.513	2.37	102.6
Waste water	1.247	0.500	1.721	4.67	98.51

^a Mean of five measurements

^b Mean of five measurements, relative standard deviation for $n=5$

at PAMAM-CoTe/GCE (0.001 μM) [30], indicating that this proposed method could potentially be used for monitoring of BPA concentration sensitively. The low detection limit could be attributed to the enhanced adsorption capacity of LDH modified with SDS.

Reproducibility, stability, and interference

The fabrication reproducibility of eight electrodes, independently made, gave an acceptable reproducibility with a relative standard deviation of 4.62% for the determination of 2.5 μM BPA by amperometry. The stability of the modified electrode was also investigated by measuring the current response of 2.5 μM BPA every 10 days. Between measurements, the electrode was stored at 4°C in a refrigerator. The response current decreased to 97% after 10 days, while 93% of the original response retained after 20 days. The electrode still retained 88% of its original response even after 30 days. The excellent reproducibility and stability of the modified electrode may be mainly attributed to the high thermal stability and the strong adsorption of the SDS-LDH. Under optimal conditions, the interference of some metal ions and organic compounds on the oxidation of BPA was evaluated. The results suggested that 100-fold concentration of phenol, hydroquinone, hydroxyphenol, pyrocatechol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-di-tert-butylphenol, and dioctyl phthalate had no influence on the signals of BPA with deviations below 5%. Otherwise, some ions such as 250-fold concentration of Na^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Zn^{2+} , Cu^{2+} , Cl^- , SO_4^{2-} , and NO_3^- had no influence on BPA determination.

Practical application

In order to confirm the sensitivity and generality of the proposed method, the amperometric procedure was applied for the determination of BPA in real water samples. Four kinds of water samples were collected from Taian region (China). One milliliter of the sample solution was added to 10 mL PBS (pH9.0) and then was analyzed with the proposed method. The results were shown in Table 1. The recoveries of BPA standard added into the samples were in the range of 96.42% to 102.6%, suggesting that the proposed procedure is very sensitive, selective, and accurate enough for practical application. Therefore, the Mg-Al-SDS/GCE is able to predict the concentrations of BPA in the real matrix samples.

Conclusion

In the presented paper, electrochemical behavior of BPA was investigated at Mg-Al-SDS/GCE. The electrochemical

response of BPA could be facilitated by the cationic clay of Mg-Al-SDS via electrostatic/hydrophobic interaction, testified by the negatively shifted oxidation peak potential and the significantly enhanced oxidation peak current compared with the bare electrode and Mg-Al-LDH-modified electrode. The detection limit obtained in this work was further decreased. Advantages of the method such as being simple, sensitive, accurate, and rapid have been demonstrated by the successful application in the amperometric determination of BPA in water samples.

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