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Sensitive Determination of Rhodamine B in Real Samples at the Surface of a Multi-walled Carbon Nanotubes Paste Electrode

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Abstract- This paper reported a selective and sensitive electrochemical approach for detection of rhodamine B (RhB) in real samples based on a multi-walled carbon nanotubes paste electrode (MWCNT/CPE). Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and chronocoulometry were used to investigation of electrochemical behavior of RhB. The modified electrode showed an excellent electrocatalytic property toward the oxidation peak current of RhB. Analytical parameters such as linearity, selectivity, repeatability, and stability are also investigated. After optimizing the experimental conditions, the anodic peak current of RhB was linear to its concentration in the range of 0.1–15.0 µM, and the limit of detection was 20.0 nM (S/N=3) in 0.1 M phosphate buffer solution (pH=3.0). Furthermore, the proposed sensor was successfully applied for the detection of RhB in real samples (water samples and Hair colors) with the recoveries of 95.0–110.0%, indicating a promising potential in practical application.

Keywords- Rhodamine B, Voltammetric determination, Modified electrode, Multi-walled carbon nanotubes, Hair colors

1. INTRODUCTION

Rhodamine B (RhB; Fig. 1) is one of the most important fluorescent and water-soluble xanthene organic dyes, which is mainly applied as a colorant in the textile, paper, and food industries as well as a fluorescent dye in biological and analytical chemistry [1-4]. It is also a common analytical reagent that is widely used in such fields as environmental protection, mining, steel, and pharmaceutical [5,6]. RhB has reproductive and developmental toxicity, neurotoxicity, and carcinogenicity towards animals and humans [7], and according to the International Agency for Research on Cancer, RhB is carcinogenic: ingestion, inhalation, and skin contact of the substance may cause acute and chronic poisoning and injury [8,9]. However, due to its low cost and high effectiveness, this harmful dye is still illegally used in some parts of the world [10]. Therefore, sensitive, simple, fast, and reliable methods for the determination of RhB in real samples are highly demanded.

Numerous analytical techniques have been suggested for this purpose, such as high-performance liquid chromatography (HPLC) [11,12], fluorescence spectrophotometry [13], UV-VIS spectrophotometry [14-16], electrokinetic capillary chromatography [17-19], gas chromatography with mass spectrometry [20], surface-enhanced Raman scattering spectroscopy [21], electrogenerated chemiluminescence [22], and electrochemical sensors. However, most of these techniques are high cost, which need complicated and expensive instrumentation, time-consuming sample preparation, and unsuitable for in situ analysis [23,24]. By contrast, the electrochemical techniques have received much attention and exhibited promising application in determining RhB because of lots of merits such as low cost, fast and quick response, easy operation, good selectivity, and high sensitivity [25-27].

Some electrodes have been developed for the electrochemical detection of RhB, but to the best of our knowledge, there is no report about the electrochemical determination of RhB by carbon paste electrode (CPE). CPEs are one of the most usually used electrodes because of its simple development, low price, easy modification, good sensitivity, easy renewability, low background current and quick response [28,29]. Various nanomaterials was used to improvement of their electrochemical characteristics of electrodes to different analytes [30]. Multi-walled carbon nanotube (MWCNT), a rapidly rising star in the field of materials, shows exceptional electrical conductivity and large specific surface areas with potential applications in modifying sensors [31,32].

The purpose of this research is to optimize a sensitive, reproducible and selective electrode for determination of RhB in real samples by voltammetric methods. Based on the good electrocatalytic activity of MWCNT modified CPE (MWCNT/CPE) toward the electrochemical oxidation of RhB, a sensitive electrochemical method has been proposed for the determination of RhB.

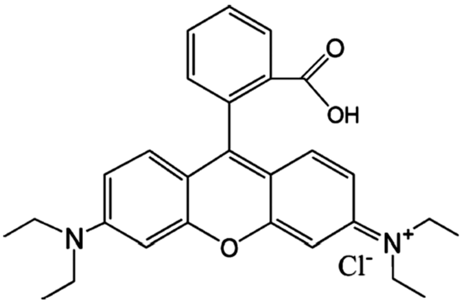

Fig. 1. Molecular structure of Rhodamine B

2. EXPERIMENTAL

2.1. Reagents

All chemicals and reagents were of analytical grade and used as received without any purification. RhB (C.I. 45170) was dissolved in demineral water to prepare a 1.0×10^{-3} $moll^{-1}$ standard solution. Pure fine graphite powder (Merck) and paraffin oil (Merck, density: 0.88 g cm^{-3}) were used as binding agents for the graphite pastes. Multi-wall carbon nanotubes (MWCNTs) were obtained from the Chinese Academy of Sciences and had outside diameters of 10–20 nm, lengths of less than 1–2 mm and purities of over 95%. Deionized water was used for all experiments. Phosphate buffer solution (PBS; 0.1 M) was prepared daily by diluting 3.4 ml 85% phosphoric acid (Merck) in 500 ml of deionized water and its pH value was adjusted with HCl or NaOH solutions using a pH meter instrument.

2.2. Apparatus

All the electrochemical measurements were performed using an Autolab potentiostat-galvanostat PGSTAT 35 (Eco chemie Utrecht, Netherlands). A conventional three-electrode electrochemical cell was used with a KCl-saturated Ag/AgCl as a reference electrode (Metrohm), a Pt wire (Metrohm) as the counter electrode and an unmodified or modified carbon paste as a working electrode (2 mm in diameter). A digital pH meter (Metrohm model 691) was used to adjust pH of the PBS solurions. Deionized water was formed with an ultrapure water system (smart 2 pure, TKA, Germany). Samples were dispersed with an ultrasonic bath (Bandelin Sonorex, Germany) at a constant frequency of 35 kHz during experimentation. Data were collected at room temperature.

2.3. Preparation of the electrode

At first, 2.0% (w/w) of MWCNT was mixed by hand with 78.0% (w/w) of graphite powder in a mortar and pestle. The mixture was added by 20.0% (w/w) of paraffin oil and mixed for 20 min to appear a uniformly-wetted paste. The paste was packed firmly into a cavity (2.0 mm inner diameter and 10 cm long) at the end of a polyethylene tube. A copper wire was placed into the carbon paste to hold the electrical contact. In addition, a new surface was created by inserting additional paste out of the tube and polishing with a weighing paper. The same way was also applied to prepare unmodified CPE in the absence of MWCNT for comparison the products.

2.4. Sample Preparation

In this work, two brown Hair colors were purchased from a local market and applied as real samples. The samples were treated as described. The 0.50 g of Hair color was carefully weighed and added into 10.0 mL ethanol followed by ultrasonication for 20 min. Then, the solution was transferred in a 100 mL volumetric flask and diluted with PBS (pH=3.0). For electrochemical determination, 10.0 mL from this sample solution was transferred into voltammetric cell.

2.5. Analytical procedure

For the RhB analysis via the developed method, the electrode was inserted into an electrochemical cell, containing of 10 mL of 0.1 M PBS (adjusted to pH=3.0) and, a certain volume of RhB stock solution was transferred into the cell. Then, differential pulse voltammetry (DPV) technique was performed for the determination of RhB. For this aim, the differential potential was scanned in the range of 0.6–1.3 V (*vs.* Ag/AgCl) and the oxidation peak currents at 1.04 V were recorded for the electrochemical oxidation of RhB. DPV employed the following parameters: step potential=6.0 mV, modulation amplitude=50 mV. For the cyclic voltammetry (CV), the potential range was from 0.6–1.3 V at scan rate of 60 mVs^{-1}. All measurements were carried out at room temperature.

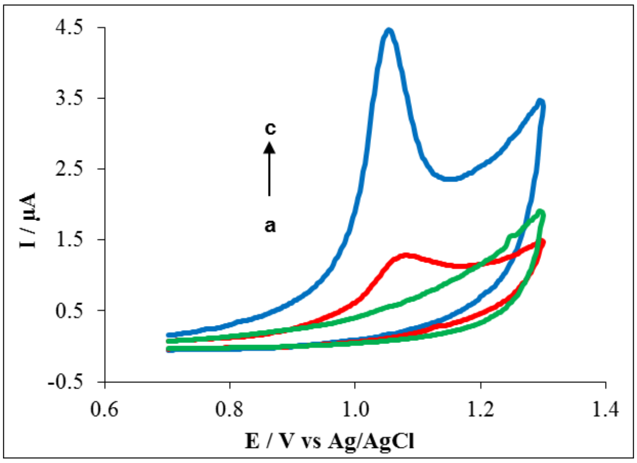

Fig. 2. Cyclic voltammograms of (a) MWCNT/CPE in PBS (pH=3.0); (b) CPE in the presence of 5.0 µM RhB; (c) MWCNT/CPE in the presence of 5.0 µM RhB (scan rate 60 mVs^{-1})

3. RESULTS AND DISCUSION

3.1. Electrochemical Behavior of RhB at the Modified Electrode

The electrochemical performance of the modified electrode for 5.0 µM of RhB in PBS solution (pH=3.0) were investigated by cyclic voltammetry (CV). As can be seen in Fig. 2, a small anodic peak was observed for CPE, while the peak current significantly increased at the surface of the MWCNT/CPE electrode that indicated the effect of modified electrode in the electrocatalysis of RhB.

3.2. pH effect

The pH influence of accompanying electrolyte on anodic peak currents and potentials of RhB was examined to acquire the most favorable peak current and shape. For these, differential pulse voltammetric (DPV) analysis was carried out in pH ranges of 2.0 to 7.0 in the presence of PBS. A comparison between the anodic peak potential at different pH values of MWCNT/CPE (Fig. 3) shows that the pH of the solution has a significant influence on the peak potential of the catalytic oxidation of RhB.

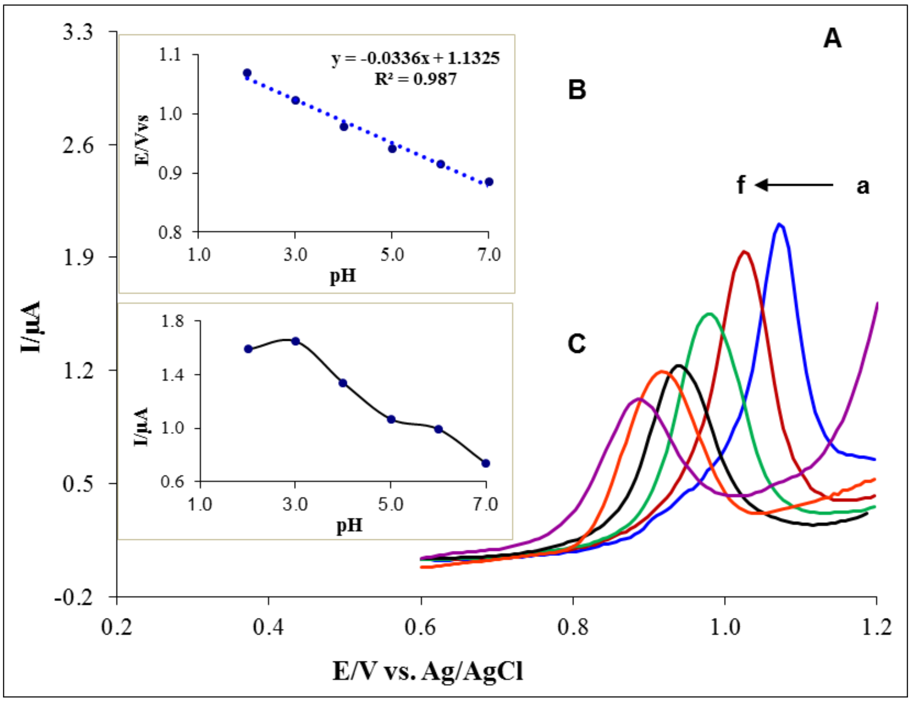

Fig. 3. (A) DPV of a solution of 5.0 µM RhB at various buffered pHs with a constant scan rate 60 mVs^{-1}, a to f correspond to pH values of 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0, respectively; (B) electrochemical potential, E (V) *vs.* pH; and (C) intensity, I (µA) *vs.* pH

It shows that pH=3.0 has a maximum value in the oxidation current. The anodic peak potentials shifted negatively with the increase of the solution pH, indicating that the oxidation of RhB at the MWCNT/CPE is a pH dependent reaction and this relationship was expressed by Eq. (1) in (Fig. 3B):

$$E_{pa}\,(v) = -0.0336x + 1.1325 \qquad R^2 = 0.987 \qquad (1)$$

The slope value of dE_{pa}/dpH plot as 0.033 V pH^{-1} is close to half of 0.059 V pH^{-1}, corresponding to the 1 H^+ per two electrons stoichiometry [33].

3.3. Effect of Scan Rate on the Oxidation of RhB

The effect of applied scan rate on the oxidation of 5.0 μM RhB in 0.1 M PBS (pH=3.0) was studied in the range of 10-300 mVs^{-1} by cyclic voltammetry at the MWCNT/CPE. The modified electrode showed increases in the current signals with increasing scan rate as showed in Fig. 4A. The plot of anodic peak current (I_{pa}) of 5.0 μM RhB increase linearly with square root of scan rate (inset B), suggesting that the electro-oxidative reaction of RhB on the electrode surface was a diffusion-controlled process. Moreover, the log I_{pa} is linear to log ν (inset C), and the regression equation is: log I_{pa}=0.7038 log ν+1.0443 (R^2=0.990).

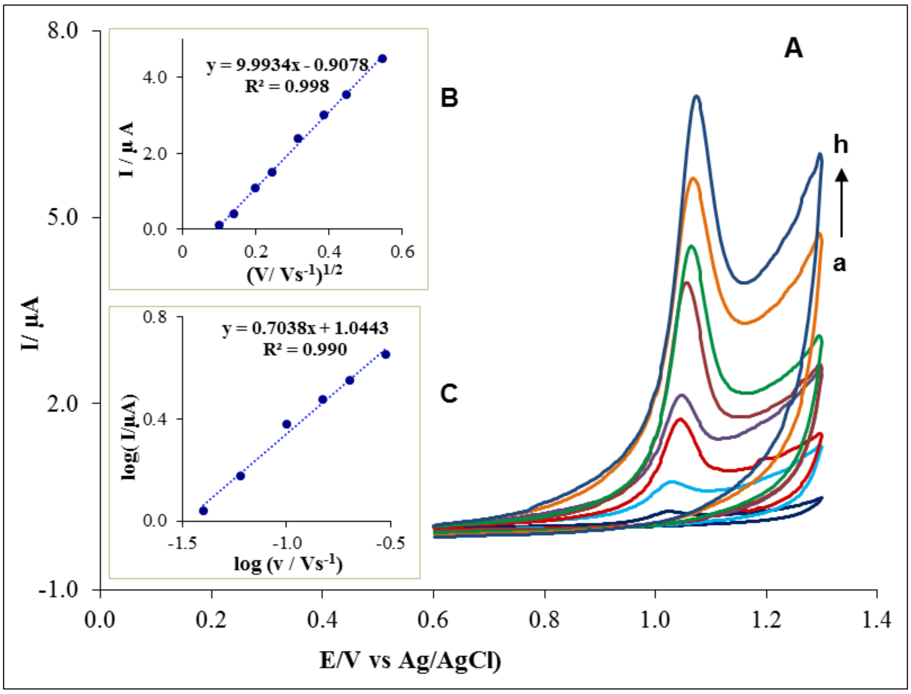

Fig. 4. (A) Cyclic voltammetry of 5.0 μM RhB at scan rates of 10.0, 20.0, 40.0, 60.0, 100.0, 150.0, 200.0, and 300 mVs^{-1} (a to h) in the presence of PBS (pH=3.0) at MWCNT/CPE; (B) Plot of peak current *vs.* $(v/Vs^{-1})^{1/2}$; (C) Plot of log I *vs.* log ν

The slope is between 0.5 and 1.0, meaning that it virtually belongs to a mixed system of diffusion and adsorption [33]. Also, there is a linear relationship between Ep and the logarithm of the scan rate, and the regression equation is: E_p=1.0913+0.0372 log ν (E_p in V, ν in Vs^{-1}, r=0.989). Such a behavior reveals the irreversible nature of the electrochemical process for RhB on the surface of MWCNT/CPE [34].

3.4. Chronocoulometry Measurements

The oxidation reaction of RhB at the MWCNT/CPE was investigated by chronocoulometry. The chronocoulograms of various solution of RhB containing 0.025, 0.040, 0.060, 0.090, and 0.13 mM in PBS (pH=3.0) by setting the working electrode potential at 1.3 V shows in Fig. 5A. The diffusion coefficient, D, of RhB was obtained using the Cottrell equation (Eq. (2)) [35]:

$$Q = 2nFA\ C_O\ D^{1/2}\ \pi^{-1/2}\ t^{1/2} \tag{2}$$

where D (cm^2s^{-1}) and C (M) are the diffusion coefficient and the bulk concentration, respectively. Fig. 5B demonstrates experimental plots of Q *vs.* $t^{1/2}$ for different concentrations of RhB. Using the slopes of the resulting plots and Cottrell equation, the value of D was obtained 3.1×10^{-5} cm^2s^{-1} (Fig. 5C).

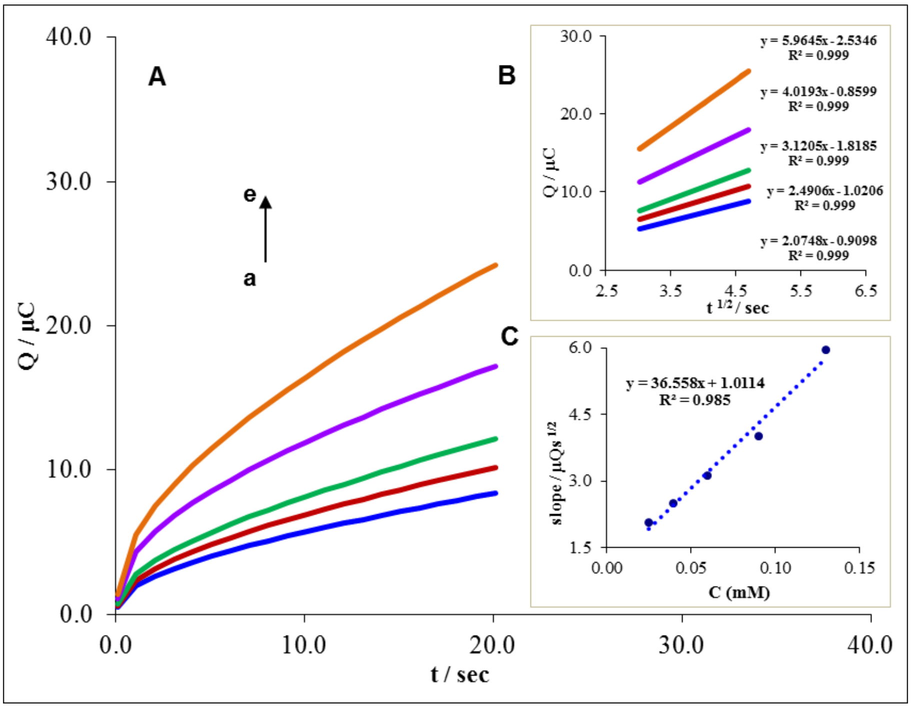

Fig. 5. (A) Chronocoulograms obtained for various concentrations of RhB at MWCNT/CPE in PBS (pH=3.0), with a potential step at 1.3 mV. a to e correspond to 0.025, 0.040, 0.060, 0.090, and 0.13 mM of RhB; (B) plots of Q *vs.* $t^{1/2}$ ($s^{1/2}$) obtained from chronocoulograms a–e; and (C) a plot of the slope of the straight lines against the concentration of RhB

3.5. Determination of RhB

Under the optimized conditions, the quantitative determination of RhB was performed by DPV (Fig. 6). The I_p of RhB increased linearly in the concentration range of 0. 1–15.0 μM and the linear regression equation of RhB is described by Eq. (3):

$$Ip\ (\mu A) = 0.1041\ C\ (\mu M) + 0.2138 \qquad R^2=0.996 \qquad (3)$$

The detection limit for RhB was found to be 20.0 nM. The determination ability of MWCNT/CPE was compared with other modified electrodes. As can be observed from Table 1, this modified electrode has a lower detection limit than other modified electrodes which are listed in this table.

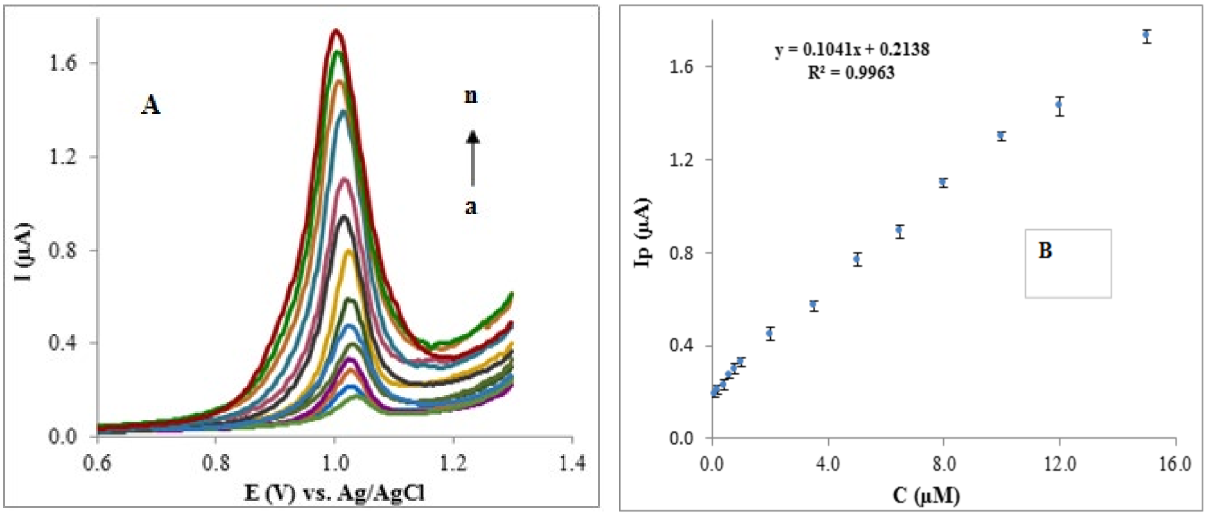

Fig. 6. DPV of MWCNT/CPE in a PBS (pH=3.0) containing different concentrations of RhB from a to n: 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.5, 5.0, 6.5, 8.0, 10.0, 12.0 and 15.0 μM (A); The linear relationship between RhB concentrations and peak currents (B)

Table 1. Comparison of the behavior of various electrodes in the detection of RhB

Electrode	**Technique**	**Linear range (μM)**	**Detection Limit (nM, S/N=3)**	**Ref.**
SPZP/NAF/GCE	SWSV	0.01-5.0	4.3	[36]
GCE	DPV	0.01-2.0	6.1	[37]
Cu-carbon sphere/GCE	DPV	0.3-30.0	100	[38]
β-CD-AuNPs/HCNS/GCE	DPV	0.01-2.0	2.0	[39]
MWCNT-COOH/IL/PGE	DPV	0.005-2.0 2.0-60.0	1.0	[7]
MWCNT/CPE	DPV	0.1-15.0	20.0	This work

SPZP/NAF/GCE, silica-pillared zirconium phosphate/Nafion glassy carbon electrode; SWSV, square wave striping voltammetry; β-CD-AuNPs/HCNS, β-cyclodextrin functionalized nanogold/hollow carbon nanospheres; MWCNT-COOH/IL/PGE, multi-walled carbon nanotube and ionic liquid modified pencil-graphite electrode

3.6. Determination of RhB in real samples

To further explore the practical applications, the MWCNT/CPE was used for detection of RhB in water and Hair colors. The samples were prepared in accordance with procedures described in the "Experimental" section. Then, 10.0 mL of this solution was added to the electrochemical cell and DPV was performed. No differential pulse voltammetric peak corresponding to RhB was observed when the samples were analyzed, indicating the absence of RhB in these samples. Next, different amounts of RhB were spiked to the electrochemical cell. The results were presented in Table 2. The recovery percent values of RhB were obtained between 95.0 and 110.0, demonstrating that this method is reliable for quantitative analysis of RhB in real samples.

Table 2. Determination results of RhB in real samples (n=3)

Sample no.	Added (μM)	Found (μM)	Recovery (%)
Water sample	0.00	Not detected	-
	2.00	2.05	102.5
	4.00	3.80	95.0
	8.00	8.25	103.1
Hair color (BES Company)	0.00	Not detected	-
	2.00	2.10	95.0
	4.00	4.30	107.5
	8.00	7.85	98.1
Hair color (Collection Company)	0.00	Not detected	-
	2.00	2.20	110.0
	4.00	3.90	97.5
	8.00	7.8	97.5

3.7. Interference Study

In order to estimate the selectivity of MCNT/CPE to the RhB determination, the influence of various foreign species has been investigated via the DPV method by adding a known concentration of important interfering substances into the analytical solution containing 5.0 μM RhB and the tolerance limit of each foreign substance was obtained [40]. The results showed that the concentrations of Ca^{2+}, Mg^{2+}, K^{+}, Fe^{2+}, NO_3^-, Cl^-, CO_3^{2-} have not significantly influence on the peak current and peak potential of RhB. Also, the interference of some dyes on the determination of RhB was investigated. The tolerated concentration of foreign substances was taken in Table 3.

Table 3. Tolerated concentration of foreign substances in the determination of RhB

Foreign Species	**Tolerance level ratio**
Ca^{2+}, Mg^{2+}, Fe^{2+}, K^{+}, NO_3^{-}, CO_3^{2-}, Cl^{-}	200
Red 10B	100
Direct Orange 26	20
Direct Red 80	15
Sunset yellow, Food Red 106	5

3.8. Reproducibility, Repeatability and Stability

To investigate the reproducibility of technique, a MWCNT/CPE was made and the anodic peak current of 5.0 μM RhB was obtained for six times. The obtained relative standard deviation (RSD) of measurements was 3.9%, suggesting that this method is highly reproducible. Further repeatability of MWCNT/CPE towards the estimation of RhB has been analyzed by fabrication six different electrodes under the same experimental condition, and the RSD value found to be equal to 2.3%. These results have shown that the prepared electrode has good stability, reproducibility and could be used for determination of RhB. The stability of the prepared modified electrode has been evaluated over a 2-week period by measuring the anodic peak currents periodically. The obtained results showed that the initial response was diminished by only 5.3% for RhB after 2-week period, indicating the high stability of the MWCNT/CPE.

4. CONCLUSION

In this study, a simple and sensitive electrochemical method was described for determination of RhB based on a carbon paste electrode modified with multi-walled carbon nanotubes. The resulting electrode presents advantages of easy fabrication, high sensitivity, selectivity, and reproducibility of the voltammetric response. This method also was successfully applied in the analysis of RhB in real samples with satisfying recoveries, which proves the method is feasible to be used for real samples.

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