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Simple sensor for simultaneous determination of dihydroxybenzene isomers

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Abstract A simple sensor based on bare carbon ionic liquid electrode was fabricated for simultaneous determination of dihydroxybenzene isomers in 0.1 mol L^{-1} phosphate buffer solution (pH 6.0). The oxidation peak potential of hydroquinone was about 0.136 V, catechol was about 0.240 V, and resorcinol 0.632 V by differential pulse voltammetric measurements, which indicated that the dihydroxybenzene isomers could be separated absolutely. The sensor showed wide linear behaviors in the range of 5.0×10^{-7}–2.0×10^{-4} mol L^{-1} for hydroquinone and catechol, 3.5×10^{-6}–1.535×10^{-4} mol L^{-1} for resorcinol, respectively. And the detection limits of the three dihydroxybenzene isomers were 5.0×10^{-8}, 2.0×10^{-7}, 5.0×10^{-7} mol L^{-1}, respectively ($S/N = 3$). The proposed method could be applied to the determination of dihydroxybenzene isomers in artificial wastewater and the recovery was from 93.9% to 104.6%.

Introduction

As proverbial hazardous substances, dihydroxybenzene isomers are harmful to human health and environment [1–3]. Hydroquinone, catechol, and resorcinol usually coexist in environmental samples and they have similar structures and properties. Therefore, the simultaneous determination of isomers is an interesting subject in electrochemistry. Due to the operating complexity, time waste, and reagent consumption of the separation, it is necessary to develop a simple, rapid, and nonseparation method for simultaneous determination of isomers. Various chemically modified electrodes have been proposed as an efficient approach and they have attracted considerable interest during the past years [4–19].

Recently, ionic liquids have been proved to be very interesting and efficient pasting binders in place of nonconductive organic binders for the preparation of carbon composite electrodes [20, 21]. Due to its low cost, ease of fabrication, and renewable surface, the carbon ionic liquid electrode (CILE) has been widely applied in the electroanalytical community [22–25]. The CILE not only provides very low background comparable to common carbon paste electrodes, but also shows surprisingly high electrochemical performance [20]. Owing to the strong adsorption of dihydroxybenzene isomers, they do not easily leave from the electrode surface. In order to ensure the reproducibility of the sensor, the regeneration procedure must be carried out after each measurement. Compared with other modified electrodes, the surface of CILE can be easily renewed, and

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there is no need to modify the electrode further. Based on its significant superiority, CILE was used as a simple but sensitive sensor in this paper.

Electrochemical methods, such as cyclic voltammetry [4–7], linear sweep voltammetry (LSV) [8–10], amperometric i–t curve measurement [11–14], and differential pulse voltammetry (DPV) [15–18], have been widely applied for the determination of dihydroxybenzene isomers. DPV, which has higher current sensitivity and better resolution, is proved to be one of the most favorable techniques for the determination of the dihydroxybenzene isomers. In this paper, a simple sensor based on bare CILE was first proposed for simultaneous determination of dihydroxybenzene isomers using DPV. In order to obtain a satisfied result, the effects of supporting electrolyte and pH, accumulation potential and time, and carbon paste composition were systematically discussed on the simultaneous determination. The proposed method was applied to simultaneous determination of the compounds in wastewater samples with high selectivity.

Experimental

Reagents

The ionic liquid N-octylpyridium hexafluorophosphate (OPPF$_6$) was purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). Graphite powder (extra pure) was obtained from Shanghai Chemical Reagents (Shanghai, China). Hydroquinone (HQ), catechol (CC), and resorcinol (RC) were obtained from Tianjin Kemiou Chemical Co. (Tianjin, China) and HQ, CC, and RC solutions were prepared immediately before use in the experiments. The
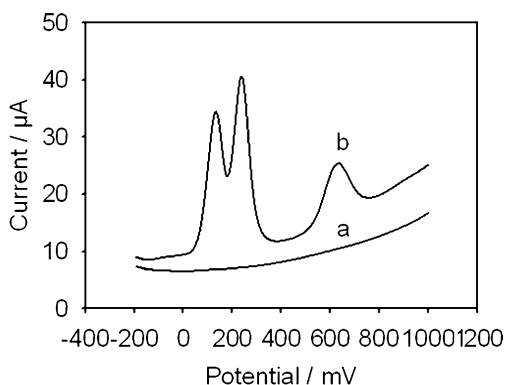

Fig. 1 DPVs of the CILE without (*a*) and with (*b*) 200 μM HQ, CC, and RC in 0.1 mol L^{-1} PBS (pH 6.0). *Amplitude* 50 mV, *pulse width* 50 ms, *pulse period* 0.2 s
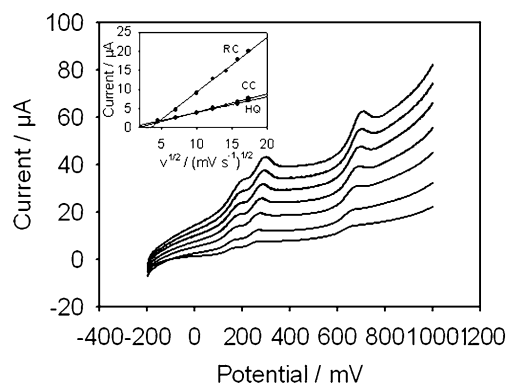

Fig. 2 LSVs of 100 μM HQ, CC, and RC in 0.1 mol L^{-1} PBS (pH 6.0) with different scan rate: 20, 50, 100, 150, 200, 250, and 300 mV s^{-1} (*from bottom to top*). *Inset* plots of peak current with square root of the scan rate

phosphate buffer solutions (PBS) of various pH values, 0.1 mol L^{-1} was used as the supporting electrolytes. The synthetic wastewater samples were prepared by added known amounts of dihydroxybenzene isomers in local tap water without any pretreatment. All other chemicals were of analytical grade and used without further purification. Double-distilled water was used throughout.

Apparatus

The electrochemical measurements were carried out with CHI660A electrochemical workstation (CH Instruments, Shanghai Chenhua Instruments Corporation, China). A conventional three-electrode system was employed comprising a CILE (1.8 mm in diameter) as working electrode, a platinum wire as counter electrode, and a Ag/AgCl (3 mol L^{-1} KCl) electrode as reference electrode. All potentials were reported with respect to the reference electrode. A magnetic stirrer (model 79–1) was used to stir the testing solution during the preconcentration step. All the experiments were carried out at room temperature.

Electrode preparation

CILE was prepared according to the following procedure. Various electrodes were prepared by mixing the OPPF$_6$ with the graphite powder to give an appropriate ratio OPPF$_6$/carbon paste (from 25% to 75% (*w/w*)). The mixtures were ground in a mortar and then a portion of the resulting paste was packed firmly into the cavity (1.8 mm in diameter) of a Teflon holder. The electrode was then heated simply by using a hair drier for 2 min. It was then left to cool to room
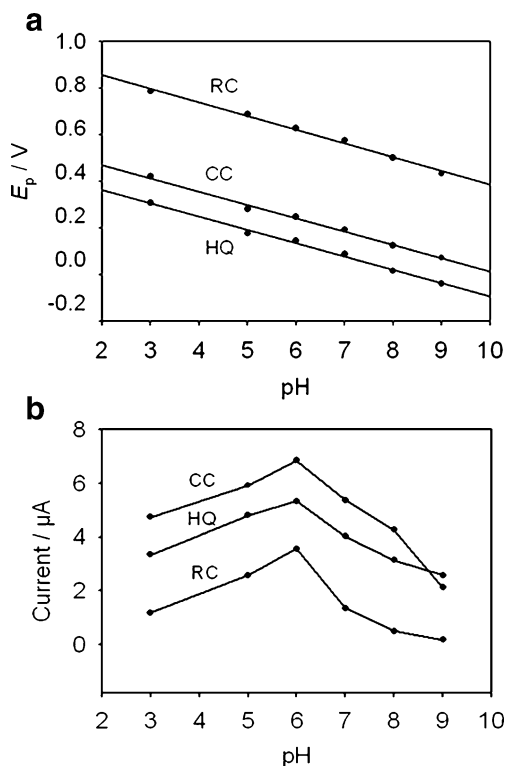
Fig. 3 Effect of pH on the peak potentials (a) and peak currents (b) of 100 μM HQ, CC, and RC, respectively. The DPVs conditions were the same as in Fig. 1

Fig. 5 Effect of carbon paste composition on the peak currents of 100 μM HQ, CC, and RC, respectively. The DPVs conditions were the same as in Fig. 1

grams were recorded from −0.2 to 1.0 V after 10 s quiescence in 0.1 mol L^{-1} PBS (pH 6.0). Experimental parameters: amplitude, 50 mV; pulse width, 50 ms; pulse period: 0.2 s. Peak currents were measured at 0.136 V for hydroquinone, 0.240 V for catechol, and 0.632 V for resorcinol.

In order to ensure the reproducibility of the sensor, the regeneration procedure was carried out after each measurement.

Results and discussion

Electrochemical behaviors of dihydroxybenzene isomers

In order to evaluate the sensitivity and selectivity of the sensor for the simultaneous determination of dihydroxybenzene isomers, the electrochemical behaviors of mixed components of dihydroxybenzene isomers (each concentration of 200 μM) were investigated by DPV (as shown in Fig. 1). At the sensor, three well-defined oxidation peaks appeared around the potentials of 0.136, 0.240, and 0.632 V, which attributed to the oxidation of hydroquinone, catechol, and resorcinol, respectively. The results indicated

temperature. The electric contact was established via a copper wire. A new surface was obtained by smoothing the electrode onto a weighing paper.

Analytical procedure

LSV and DPV were chosen for studying the electrochemical behaviors of dihydroxybenzene isomers. The determination of dihydroxybenzene isomers using DPV was carried out by using the following steps: (a) the open-circuit accumulation step proceeded for 30 s; (b) the differential pulse voltammo-

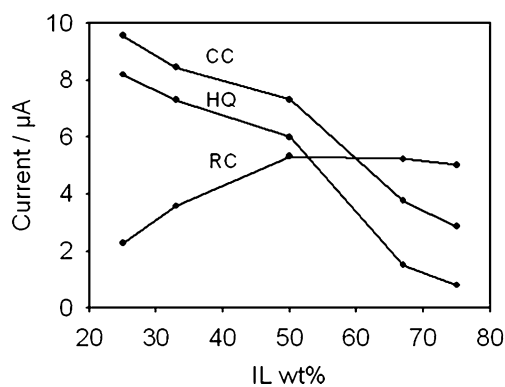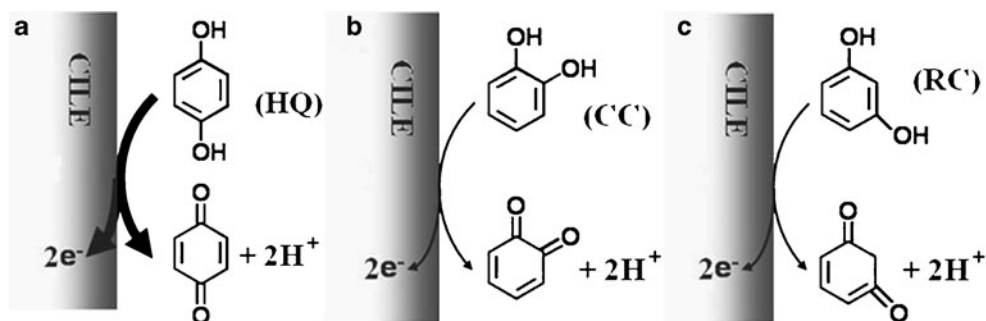Fig. 4 Schematic diagrams for a HQ, b CC, and c RC electro-oxidation at CILE

Table 1 Comparable methods for determination of dihydroxybenzene isomers

Methods	Component	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	References
Integrated MWCNT electrode	Catechol	1.0×10^{-6}–1.0×10^{-3}	6.0×10^{-7}	[6]
CMK-3/GCE	Catechol, hydroquinone	5×10^{-7}–3.5×10^{-5} (CC) 1×10^{-6}–3×10^{-5} (HQ)	1×10^{-7} (CC, HQ)	[7]
Poly-ACBK/MWNTs/GCE	Dihydroxybenzene isomers	1×10^{-6}–1×10^{-4}	1×10^{-7} (HQ) 1×10^{-7} (CC) 9×10^{-8} (RC)	[9]
Cobalt hydroxide/GCE	Hydroquinone	5.0×10^{-6}–1.25×10^{-4}	5.0×10^{-7}	[10]
Fe$_3$O$_4$–SiO$_2$-Laccase/CPE	Hydroquinone	1×10^{-7}–1.375×10^{-4}	1.5×10^{-8}	[11]
OMC/GC	Dihydroxybenzene isomers	1.0×10^{-5}–2.0×10^{-4} (HQ) 1.0×10^{-5}–3.0×10^{-4} (CC) 1.0×10^{-5}–1.2×10^{-4} (RC)	7.6×10^{-8} (HQ) 1.0×10^{-7} (CC) 9.0×10^{-8} (RC)	[12]
Try/PANI–IL–CNF/GCE	Catechol	4.0×10^{-10}–2.1×10^{-6}	1×10^{-10}	[13]
Nanograss array BDD electrode	Catechol	5×10^{-6}–1×10^{-4}	1.3×10^{-6}	[14]
MWNT/GCE	Hydroquinone, catechol	1.0×10^{-6}–1.0×10^{-4} (HQ) 6.0×10^{-7}–1.0×10^{-4} (CC)	7.5×10^{-7} (HQ) 2.0×10^{-7} (CC)	[15]
PASA/MWNTs/GCE	Hydroquinone, catechol	6.0×10^{-6}–1.0×10^{-4} (HQ) 6.0×10^{-6}–1.8×10^{-4} (CC)	1×10^{-6}	[16]
Zn/Al LDHf/GCE	Catechol, hydroquinone	3.0×10^{-7}–1.0×10^{-3} (CC) 1.2×10^{-5}–8×10^{-4} (HQ)	1.2×10^{-6} (CC) 9.0×10^{-6} (HQ)	[18]
SWNT/GCE	Dihydroxybenzene isomers	4.0×10^{-7}–1.0×10^{-5} (HQ) 4.0×10^{-7}–1.0×10^{-5} (CC) 4.0×10^{-5}–1.0×10^{-4} (RC)	1.2×10^{-7} (HQ) 2.6×10^{-7} (CC) 3.0×10^{-7} (RC)	[19]
CILE	Dihydroxybenzene isomers	5.0×10^{-7}–2.0×10^{-5} (HQ) 5.0×10^{-7}–2.0×10^{-5} (CC) 3.5×10^{-6}–1.5×10^{-4} (RC)	5.0×10^{-8} (HQ) 2.0×10^{-7} (CC) 5.0×10^{-7} (RC)	This work

that dihydroxybenzene isomers were separated absolutely and they could be examined simultaneously at the sensor.

Optimization of conditions

Effect of scan rate

The influence of the scan rate on the oxidation peak currents (i_{pa}) was investigated using LSV between −0.20 and +1.0 V at CILE in 0.1 mol L^{-1} PBS (pH 6.0). As shown in Fig. 2, the oxidation peak currents of dihydroxybenzene isomers increased linearly with the square root of scan rate from 20 to 300 mV s^{-1}, respectively, The regression equations were $i_p(\mu A)=0.4102v^{1/2}$–0.2255 (v in mV s^{-1}) for HQ, $i_p(\mu A)=0.4798v^{1/2}$–0.8248 (v in mV s^{-1}) for CC, and $i_p(\mu A)=1.4395v^{1/2}$–5.1873 (v in mV s^{-1}) for RC, with the correlation coefficient 0.9935, 0.9965, and 0.9969, respectively, indicating that the oxidation processes of dihydroxybenzene isomers were a diffusion-control process. It was also found that the oxidation peak potentials of dihydroxybenzene isomers shifted positively as the scan rate increased and separation between peak potentials of hydroquinone, catechol, and resorcinol were nearly independent on the scan rate.

Effects of supporting electrolyte and pH

DPV was used to investigate the effects of different supporting electrolytes. Different supporting electrolytes were tested: HClO$_4$, acetate buffer, Britton–Robinson buffer, and phosphate buffer solution. We found that in PBS, the peak currents of the dihydroxybenzene isomers were larger and the peak shapes were sharper. Therefore, PBS (0.1 mol L^{-1}) was chosen as the supporting electrolyte in this paper.

Effects of pH on the peak potential and the peak current of dihydroxybenzene isomers were also tested from 3.0 to 9.0 (as shown in Fig. 3). All peak potentials shifted towards negative values with increasing pH. The peak potentials of dihydroxybenzene isomers were proportional with the solution pH in the range of 3.0–9.0. The three lines were almost parallel, which meant that the difference of the potentials was stable in various pH solutions. The linear regression equations were $E_p(V)=0.4765−0.0570$ pH ($r^2=0.9937$) for HQ, $E_p(V)=0.5835−0.0569$ pH ($r^2=0.9933$) for CC, and $E_p(V)=0.9755−0.0591$ pH ($r^2=0.9929$) for RC. All the slopes of the above equations are very close to −59 mV, which indicated that the uptake of electrons was accompanied by an equal number of protons. These results indicated that two protons take part in the two-electron redox reaction of HQ, CC,
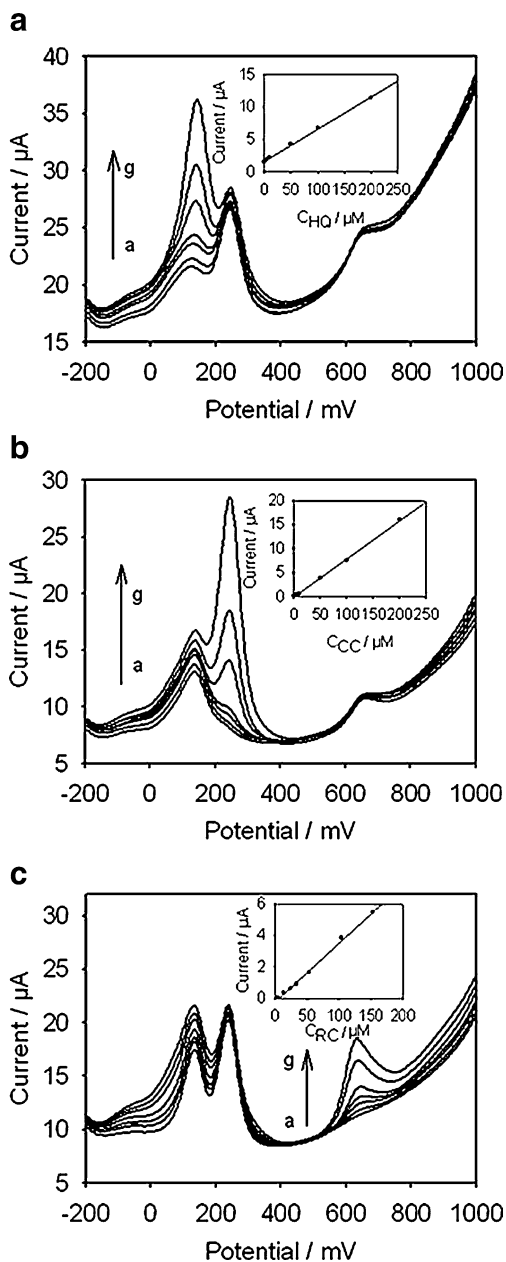
Fig. 6 **a** DPVs of (*a*) 0.5, (*b*) 1, (*c*) 5, (*d*) 10, (*e*) 50, (*f*) 100, and (*g*) 200 μM HQ in the presence of 50 μM CC and RC, respectively. *Inset* calibration plots of HQ. **b** DPVs of (*a*) 0.5, (*b*) 1, (*c*) 5, (*d*) 10, (*e*) 50, (*f*) 100, and (*g*) 200 μM CC in the presence of 50 μM HQ and RC, respectively. *Inset* calibration plots of CC. **c** DPVs of (*a*) 3.5, (*b*) 13.5, (*c*) 23.5, (*d*) 33.5, (*e*) 53.5, (*f*) 103.5, (*g*) 153.5 μM RC in the presence of 50 μM HQ and CC, respectively. *Inset* calibration plots of RC

and RC, respectively [26, 27]. The electrooxidation mechanism of dihydroxybenzene isomers could be expressed as Fig. 4. Meanwhile, the peak current increased gradually until it attained the maximum at pH 6.0, then it decreased rapidly. Possible reasons were summarized as follows: at low pH values, the oxidation potentials were high and the interference was serious. However, when the pH exceeded 7.0, the dihydroxybenzenes began to be oxidized; and above pH 9.0, the oxidation peaks of hydroquinone and catechol overlapped and the peak current decreased sharply, and the oxidation peak of resorcinol hardly disappeared. Therefore, a weak acidic solution was better for the experiments. Thus, pH 6.0 was chosen as the optimum pH value in the electrochemical detection of dihydroxybenzene isomers.

Effects of accumulation potential and time

The effect of the accumulation potential on the peak current of dihydroxybenzene isomers was studied by DPV in the potential range of −600 to 0 mV. The results indicated that the peak current was nearly independent of accumulation potential. In fact, the observed peak current under the accumulation potential was equal to that observed for the open circuit accumulation. Hence, open-circuit condition was employed as an optimum accumulation condition for further studies.

The influence of accumulation time was also investigated. With accumulation time increasing, the peak current increased rapidly within 30 s and then changed slowly. Thus, the preconcentration was performed on open-circuit for 30 s.

Effect of carbon paste composition

The effect of the carbon paste composition on the voltammetric response of the sensor was evaluated. Electrodes with a ratio of ionic liquid (IL)/carbon paste varying from 25% to 75% (*w/w*) were prepared. As shown in Fig. 4, with the IL percentage increasing, the oxidation peak current of CC and HQ decreased; on the contrary, the peak current of RC increased with increasing IL percentage up to 50% and leveled off at higher concentrations.

The phenomenon would be primarily attributed to the following reasons. All of the prepared electrodes yielded consistent composites and improved electrochemical be-

Table 2 Simultaneous determination of dihydroxybenzene isomers in artificial wastewater samples

Sample	Added (μM)			Found[a] (μM)			Recovery (%)		
	HQ	CC	RC	HQ	CC	RC	HQ	CC	RC
1	10.00	10.00	20.00	9.39	10.12	20.56	93.9	101.2	102.8
2	20.00	30.00	30.00	20.92	29.13	29.58	104.6	97.1	98.6
3	30.00	20.00	40.00	29.31	20.78	40.72	97.7	103.9	101.8

[a] Average of three measurements

havior after compression and heating to the melting point of $OPPF_6$ [20]. However, as the content of IL increased, the background current of the electrode became lower, so the peak current of RC increased accordingly. In addition, the electroactivity area of the electrode surface was limited and three dihydroxybenzene isomers competed at the same time; so the current of the one increased, and the others' could decrease. In order to simultaneously and sensitively determine the three dihydroxybenzene isomers, the electrode prepared with $OPPF_6$/carbon paste ratio of 50% (w/w) was used in further studies.

Calibration graphs

The DPV was used for simultaneous determination of the dihydroxybenzene isomers at the sensor. The calibration experiments were carried out by varying the concentration of one isomer in the presence of the other two in optimized conditions. Figure 5a shows DPV curves of different concentrations of HQ in pH 6.0 PBS coexisting 5.0×10^{-5} mol L^{-1} CC and RC. The result (the inset in Fig. 5a) showed that peak current was proportional to the concentration of HQ in the range of $5.0 \times 10^{-7} – 2.0 \times 10^{-4}$ mol L^{-1}. The regression equation was $I(\mu A) = 0.0494 C(\mu M) + 1.6183$, $r^2 = 0.9983$. Similarly, as shown in Fig. 5b, c, the peak current increased linearly with the increasing concentration in the range of $5.0 \times 10^{-7} – 2.0 \times 10^{-4}$ mol L^{-1} of CC and $3.5 \times 10^{-6} – 1.535 \times 10^{-4}$ mol L^{-1} of RC. The regression equation were $I(\mu A) = 0.0796 C(\mu M) – 1.094$, $(r^2 = 0.9990)$ for CC, $I(\mu A) = 0.0372 C(\mu M) – 0.2154$, and $(r^2 = 0.9955)$ for RC. The detection limits of HQ, CC and RC were estimated to be 5.0×10^{-8}, 2.0×10^{-7}, and 5.0×10^{-7} mol L^{-1}, respectively. The analytical performances of the proposed method were compared with other modified electrode reported in the literatures [6–19]. The results were all summarized in Table 1. As can be observed, the proposed method showed better electrocatalytic activities toward the simultaneous determination of dihydroxybenzene isomers with wide linear range and low detection limit. The HQ, CC and RC exhibited an excellent record with the signal height of the other two isomers remaining unchanged, which indicated that the responses to the dihydroxybenzene isomers were relatively independent.

The reproducibility of the sensor was estimated by the response to 50 μM HQ, CC, and RC. The relative standard deviations (RSD) of eight times' successive determinations with the same electrode were 2.1% for HQ, 2.7% for CC, and 2.5% for RC, respectively. Eight different electrodes were fabricated for determining 50 μM HQ, CC, and RC, and the RSDs were 3.7% for HQ, 4.5% for CC, and 3.9% for RC, respectively. The long-term stability of the sensor was also investigated in the same solution. When the electrode was kept in the air for 2 weeks, the peak currents remained more than 96% of their initial values. The results revealed the good reproducibility and stability of the sensor (Fig. 6).

Interferences

The influence of possible interferents in wastewater was tested by analyzing a standard solution of 50 μM HQ, CC and RC in pH 6.0 PBS. The determination of the each solution was repeated three times and the average current values were obtained. The results showed that 5 mM Ca^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, NH_4^+, Na^+, K^+, PO_4^{3-}, SO_4^{2-}, NO_3^-, Cl^-, and 50 μM glucose; ascorbic acid had no influence on the determination of the dihydroxybenzene isomers (signals change below 5%).

Analytical applications and recovery test

To demonstrate the analytical applicability of the proposed method, the concentrations of dihydroxybenzene isomers in the artificial wastewater samples were determined. The analytical results were shown in Table 2, and the recoveries of 93.9–104.6% were obtained. These results indicated that it was feasible to apply the proposed method in the determination of real samples.

Conclusion

The electrochemical response of dihydroxybenzene isomers was examined at a CILE by DPV. The simple sensor exhibited excellent catalytic activity to dihydroxybenzene isomers. In addition, the sensor had good reproducibility and stability. Based on this, a simple, rapid, sensitive, and reliable electrochemical method was proposed for simultaneous determination of the dihydroxybenzene isomers, and it could be applied in the analysis of real samples.

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