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Simultaneous Detection of Diethylstilbestrol and Malachite Green Using Conductive Carbon Black Paste Electrode

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The voltammetric responses of diethylstilbestrol (DES) and malachite green (MG) were investigated at the conductive carbon black paste electrode (CCBPE), which exhibited an attractive electroanalytical ability. The mechanisms of the electrode reactions were studied. And the experimental parameters influencing the voltammetric responses of the two species, including supporting electrolyte, pH, accumulation time and potential, etc., were optimized. Based on the results, a simple and rapid method for detecting DES and MG simultaneously was established. Under optimal conditions, linear voltammetric responses of DES and MG were obtained in the range of 16-465 nM and 10-510 nM, respectively. For DES and MG the limit detections were 8 nM and 6 nM (s/n=3), respectively. The concentrations of DES and MG in real fishery water samples were tested successfully, indicating that the new method was strongly promising in the environmental monitoring application.

Keywords: Diethylstilbestrol; Malachite green; Conductive carbon black paste electrode; Electroanalysis; Environmental monitoring

1. INTRODUCTION

Diethylstilbestrol (DES, Fig. 1A) is a kind of synthetic non-steroidal estrogens [1]. It has been widely used not only in livestock production to promote growth but also as a treatment for estrogen-deficiency [2]. Many investigations have reported that it had harmful effects on human and animals' health [1, 3]. Although the use of this compound has been banned for years, DES has been recently encountered in Chinese river waters [4].

Malachite green (MG, Fig. 1B) is a kind of synthetic triphenylmethane dye that has been extensively used in aquaculture or food industry as an effective antifungal, anti-microbial and anti-parasitic agent since 1930s [5]. It has also been used all over the world in the fish farming industry as a fungicide, ectoparasiticide and disinfectant [6]. Recent studies suggested that it was toxic to microbial and mammalian cells, promoting the hepatic tumor formation in rodents and reproductive abnormalities in rabbits and fish [7]. Because of its potential mutagenity, teratogenicity, genotoxicity and carcinogenicity, the use of MG has been banned in many parts in the world, including China, the United States, Europe and Canada. However, MG was often illegally used in the fish farming industry due to the low cost, easy availability, high efficacy against fungus, bacteria and parasite [8].

(A) (B)

Figure 1. Chemical structures of DES (A) and MG (B).

The presence of DES and MG in the environment, e.g. fishery water, has become a concern because of their potential to alter the normal endocrine function of animals and humans. Therefore, it is of importance to monitor the amount of them. Generally, the analytical determination of DES has been carried out using gas chromatography–mass spectrometry (GC-MS) [9], liquid chromatography-mass spectrometry (LC-MS) [10], HPLC [11, 12], Enzyme-linked immunoassay [13] or liquid chromatography–tandem mass spectrometry (LC–MS/MS) [14]. For determining MG, HPLC [15, 16], HPLC-MS [17, 18] and Raman microfluidic sensor [19] have often been employed. As it's well known, some of the problems associated with these analytical methods, such as expensive apparatus, long sample preparation time, lengthy measurement time and indirect measurements, made these detection systems less attractive. Recently, electrochemical method, which was another attractive candidate due to its simple and cost-effective characteristics, was developed for determining the two species. In 2002, Zhang et al [20] reported on the voltammetric determination of DES at carbon paste electrode using cetylpyridine bromide as medium. In the following year, Biryol et al [21] also reported the voltammetric investigation of DES. In 2005, Bin et al [22] reported electrochemical behaviors of diethylstilbestrol and its application in pharmacokinetics. Before long, Fei et al [2] proposed the electrochemical determination of DES by a single-walled carbon nanotube/platinum nanoparticle composite film electrode. In 2008, Huang et al [23, 24] reported the electrochemical determination of MG using modified electrodes. By the electrochemical techniques they all obtained satisfactory results. However, the two target species usually coexist in some fishery water. To our best knowledge, there is no report on simultaneous determination of the two by electrochemical method.

As we have reported not long ago, paste electrode made from conductive carbon black (CCBPE) exhibited more attractive voltammetric analytical ability than that from carbon nanotubes and graphite powder due to the attractive high signal/noise ratio [25]. Herein we developed a highly sensitive detection system for determining DES and MG simultaneously based on the cost-effective CCBPE. The electrochemical responses of DES or MG were investigated carefully at the electrode. And the factors influencing the analysis were optimized systematically. Based on these, the concentrations of DES and MG in real fishery water samples were tested simultaneously. This showed that the new protocol was strongly promising in the environmental monitoring application with obvious advantages: simplicity of operation, low cost, rapid response and high sensitivity.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

Cyclic voltammetry (CV), differential pulse voltammetry (DPV), linear sweep voltammetry (LSV) and square wave voltammetry (SWV) were performed using a CHI 660D Electrochemical Analyzer (CH Instruments, Shanghai, China) with a three-electrode arrangement, consisting of a paste working electrode (Φ = 6 mm), a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode. A model pHS-25 digital pH meter (Shanghai Leici Factory, China) was used for pH measurement. Scanning electron microscopic (SEM) measurements were carried out on a JSM-6700F scanning electron microscope (Japan Electron Company).

CCB (HG-1P, density: 1.7-1.9 g/cm^3; particle size: 35-50 nm; BET surface area: 110-130 m^2/g; ash: 1.75%) was purchased from Guanghua Chemical Plant (Zibo, China). DES and MG were purchased from Sigma (USA). The other usual reagents were purchased from Shanghai Chemical Reagent Co. (Shanghai, China) and were all of analytical reagent grade. Solutions were all prepared with sterilized ultrapure water (Resistivity: 18.2 MΩ cm^{-1}) from Poseidon-R70 water purification system (Research Scientific Instruments Co. Ltd, Xiamen, China).

2.2. Sample collection and storage

The six water samples were collected in glass bottles at different fishery locations. The collected water samples were immediately treated by mean of centrifugation at the day of collection to remove suspended particles. Unless stated otherwise, the samples were stored at 4 °C in a refrigerator and analyzed within 72 h.

2.3. Fabrication of paste electrodes

The conductive carbon black paste electrodes (CCBPEs) were fabricated by conventional method described in previous report [25]. In brief, CCB powder and paraffine were hand-mixed carefully in a mortar at an appropriate ratio, followed by being packed tightly into a glass tube (6 mm,

i.d.). The paste electrodes were kept at room temperature before used. Their surfaces were smoothed on a weighing paper prior to use.

2.4. Electrochemical measurements

Unless otherwise indicated, LSV and CV experiments were performed at a scan rate of 0.100 V/s. The SWV measurements were performed at an amplitude of 2.5 mV, a frequency of 15Hz and a Incr E of 4mV. The sample mixtures were stirred with a Teflon coated magnetic stirring bar at about 300 rpm. Before all the electrochemical scans, the paste electrode was renewed. All experiments were conducted at room temperature (25 ± 0.5 °C).

3. RESULTS AND DISCUSSION

3.1. Characterization of the CCBPE

In order to gain ideal electroanalytical ability as well as mechanical robustness, the carbon materials ratio in all the CCBPEs were optimized [25]. In our experiment, the optimized percentage composition of paraffine in the CCBPE was 47%. The nature of the electrode surface is of great importance for the analytical electrochemical properties. Therefore, firstly the morphological characterizations of the CCBPE were performed. Fig. 2 is the typical morphological feature of the CCBPE. It can be seen that the CCBPE shows a more uniform and rough surface topography, which is in good agreement with previous reports [25, 26]. In addition, on the surface of the CCBPE there are few large cavities and cracks.

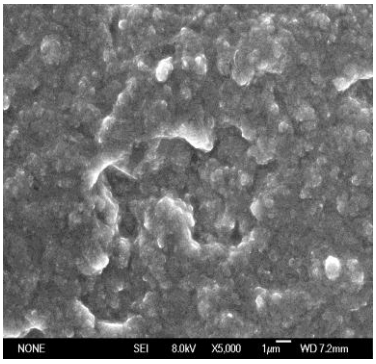

Figure 2. SEM image of the CCBPE. Accelerating voltage, 8.0 kV.

Secondly, the electrochemical area of the CCBPE was evaluated using chronoamperometry in a 1.0 mM ferrocene monocarboxylic acid solution. The slope of the linear region of the $I–t^{-1/2}$ plot in the short time region provides the product $nFAC_0D^{1/2}\pi^{-1/2}$ using the Cottrell equation:

$$i_d = nFAC_0D^{1/2}(\pi\tau)^{-1/2}$$

where C_0=1.0 mM, D=7.96×10^{-10} cm^2/s [27], are the concentration and diffusion coefficient of ferrocene monocarboxylic acid, respectively; and the other parameters have their usual meanings. Then, 0.343 cm^2 was obtained for the electrochemical area of the CCBPE. As expected, it is notable larger than the geometric area (0.283 cm^2).

3.2. Electrochemical response of DES at the CCBPE

Fig. 3 shows the successive CV response of 155 nM DES at the CCBPE in 0.2 M Britton-Robinson (B-R) buffer solution of pH 4.0. At the first cycle, there are a pair of well-shaped redox peaks at about 0.560 V and 0.140 V. Then, at the second cycle, the well-shaped oxidation peak shifts to about 0.475 V with a little decrease of the anodic peak current (i_{pa}). At the same time the reduction peak current (i_{pc}) decreases, too. With the CV scan going on, both the oxidation peak at about 0.475 V and the reduction peak at about 0.140 V decrease regularly. Meanwhile, from the cure of the second cycle a new oxidation peak at about 0.620 V appears. The value of the i_{pa} increases regularly with the increase of the scan cycles. This phenomenon is different from DES at the CNT/platinum nanoparticle composite film electrode [2] and the glassy carbon electrode [21].

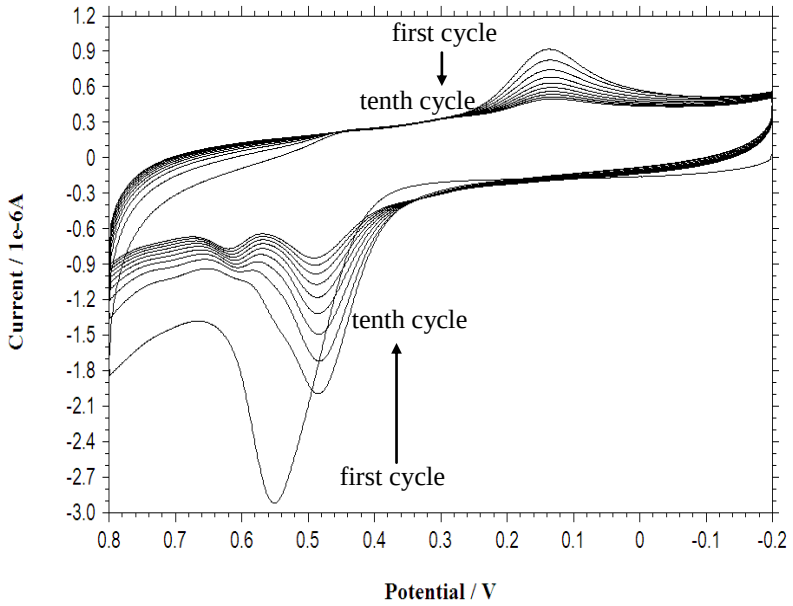

Figure 3. Successive cyclic voltammograms of 155 nM DES at the CCBPE in 0.2 M B-R buffer solution of pH 4.0. Scan rate: 0.100 V/s. Precondition for accumulation: 0.3 V, 180 s. Quiet time: 5 s.

The effect of scan rate v was studied with CV in the range of 0.010-0.200 V/s. As shown in Fig. 4, the anodic peak potential (E_{pa}) of DES shifts positively with the increase of scan rate v. Meanwhile, the reduction peak potential (E_{pc}) shifts negatively with the increase of scan rate v. The relationship between the scan rate v and the E_{pa} was calculated. It is found that the E_{pa} depends linearly on scan

rates (Fig. 4 Inset) with a linear regression equation: E_{pa} (V) = 0.320 v (V/s) + 0.508 (R^2 = 0.9941). According to the Rardles-Sevcik equation [28], the electron transfer coefficient α is 0.24. The i_{pa} of DES is proportional to v over the same range with the equation of i_{pa} (μA) = 18.433 ν (V/s) + 0.028 (R^2 = 0.9988), indicating that the electrode process is controlled by adsorption.

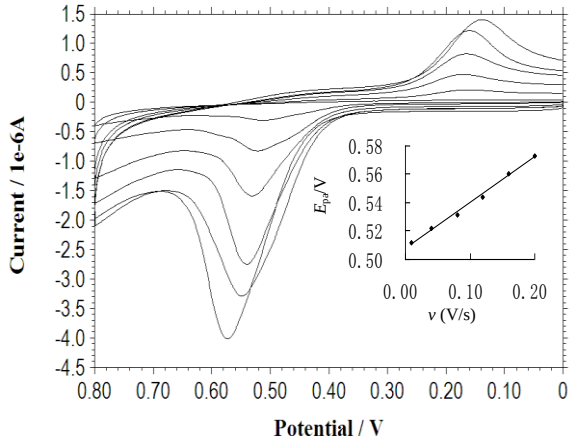

Figure 4. Cyclic voltammograms of 155 nM DES at different scan rate v. From inner to outside: 0.010 V/s, 0.040 V/s, 0.080 V/s, 0.120 V/s, 0.160 V/s and 0.200 V/s, respectively. Inset: the plot of E_{pa} *vs*. scan rate v. Other conditions are as in Fig. 3.

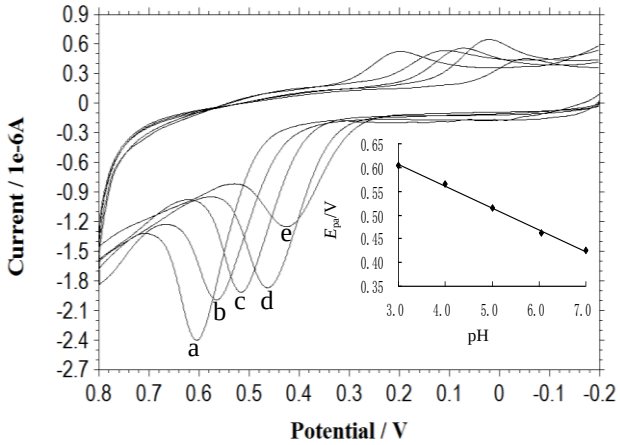

Figure 5. Cyclic voltammograms of 155 nM DES at the CCBPE in 0.2 M B-R buffer solution of different pH. B-R buffer soluteion pH (from a to e): 3.0, 4.0, 5.0, 6.0 and 7.0. Inset: the plot of E_{pa} *vs*. pH. Other conditions are as in Fig. 3.

The E_{pa}s of DES at the CCBPE shift negatively as solution pH increases in the range of 3.0-7.0 (Fig. 5). It can be calculated that there is a linear relationship (Fig. 5 Inset) between the E_{pa}s and the pH with a linear regression equation: E_{pa} (V) = -0.046 pH + 0.744 (R^2 = 0.9980). The slope is a negative value, indicating that the electrochemical process of DES at the CCBPE is an oxidative process. Meanwhile, the absolute value of the slope approached 59 mV, indicating that the proton number

participating the electrode reaction is the same as the electron number [29]. Moreover, it is found that the sensitivity of current response is the highest at low pH.

Between the two redox peaks, the oxidation peak presents higher sensitivity. Thus it was chosen for analyzing and detecting DES. The relationship between the concentration of DES and the i_{pa} was obtained by LSV in 0.2 M B-R buffer solution of pH 4.0. It is found that in the range of 3.1-555 nM there is a linear regression equation of i_{pa} (nA) = 12.129 C_0 (nM) - 38.395 (R^2 = 0.9964) with a detection limit of 1.55 nM (s/n=3), which is far lower than those reported previously [2, 21, 22].

3.3. Electrochemical response of MG at the CCBPE

Fig. 6 shows the CV response of 1.0 μM MG at the CCBPE in 0.2 M B-R buffer solution of pH 7.0. There is a well-shaped redox peak at 0.847 V within the potential window from 0.20 V to 1.00 V. Clearly it's an irreversible electrode process, which is in good agreement with previous reports [23, 24]. From the successive cyclic voltammograms (Fig. 6 Inset) we can see that there is a redox peak only at the first scan. This may be caused by the fact that the adsorption of oxidative product occurs at the electrode surface, resulting in an impossible further access of MG.

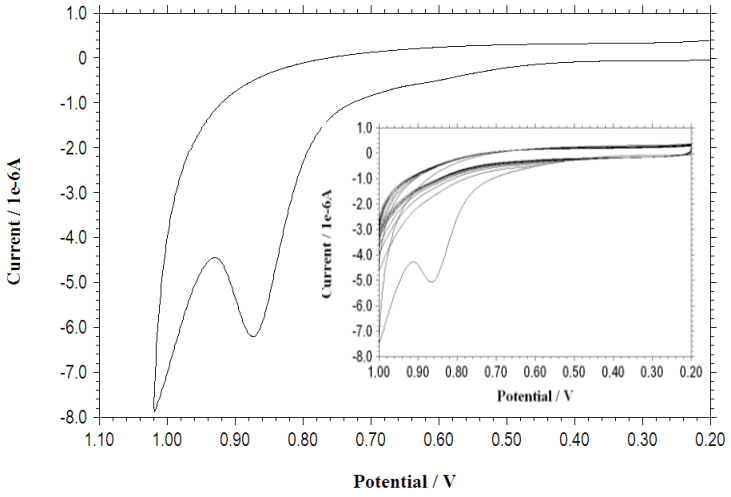

Figure 6. Cyclic voltammogram of 1.0 μM MG at the CCBPE in 0.2 M B-R buffer solution of pH 7.0. Scan rate: 0.100 V/s. Precondition for accumulation: 0.3 V, 180 s. Quiet time: 5 s. Inset shows the successive cyclic voltammograms.

The effect of scan rate v on the CV response of MG was also studied. In the range of 0.010-0.200 V/s, the E_{pa} of MG shifts positively with the increase of scan rate v (Fig. 7). And its value depends linearly on scan rate v (Fig. 7 Inset) with a linear regression equation: E_{pa} (V) = 0.225 v (V/s) + 0.868 (R^2 = 0.9951). According to the Rardles-Sevcik equation [28], the electron transfer coefficient α is 0.46. The i_{pa} of MG is proportional to scan rate v over the same range with the equation of i_{pa} (μA) = 39.654 ν (V/s) + 0.374 (R^2 = 0.9976), indicating that the electrode process is controlled by

adsorption. This is different from the electrode reaction of MG at the boron-doped diamond thin-film electrode in phosphate buffer of pH 2.0 [30].

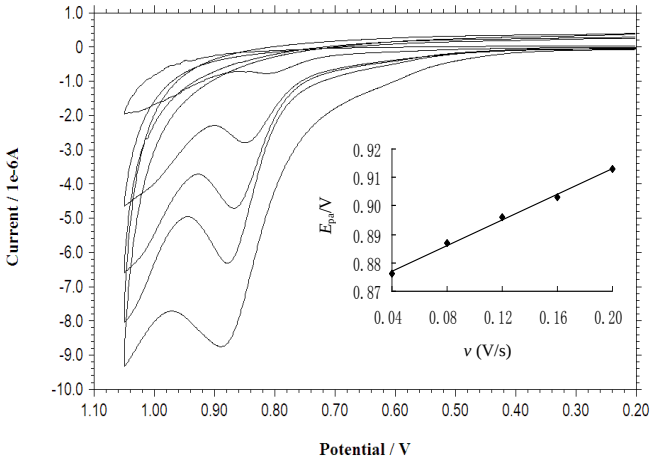

Figure 7. Cyclic voltammograms of 1.0 μM MG at different scan rate *v*. From inner to outside: 0.010 V/s, 0.040 V/s, 0.080 V/s, 0.120 V/s, 0.160 V/s and 0.200 V/s, respectively. Inset: the plot of E_{pa} *vs*. scan rate *v*. Other conditions are as in Fig. 6.

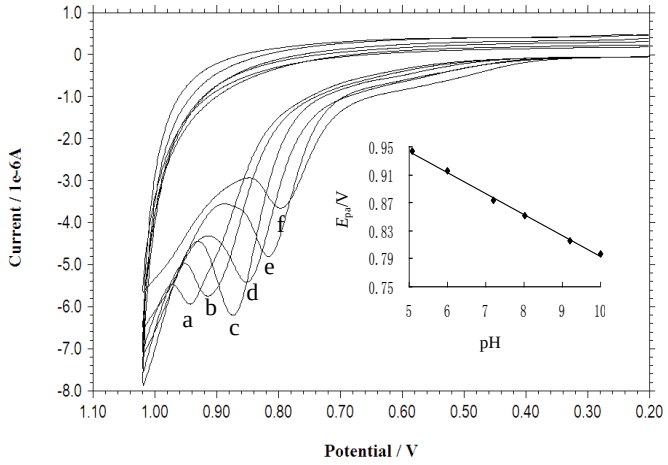

Figure 8. Cyclic voltammograms of 1.0 μM MG at the CCBPE in 0.2 M B-R buffer solution of different pH. B-R buffer soluteion pH (from a to f): 5.1, 6.0, 7.2, 8.0, 9.2 and 10.0. Inset: the plot of E_{pa} *vs*. pH. Other conditions are as in Fig. 6.

The effect of pH on the CV response of MG was also studied at the CCBPE using B-R buffer as supporting electrolyte. As showed in Fig. 8, the E_{pa}s of MG shift negatively as solution pH increases in the range of 5.08-10.0. It can be calculated that there is a linear relationship (Fig. 8 Inset) between the E_{pa}s and the pH with a linear regression equation: E_{pa} (V) = -0.030 pH + 1.094 (R^2 = 0.9978). The slope is a negative value, indicating that the electrochemical process of MG at the CCBPE is an oxidative process. Meanwhile, the number of protons participating in the electrode reaction is the same

as the electron number [29]. Moreover, it is found that the sensitivity of current response is the highest at pH 7.2.

Using 0.2 M B-R buffer solution of pH 7.0 as supporting electrolyte, the relationship between the concentration of MG and the i_{pa} was obtained by SWV at the CCBPE. It is found that in the range of 10 ~ 900 nM there is a linear regression equation of i_{pa} (μA) = 4.885 C_0 (μM) - 0.015 (R^2 = 0.9910) with a detection limit of 4 nM (s/n=3). Though this value of detection limit (1.46 μg/L) is similar to those electrochemical methods reported previously [23, 24, 30], the accumulation time in our experiments is shorter (3 min). According to the Irish regulation, in Ireland the concentrations of MG in fish farm water should not exceed 100 μg/L [31]. Therefore, the method reported here is competent for monitoring MG in water environment.

3.4. Simultaneous detection of DES and MG at the CCBPE

In order to obtain ideal analytical data for simultaneous measurement of DES and MG, some of the important factors were optimized systematically.

Analytical performances at the CCBPE for simultaneous measurement of DES and MG were carried out by CV, DPV, LSV and SWV, respectively. The results indicate that the highest sensitivity for both the two species can be obtained using SWV technique. Thus, SWV mode was employed in all the simultaneous detecting performances.

The buffer solutions were found to induce a remarkable effect on the electrocatalytical activity. A few kinds of buffer solution with the same concentration and pH, including Tris-HCl, HAc-NaAc, PBS, TE, Na_2HPO_4-$C_6H_8O_7$ and $C_6H_8O_7$-$Na_3C_6H_5O_7$, were used as supporting electrolyte, respectively. The results of SWV scan show that in the B-R buffer solution both DES and MG have the highest sensitivity. Then a series of B-R buffer solutions with different concentration and pH were tested. It is found that 0.2 M B-R buffer solution of pH 6.5 is the most suitable supporting electrolyte for simultaneous detection of DES and MG.

With extending accumulation time the i_{pa} of DES at the CCBPE increases almost straightly in the first 120 s. Then the i_{pa} tends to level off. For MG the i_{pa} increases almost straightly in the first 150 s. In order to obtain high sensitivity and ideal efficiency, 180 s was selected for analytical performance. Certainly, increasing the accumulation time can increase the detection limit further.

The effect of accumulation potential was also studied in the range of -0.7-0.3 V. The results demonstrate that 0.3 V is the most suitable potential for accumulating DES and MG together.

The analytical experiments for DES were carried out by varying its concentration in the presence of 0.1 μM MG at the CCBPE using 0.2 M B-R buffer solution of pH 6.5 as supporting electrolyte. Fig. 9 shows SWVs obtained with increasing concentrations of DES. It can be seen that DES exhibits an excellent voltammetric response with the signal height of MG remaining unchanged, indicating that the responses of DES and MG at the CCBPE are relatively independent. The current-to-concentration relationship for DES is linear in the range of 16-465 nM with a regression equation of i_{pa} (μA) = 0.0054 C_0 (nM) - 0.1109 (R^2 = 0.9957). The detection limit is 8 nM. About 0.50 mm paste was pushed out of the holder, following by smoothing at weighing paper. Then the renewed electrode was

scanned in the solution again to evaluate the reproducibility. The relative standard deviation (RSD) for 11 parallel detections of 100 nM DES at the same CCBPE is 4.6%. Using the electrode again after leaving it unused for 2 d, we found that the E_{pa} was almost unchanged and the i_{pa} of 100 nM DES showed a 2.7% decrease in comparison with the initial response. These indicate that the precision, reproducibility and stability of the method are satisfactory.

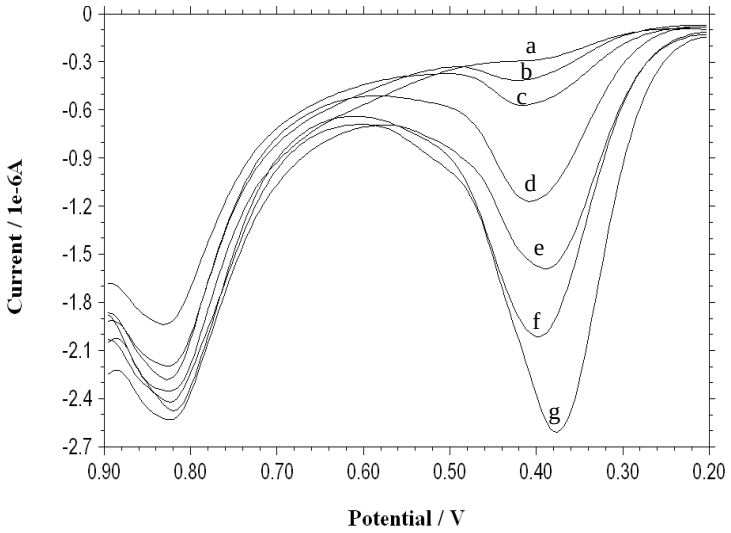

Figure 9. SWV recordings of DES at the CCBPE in the presence of 0.1 μM MG using 0.2 M B-R buffer solution of pH 6.5 as supporting electrolyte. DES concentration (nM): 16 (a), 32 (b), 64 (c), 150 (d), 250 (e), 350 (f) and 450 (g). SWV measurements: amplitude of 2.5 mV; frequency of 15Hz; Incr E of 4mV. Precondition for accumulation: 0.3 V, 180 s. Quiet time: 5 s.

With the same method, the analytical experiments for MG were carried out by varying its concentration in the presence of 155 nM DES at the CCBPE using 0.2 M B-R buffer solution of pH 6.5 as supporting electrolyte. Fig. 10 shows SWVs obtained with increasing concentrations of MG. It can be seen that MG also exhibits an excellent voltammetric response with the signal height of DES remaining unchanged, confirming that the responses of DES and MG at the CCBPE are relatively independent. The current-to-concentration relationship for MG is linear in the range of 10-510 nM with a regression equation of i_{pa} (μA) = 5.542 C_0 (μM) + 0.1207 (R^2 = 0.9906). The detection limit is 6 nM. The reproducibility and stability were also evaluated. The results show that the RSD for 11 parallel detections of 100 nM MG using the same CCBPE is 5.4%. Using the electrode again after leaving it unused for 2 d, we found that E_{pa} of MG was almost unchanged and the i_{pa} of 100 nM MG showed a 2.0% decrease in comparison with the initial response. These indicate that this working electrode is reliable for detecting DES and MG simultaneously.

The selectivity of the proposed method was evaluated. As summarized in Table 1, many foreign substances have no influence on the simultaneous detection of DES and MG. In particular, apt concentration of some inorganic ions (Na^+, K^+, NO_3^-, PO_4^-, etc.) can help to improve sensitivity. However, some organic molecules and surfactant have negative influence on the detection due to competitive adsorption or interaction.

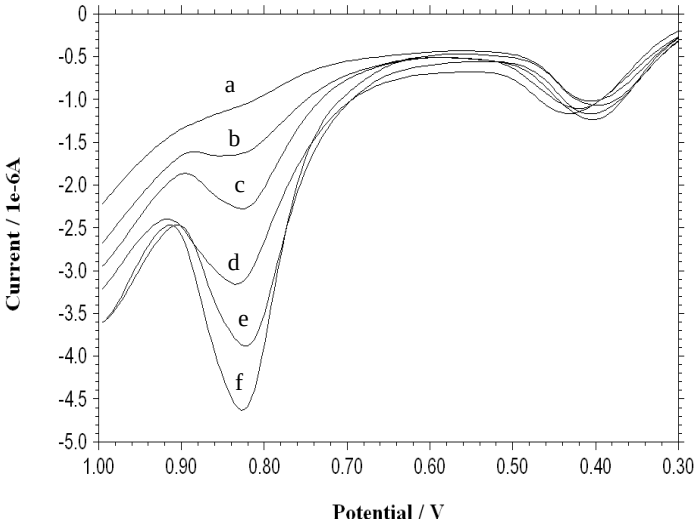

Figure 10. SWV recordings of MG at the CCBPE in the presence of 155 nM DES using 0.2 M B-R buffer solution of pH 6.5 as supporting electrolyte. MG concentration (nM): 10 (a), 50 (b), 100 (c), 200 (d), 350 (e) and 500 (f). Other conditions are as in Fig. 9.

Table 1. Effect of interfering species on the simultaneous detection of 0.1 μM DES and 0.1 μM MG. Other conditions are as in Fig. 9.

Substances	Tolerance level (μM) [a]	Substances	Tolerance level (μM) [a]
Na^+, K^+, NO_3^-, PO_4^-, Cl^-	- [b]	Ascorbic acid	0.1
SO_4^{2-}, CO_3^{2-}	50	Dopamine	0.1
Fe^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}	20	Methylene blue	0.01
Fe^{3+}	15	Sodium dodecylsulphate	0.01

[a] Changes of the i_{pa}s exceed 10%.
[b] The i_{pa}s of DES and MG increase slightly with the increase of these substances in the concentration range of 0.1-500 μM.

3.5. Application in the fishery water samples analysis

In order to verify its application in practical sample analysis, the proposed method was used to detect DES and MG simultaneously in some fishery water samples. It is found that the method of pretreatment may affect the detecting results significantly. For example, the recovery was no more than 20% when we pretreated the water samples by filtering through Millipore membranes (0.45 μm). In our experiments the samples were treated by mean of centrifugation as mentioned in the experimental section. Then 5 mL pretreated sample was added into the same volume of 0.4 M B-R buffer solution (pH 6.5). After an accumulation at 0.3 V for 180 s with stirring, the concentration of the two species was determined by standard addition method. It is found that the RSD of each sample for 8 parallel detections is less than 7%. As shown in Table 2, the values of the recovery are between

84% and 95%. Though the recovery at present is a little low, we believe that it can be improved by developing the pretreatment method further.

Table 2 Concentration of DES and MG in fishery water samples.

Fishery water	DES(μg/L)				MG(μg/L)			
	Detected	Spiked	Found	Recovery	Detected	Spiked	Found	Recovery
1	ND[a]	10	8.4	84%	8.7	10	17.0	91%
2	7.2	10	15.1	88%	6.9	10	16.1	92%
3	ND	10	9.4	94%	ND	10	8.8	88%
4	ND	15	13.5	90%	ND	15	13.3	89%
5	16.9	15	30.8	93%	ND	15	12.7	85%
6	10.2	15	23.1	92%	7.7	15	21.5	95%
Mean				90.2%				90.0%

[a] ND = no detected.

4. CONCLUSION

Both DES and MG have sensitive electrochemical response at the CCBPE, which demonstrates attractive ability for voltammetric analysis due to the remarkably high signal/noise ratio. The redox peaks of the two species don't interfere. Thus an electrochemical method for detecting DES and MG simultaneously can be established. Compared to those conventional protocols [9-19], the new-proposed method has some notable advantages: high sensitivity, low cost, simplicity of pretreatment, easy preparation, fast response and satisfying reproducibility. Being used to measure the concentration of DES and MG simultaneously in real fishery water samples, this method presents satisfying results. It seems to be of great potential application in the environmental monitoring.

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