

Modified Glassy Carbon Electrode with Galvanized Copper Nanowires by Palladium and Carbon Nanotubes for Speciation of Dihydroxybenzene Isomers

Najmeh Sabbaghi, Meissam Noroozifar*, Masoumeh Tohidinia and Majid Farsadrooh

Department of Chemistry, University of Sistan and Baluchestan, Zahedan, P.O. Box 98135-674, Iran

*E-mail: mnoroozifar@chem.usb.ac.ir

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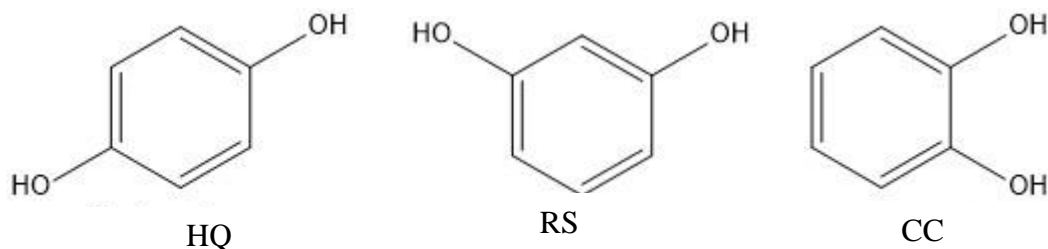
A new modified glassy carbon electrode (GCE) with galvanized copper nanowires by palladium (CuNWs-Pd) and carbon nanotubes (CNTs) has been used for the simultaneous determination of hydroquinone (HQ), catechol (CC) and resorcinol (RS) as water pollutions. The modifier, Pd/CuNWs-CNTs, was characterized by field emission scanning electron microscopy and electrochemistry. Different electrochemical techniques such as cyclic voltammetry, differential pulse voltammetry (DPV) and chronoamperometry were used for the electrochemical study of the proposed modified electrode toward HQ, CC and RS electrooxidation. Based on the experimental results, the calibration are linear with two segmented 1-99 and 99-228 μM for HQ, 1-280 μM for CC and with two segments 1-33 and 33-228 μM for RS. The detection limits were obtained 0.4, 0.6 and 0.8 μM and the diffusion coefficient calculated 6.5×10^{-5} , 1.6×10^{-5} and $8.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, for the HQ, CC and RS, respectively. Moreover, GCE/Pd/CuNWs-CNTs was successfully used for simultaneous determination of HQ, CC and RS in real samples by DPV technique.

Keywords: Galvanized copper nanowires by palladium, Electrochemical sensor, Speciation, Dihydroxybenzene isomers.

1. INTRODUCTION

Hydroquinone (HQ), catechol (CC) and resorcinol (RS) are three isomers of the dihydroxybenzene. Due to their high toxicity and low degradability of HQ, CC and RS in the real samples such as ground waters and rivers, simultaneous determination of these compounds as environmental pollutants is very important. The chemical structure of this isomer has been shown in Schematic 1. They are widely used in different industries activities such as coal mining, cosmetics, paint, pharmaceutical preparation and polymer. Based on manufacturing and application process of

HQ, CC and RS, some of them are released into the environment so that it pollutes different kind's waste waters and could enter into the human body and inhibit nerve centre system [1]. Speciation of HQ, CT and RS is very important for environmental analysis because they co-exist of these isomers in environmental samples and low degradation in environment. For examples, HQ with high concentration could incur headache, fatigue, tachycardia, decomposition, the damage to kidney and even death, CC and CT could cause DNA damaging and human carcinogen [1, 2].



Schematic 1. Chemical structure of HQ, CC and RS

For their carcinogenicity and toxicokinetic effects of these compounds on human and difficult to degrade in environment, US Environmental Protection Agency (EPA) and the European Union (EU) have been included them in the lists of priority environmental pollutants [3]. There are many analytical techniques such as spectrophotometry [4], fluorescence [5], high performance liquid chromatography (HPLC) [6] and electrochemical methods [7–8] have been reported for determination of these isomers. Electrochemical voltammetry methods have attractive advantages such as simple and fast response, cheap, wide linear range, excellent selectivity and high sensitivity [9-11] and were widely used for simultaneous determination of a large number of compounds. The main problem for simultaneous determination of these compounds is that the oxidation potential of the two dihydroxybenzene isomers “HQ and CC” is always closes and overlapped with each other's and also the oxidation of RS is hard by using the unmodified electrodes. A superior approach to solve peak separation and oxidation problems is application of a chemically modified electrode. The modification of electrodes with nanomaterials could have been improved detection limits and decreasing over-potentials as well as resistance to surface fouling [12, 13]. The nano-material properties are depending on size, purity, chemical functionalization and surface's topological [14-15]. It is know that nano-sized metal and metal oxide such as gold, silver, copper, palladium, platinum nanoparticles, and magnetite (Fe_3O_4) nanoparticles show many interesting electronic, magnetic and chemical properties for applications in sensors for determination of bio-compounds [16]. Among these metal nanoparticles, application of copper and copper-based compounds is very interesting because of significant role of Cu in modern electronics circuits and high electrical conductivity and much more economical than gold and silver, copper, palladium, platinum [17]. Several experimental methods have been used for the preparation of copper nanoparticle, such as thermal reduction [18], sono-chemical reduction [18, 19], metal vapor synthesis [20], chemical reduction [21], vacuum vapor deposition [22], radiation methods [23], micro

emulsion techniques [24-26] and laser ablation [27]. Among these methods, the wire explosion method is found to be simple and most versatile for producing pure metal nanoparticles. They are often referred to as one-dimensional (1-D) materials such as nanowires (NWs) that the length-to-width ratio is of 1000 or more times. There are some interesting properties for NWs that cannot see in bulk materials. In the NWs, the electrons are quantum restricted and occupy energy levels that are different from bulk materials (traditional continuum, 3-D) with continuum of energy levels.

In this study, a novel modified glassy carbon electrode (GCE) with galvanized copper nanowires by palladium (CuNWs-Pd) and carbon nanotubes (CNTs) has been introduced for simultaneous voltammetric determination of HQ, CC and RS. The proposed modified electrode was successfully used analytical performance of this sensor for speciation of HQ, CC and RS in different real waters is evaluated by differential pulse voltammetry (DPV).

2. EXPERIMENTAL

2.1. Reagents and solutions

The HQ, CC and RS were purchased from Sigma-Aldrich Company and used as received. A 1.0×10^{-2} mol L⁻¹ HQ, CC and RS solution was prepared daily by dissolving appropriate amount of HQ, CC and RS in water and the solution was diluted to 100 mL with distilled deionized water in a 100 mL volumetric flask. The solution was kept in a refrigerator in dark. Multi-walled carbon nanotubes (MWCNT, purity 95%) with nanotube diameters, OD = 20–30 nm and wall thickness = 1–2 nm was purchased from Aldrich Company. Other compounds such as copper nitrate trihydrate, hydrazine, sodium hydroxide, ethylenediamine were purchased from Merck Company. Phosphate buffer solution (PBS, 0.1 mol L⁻¹) was prepared by mixing the stock solution of 0.1 mol L⁻¹ NaH₂PO₄ and 0.1 mol L⁻¹ Na₂HPO₄, and the pH was adjusted by HCl or NaOH. All other materials used were analytical reagent grade and all solutions were prepared with double distilled deionized water. All the chemicals were used without more purification.

2.2. Instrumentation

All electrochemical measurements were recorded using a conventional three-electrode cell that served the modified glassy carbon electrode (GCE) with 0.0314 cm² surface areas as the working electrode and a platinum wire as the counter electrode at room temperature. A SCE electrode served as the reference electrode. Electrochemical determinations such as DPV were done with an SAMA500 Electroanalyser (SAMA Research Center, Iran) controlled by a personal computer. All the electrochemical determination was carried out under a pure nitrogen atmosphere at room temperature. Field Emission Scanning Electron Microscopy (FESEM) was employed to study the morphology of the prepared samples. The Energy-Dispersive x-ray Spectroscopy (EDS) technique was performed to determine the bulk compositions of the Pd/CuNWs-CNTs. FESEM and EDS were carried out using MIRA3 TESCAN and SAMX electron microscope, respectively.

2.3. Synthesis of Copper nanowires (CuNWs):

For synthesis of CuNWs, 200 mg copper nitrate trihydrate in 10 mL Millipore-Q water (with resistivity 18.2 M Ω cm) was mixed to 200 mL NaOH 10 M in a 500 mL glass bottle and then 1.5 ml of ethylenediamine and 0.25 ml hydrazine (35 % m/m) were subsequently added to the solution. This solution was shaken vigorously to ensure well mixing and then was heated in a 65 °C water bath for 1h. The result product was filtrated and washed with DDW until the pH of filtrate reached 7.0. The final product was stored in a desiccator, dried overnight.

2.4. Preparation of modified GCE by Pd/CuNWs-CNTs

At first, a mixture of concentrated sulfuric acid and nitric acid (volumetric ratio of 3:1) was used for oxidative pre-treatment of CNTs at room temperature for 24 h [28]. This pre-treatment removes impurities and generates sufficient functional groups on the surface of CNTs. The treated CNTs were filtered by centrifugation (2,000 rpm) and washed with double distilled water until the pH of the filtrate reached 7. Stock solution of CNT-CuCWs containing of 1mg ml⁻¹ CNT and 1 mg.ml CuNWs was prepared by dispersing appropriate amount of CNTs and CuCWs in CH (1% m/v) and sonicated for 30 minute. The clean GCE was coated by casting 5.0 μ L of the CNT-CuCWs dispersion and then put the electrode under infrared radiation for fast drying. Then 5 μ L of chloroplatinic acid of PdCl₂ (1 mg/ ml) was putted on the electrode and dried at room temperature for 1 h to ensure a complete galvanization reaction. This modifier and modified electrode were denoted as Pd/CuNWs-CNTs and GCE/ Pd/CuNWs-CNTs. The other modified GCEs such as; GCE/CuNWs, and GCE/CuNWs-CNTs were prepared with the same method. For preparation of GCE/Pd-CNTs, the chloroplatinic acid of PdCl₂ was reduced with fresh sodium borohydride solution in presence of CNTs.

3. RESULTS AND DISCUSSION

3.1. Morphology of the CuNWs and Pd/CuNWs-CNTs

The FESEM images of the CuNWs were shown in Fig. 1a. Based on this Figure, the diameters and lengths of CuNWs are in the range 50-150 nm and 10-30 μ m, respectively. Fig. 1b shows the Pd/CuNWs-CNTs. Based on this Figure, the Pd replace and attached on CuNWs and CNTs. Figure 1c shows the elemental compositions of Pd/CuNWs-CNTs was measured by EDS. Based on the results, the percent of C, Cu and Pd (%) are 81.1, 2.95 and 11.73 (%), respectively. Also, there are 2.95 and 0.69 (%) for O and Au, respectively. Carbon is derived from the CNTs. Small amount of oxygen and Au may come from functionalization of CNTs and thin layer Au coating for FESEM processes, respectively. Also, the results was shown that Pd/CuNWs-CNTs had a residual copper content of about 2.95 wt. %.

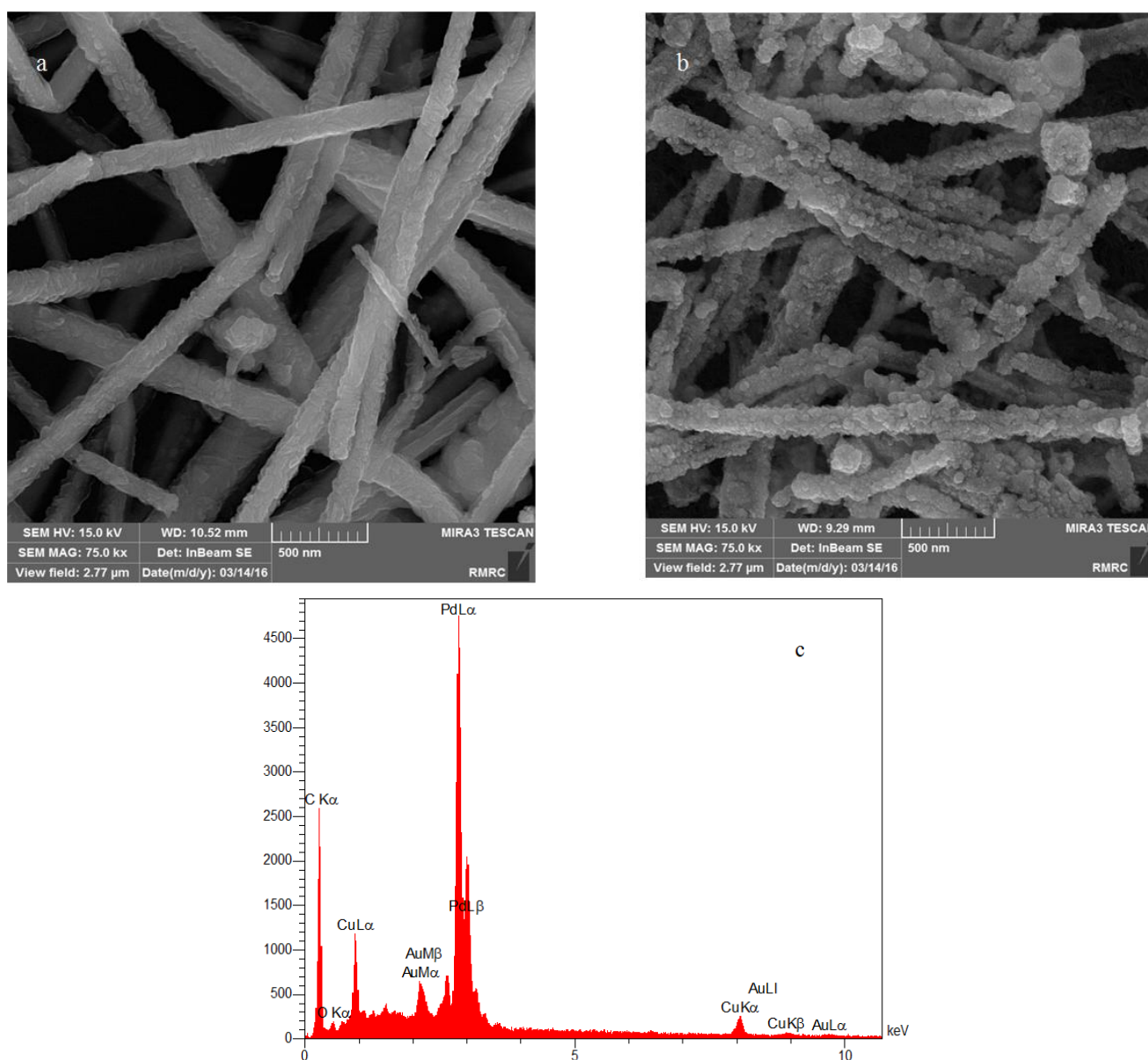


Figure 1. FESEM of images of (a) CuNWs (b) Pd/CuNWs-CNTs and (c) EDS of Pd/CuNWs-CNTs

3.1. Voltammetric behaviors modified electrode

The electrochemical behaviors of the mixed components of HQ, CC and RS at modified electrode by Pd/CNTs, CuNWs and Pd/CuNWs-CNTs in the potential range 0.1 -1.2 V/ SCE and in 0.1 M PBS of pH 7 were shown in Fig. 2a. Based on this Figure, modified electrode by Pd/CNTs showed three broad oxidation peaks for mixture of HQ, CC and RS at 0.141 , 0.245 and 0.630 V, respectively. The oxidation peaks of HQ and CC were merged with each other's with increasing the concentration of them. In contrast, the modified GCE with CuNWs showed three well peaks for HQ, CC and RS at 0.158, 0.262 and 0.654 V, respectively. The behavior of modified GCE with Pd/CuNWs-CNTs showed three well-defined and sharp peaks for HQ, CC and RS at 0.162, 0.269 and 0.659 V and two reductions for HQ and CC.

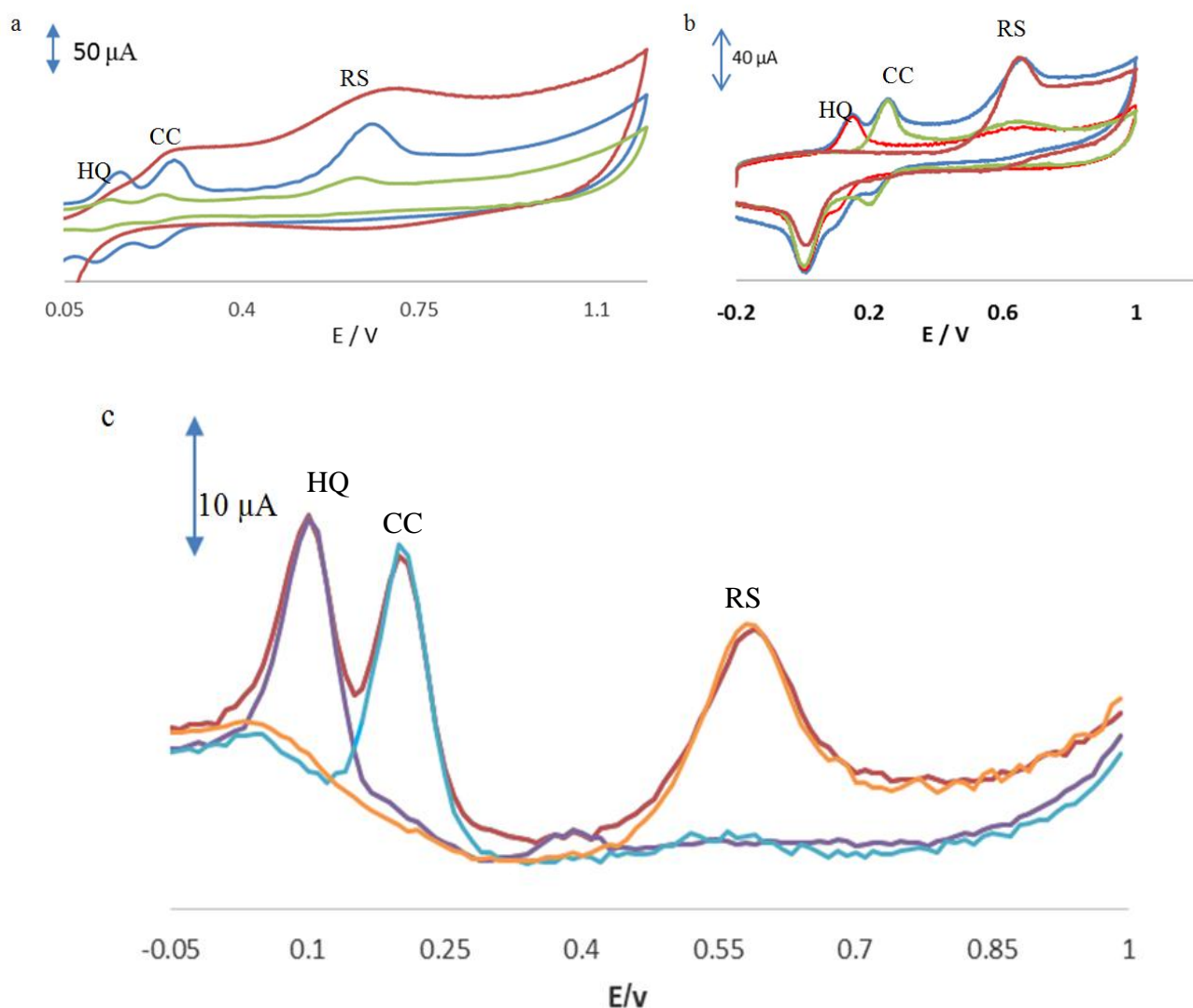


Figure 2. (a) A comparison electrochemical behaviour study of HQ(132.0 μM), CC(132.0 μM) and RS(196.0 μM) at different modified GCE with Pd/CNTs (green), CuNWs (brown) and Pd/CuNWs-CNTs (blue), (b) CVs of HQ, CC and RS in the a mixture and individual solutions (c) DPVs of HQ, CC and RS of the a mixture and individual solution in the same potential range and PBS (0.1 M) at pH 7.0.

It can be seen from Fig. 2a that the peak current for HQ, CC and RS at the GCE/Pd/CuNWs-CNTs is several times larger than that of the modified electrode with CuNWs because of catalytic property of Pd as a promoter by increasing the rate of electron transfer. Also, the CVs and DPVs of HQ, CC and RS as a mixture and individual solution in the same potential range were shown in Figs. 2b and c. Based on these Figs., the oxidation potential peaks of analytes in the mixture and individual solution are constant.

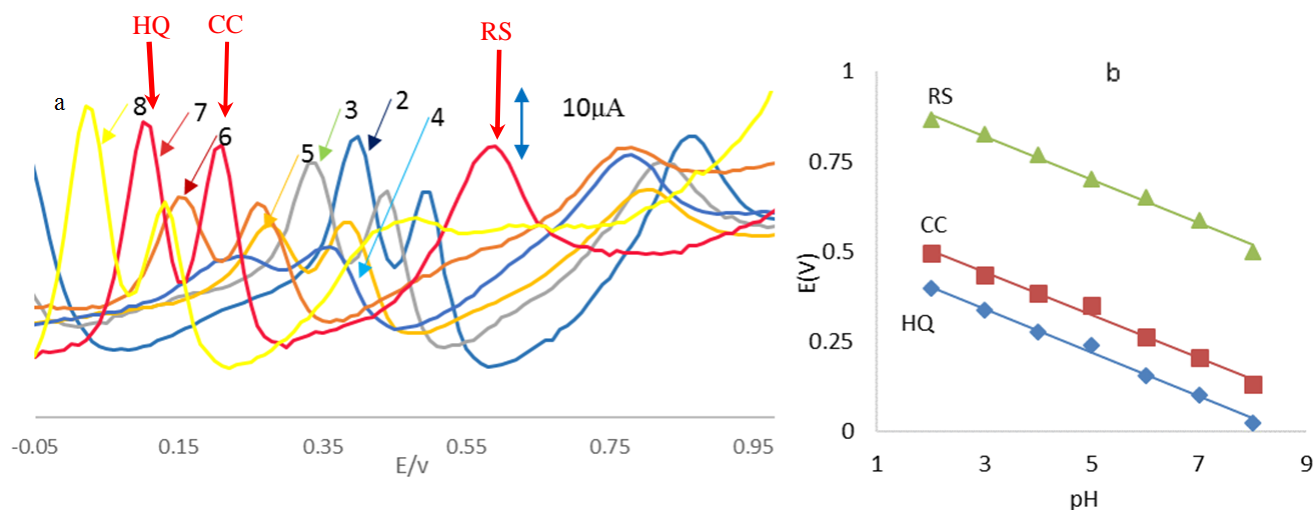


Figure 3. (a) Effect of pH on the peak separation and peak current for the oxidation of HQ(132.0 μM), CC (132.0 μM) and RS(196.0 μM); pH= 2 - 8. (b) Plot of peak potential vs. pH

3.2. Effect pH

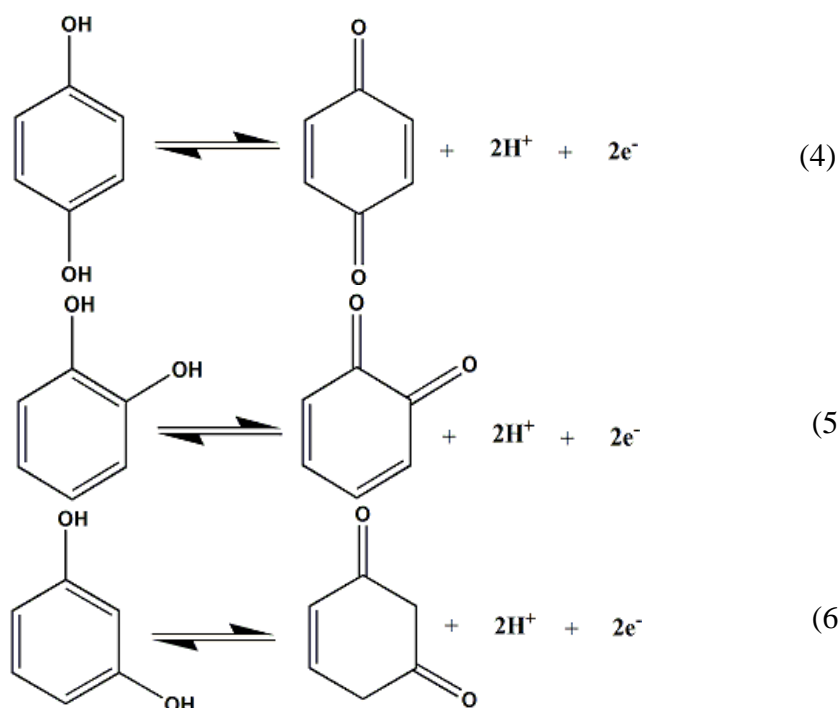
The acidity of electrolyte has a significant influence on the HQ, CC and RS electro-oxidation because protons take part in the electrode reaction. The effect of pH on GCE/Pd/CuNWs-CNTs signal was carefully investigated by cyclic voltammetry using 0.1 mol L⁻¹ buffer solutions at pH levels ranging from 2 to 8. The results were shown in Fig.3a. Based on the results, with increasing the pH from 2 to 7, the peak current of HQ, CC and RS increase but after that and with increasing pH until 8, the peak current for CC and RS decrease except for HQ with slightly increasing. In other hand, when the pH increased, the peak potentials of HQ, CC and RS shifted towards less positive values. This result was shown that those protons have taken part in their electrode processes. It can be seen from Fig. 3a, pH 7 of phosphate buffer solutions (PBS) with highest peak current, peak shape and negatively shift for all compounds; hence it was selected as optimal pH. Plot of E_p vs. pH for HQ, CC and RS in the working pH range was shown in Fig. 3b. As can be seen, the E_p of all compound have linear relationship with pH of the buffer solution and can be shown as follow;

$$E_p(\text{HQ}) = -0.061 \text{ pH} + 0.52 \quad (R^2 = 0.993) \quad (1)$$

$$E_p(\text{CC}) = -0.060 \text{ pH} + 0.62 \quad (R^2 = 0.991) \quad (2)$$

$$E_p(\text{RS}) = -0.061 \text{ pH} + 1.0 \quad (R^2 = 0.992) \quad (3)$$

Based on the equations of 1-3, the observed slopes of 0.061, 0.060 and 0.061 mV/pH for HQ, CC and RS which was close to the Nernstian slope value (0.059 mV/pH) for equal number of electrons and protons (in this study, two-electrons, two-protons for HQ, CC and RS) in electrochemical reaction [29-31]. Based on these results, the oxidation of HQ, CC and RS at the surface of GCE/Pd/CuNWs-CNTs were explained in Eqs. 4-6.



3.3. Influence of scan rate on the electrochemical behavior of HQ, CC and RS

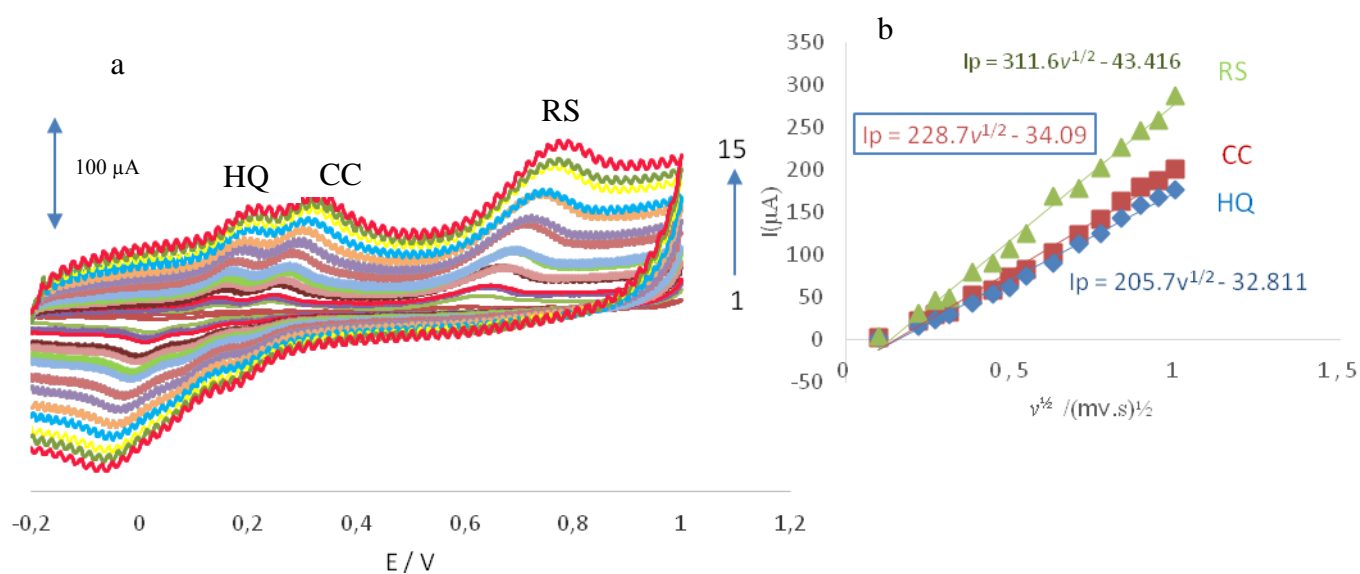


Figure 4. CVs of GCE/Pd/CuNWs-CNTs in pH 7.0 at various scan rates (from inner to outer curve): 10, 20, 30, 50, 75, 100, 125, 150, 175, 225, 325, 425, 525, 700 and 1000 mV s^{-1} , (b) The plot of peak currents vs. square root scan rates.

The influence of scan rate on the oxidation peak current of HQ, CC and RS were investigated on the GCE/Pd/CuNWs-CNTs by cyclic voltammetry (see Fig. 4).

As can be seen in Fig.4a, the peak current increases continuously with the increase of scan rate. Furthermore, the current was directly proportional to the square root of the scan rate over the range of

10–1000 mV s^{-1} as shown in Fig. 4b, which powerfully proposed that the redox reactions of HQ, CC and RS are diffusion controlled. Also the results were shown that the peak separations of HQ, CC and RS were satisfactory for its analysis at higher scan rates. Based on the results with increasing of the scan rate, potential of the oxidation peak shifted positively and potential of the reduction peak shifted negatively. These results demonstrate that a kinetic limitation exists at higher scan rates in the course of the reaction between the GCE/Pd/CuNWs-CNTs composite and HQ, CC and RS. Ultimately, due to our study to reach best efficiency for peak currents and peak separation, 100 mV s^{-1} was chosen as best scan rate.

3.4. Chronoamperometric study

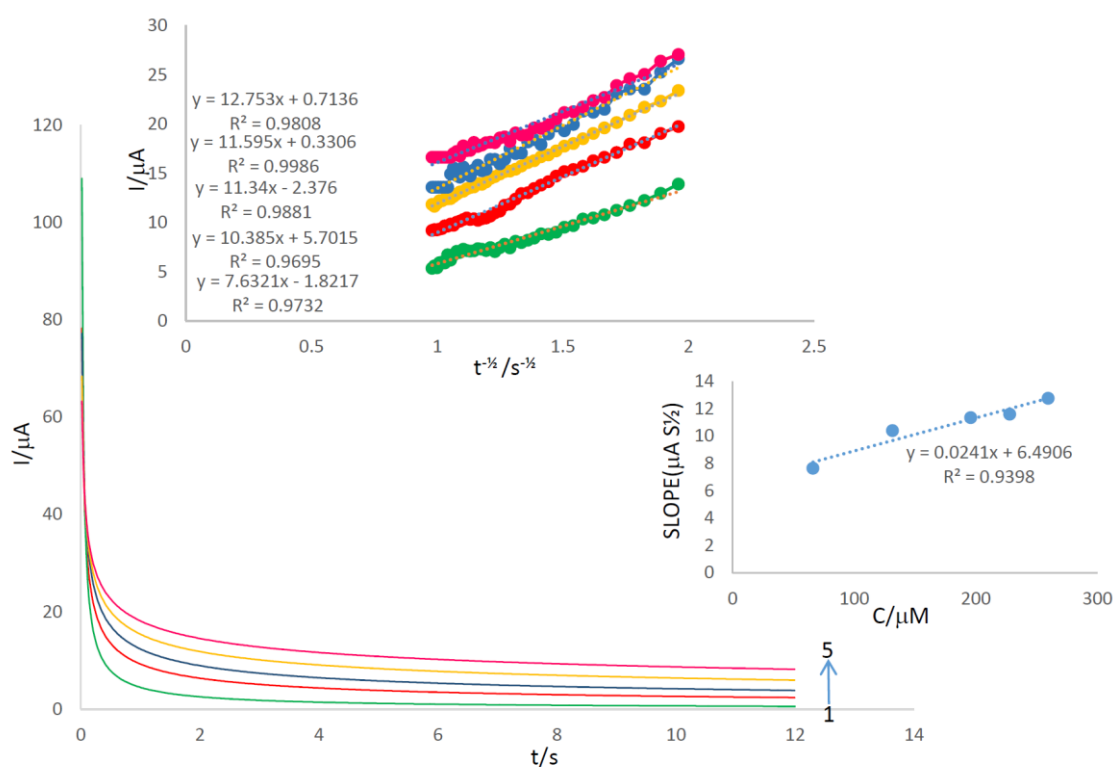


Figure 5. Typical chronoamperograms obtained at GCE/Pd/CuNWs-CNTs in 0.1 M PBS (pH 7.0) for different concentration of HQ with different concentration 1) 66.3, 2)131.6, 3)196.1, 4) 228.0 and 5) 259.7 mM of HQ, (b) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–3. (c) Plot of the slope of the straight lines against HQ concentration.

Chronoamperometric methods was used for determination diffusion coefficient (D). Chronoamperograms of HQ, CC and RS at GCE/Pd/CuNWs-CNTs were studied by setting the potential of working electrode at 0.152 , 0.253 and 0.624 V vs. SCE for the various concentration of HQ, CC and RS in PBS (pH = 7.0). A typical chronoamperogram for HQ was shown in Fig. 5 and the D for an electroactive compound can be calculated by the Cottrell equation as follow [29];

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (7)$$

where n , F , A , D , C_b and t are number of transferring electron, faraday constant (96485Cmol^{-1}), microscopic area, analyte diffusion coefficient, analyte concentration, and time. Under diffusion control for a electrochemical reaction with a mass transport limited rate, the plot of I vs. $t^{-1/2}$ will be linear, and the slope ($nfAD^{1/2}C_b\pi^{-1/2}$) of the linear region of the Cottrell's plot can be used to calculate of the D for HQ, RS and CC. The value of D_{HQ} , D_{CC} and D_{RS} were found to be 6.5×10^{-5} , 1.6×10^{-5} and $8.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

3.5. Interference studies

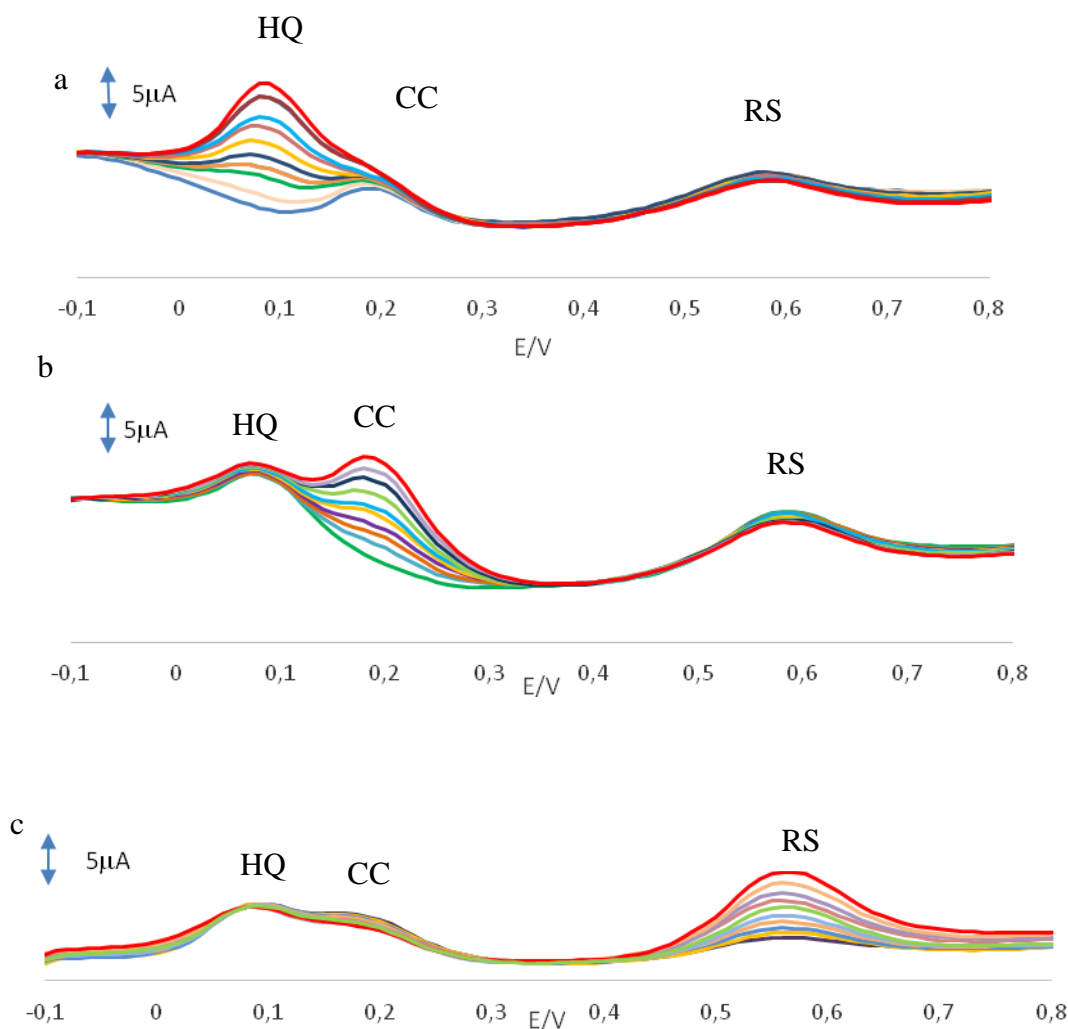


Figure 6. DPVs at the GCE/Pd/CuNWs-CNTs in 0.1 M pH 7.0 PBS (a) containing CC (66.2 μM) and RS (99.0 μM) and different concentrations of HQ(μM, from inner to outer): (6.6, 13.3, 19.9, 33.2, 46.4, 53.0, 59.6, 66.2, 72.8 and 79.3), (b) Containing HQ (66.2 μM) and RS (99.0 μM) and different concentrations of CC (μM, from inner to outer): (6.6, 13.3, 19.9, 33.2, 46.4, 53.0, 59.6, 66.2, 72.8 and 79.3) and (c) Containing HQ, CC (66.2 μM) and different concentrations of RS (μM, from inner to outer): (6.6, 13.3, 19.9, 33.2, 46.4, 53.0, 59.6, 66.2, 72.8, 79.3, 85.9, 92.4, 99.0, 105.5, 112.0 and 125.0).

As dihydroxybenzene isomers usually co-exist in real samples, the interference study of HQ, CC and RS for the selective detection of one species is very important. The results for HQ, CC and RS were shown in Fig.6. In each experiment, the concentration of one species changed, while the concentrations of the other one were kept constant. The results are shown in Fig. 6a-c. It can be seen from Fig. 6a, the peak current of HQ increases with an increase in the concentration of HQ, while the peak currents for CC and RS remain constant. Evaluation of Fig. 6a reveals that the peak current of HQ grows by increasing of HQ concentration in a mixture with constant concentration of CC and RS. As it can be seen (Fig, 6b and c) the voltammetric peak corresponding to the oxidation of CC and RS were found to increase linearly in consonance with the increase in their concentration, whereas the peak current for the oxidation of other two compounds remain constant. The same test were used for interference studies of CC or RS, while the concentration of two others isomers is constant. Based on the Fig. 6a-c, the electrooxidation of HQ, RC and CC at GCE/Pd/CuNWs-CNTs are proportional to the concentrations of HQ (or CC, RC) and the isomers have not interference in determination of each other's.. Also, the possible interferences of other species on the simultaneous determination of HQ, CC and RS were investigated by DPV. The results showed no significant interference from common cations and anions such as Zn^{2+} , Ni^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , K^+ , Na^+ (each of concentration = 0.01 mol L^{-1}), with signal deviations below 5 %.

3.6. Calibration curves of HQ, CC and RS

Under optimum conditions, DPVs technique was used for simultaneous determination of HQ, CC and RS at GCE/Pd/CuNWs-CNTs. Three oxidation peaks for HQ, CC and RS can be seen in Figure 7. The results for figures and merit of proposed electrode were summarized in Table 1.

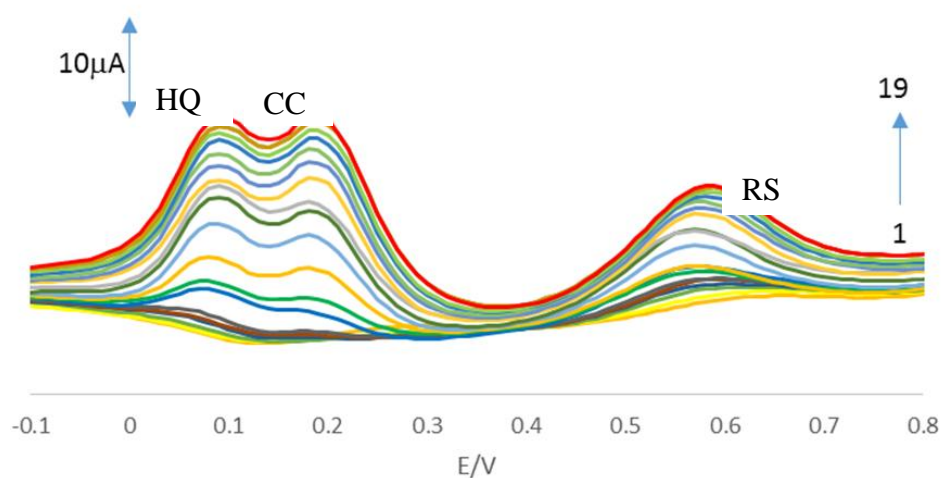


Figure 7. DPVs of the mixtures of HQ, CC and RS at the GCE/Pd/CuNWs-CNTs electrode in PBS (pH=7.0), Concentrations from inner to outer of curves: (0.0, 1.3, 2.6, 3.9, 5.3, 6.6, 7.9, 9.9, 13.3, 19.9, 26.5, 33.2, 46.4, 66.2, 99.0, 131.5, 163.9, 196.0 and 228.0 μM) for HQ, (0.0, 1.3, 2.6, 3.9, 5.3, 6.6, 7.9, 9.9, 13.3, 19.9, 26.5, 33.2, 46.4, 66.2, 99.0, 131.5, 163.9, 196.0 and 228.0) for CC and (0.0, 1.3, 2.6, 3.9, 5.3, 6.6, 7.9, 9.9, 13.3, 19.9, 26.5, 33.2, 46.4, 66.2, 99.0, 131.5, 163.9, 196.0 and 228.0) for RS.

Table 1. Figures and merit for simultaneous determination of HQ, CC and RS by GCE/Pd/CuNWs-CNTs.

Analytes	Linear range (μM)	Calibration curve	r	Detection limit (μM)
HQ	1.0-99.0	$I_p = 0.220[\text{HQ}] + 12.90$	0.991	0.4
	99.0-228.0	$I_p = 0.114[\text{HQ}] + 23.99$	0.993	
CC	1.0-228.0	$I_p = 0.151[\text{CC}] + 13.84$	0.991	0.6
RS	1.0-33.0	$I_p = 0.394[\text{RS}] + 14.86$	0.992	0.8
	33.0-228.0	$I_p = 0.063[\text{RS}] + 26.43$	0.991	

Based on Table 1, the plot of peak currents *vs.* HQ, CC and RS concentration consisted of two linear segments. The detection limits were calculated using the equation $Y_{\text{LOD}} = X_{\text{bk}} + 3S_{\text{bk}}$, where Y_{LOD} is the signal for detection limit, X_{bk} the mean of blank signal and S_{bk} the standard deviation of the blank signal. The relative standard deviations were 2.1%, 1.9% and 1.7% for HQ, CC and RS, respectively.

A comparison study of proposed modified electrode with a lot of published works for simultaneous determination of dihydroxybenzene isomers has been shown in Table 2. Based on this Table, the optimum conditions for simultaneous determination of HQ, CC and RS is DPV technique and a pH close to 7.0 of PBS.

Table 2. Performance comparison of the modified electrode for HQ, CC and RS detection with other electrodes.

Electrode	Technique	pH	Linear Range / μM			Detection Limit / μM			Ref.
			HQ	CC	Res	HQ	CC	Res	
Graphene-chitosan/GC	DPV	7 ^f	1-300	1-400	1-550	0.75	0.75	0.75	[7]
LDHF ^a /GCE	DPV	6.5 ^f	12-800	3-1500	-	9	1.2	-	[27]
MPE ^b	DPV	0.0, (HClO ₄ 1M)	50-2000	20-50	-	-	-	-	[29]
GCE	DPV	6.8 ^f	8-400	3-400	-	8	3	-	[32]
GC/CNT-RR-NF ^c	DPV	4.5 ^g	1.3-433.3	1.3-433.3	-	0.21	0.18	-	[33]
Graphene doped CILE ^d	DPV	5 ^g	10-400	10-300	10-170	1.8	0.7	0.4	[34]
MWCNTs/GCE	LSV	5.5 ^g	2-100	2-100	5-80	0.6	0.6	1	[35]
MnO ₂	DPV	7 ^f	10-70	10-70	10-70	3.1	2.2	2.1	[36]

CNx nano tubes ^c	CV	4.7 ^g	10-1000	20-1000	50-1000	1.20	2.71	5.64	[37]
Gold nanoparticles, ZnS/NiS@ZnS quantum dots and L-cysteine	DPV	7.5 ^f	0.1 to 300	0.5 to 400	-	0.024	0.071	-	[38]
CTAB Functionalized Graphene Oxide Multiwalled Carbon Nanotube	CV	7.0 ^f	0.1-400	0.1-200	1-100	0.03	0.01	0.1	[39]
Multiwalledcarbon nanotubes/polydopamine /gold nanoparticles	DPV	6.0 ^f	0.1 to 10	0.1 to 10	-	0.035	0.047	-	[40]
Polydopamine-reduced graphene oxide nanocomposite	DPV	6.5 ^f	1-230	10-250	-	0.62	0.74	-	[41]
Gold nanoparticle-graphene nanohybrid bridged 3-amino-5-mercapto-1,2,4-triazole-functionalized multiwall carbon nanotubes	DPV	7.0 ^f	54.5-1250.5	11.0-126.0	43.5-778.5	4.17	1.00	7.80	[42]
GCE/Pd/CuNWs-CNTs	DPV	7.0 ^f	1-99 99-228	1-280	1-33 33-228	0.4	0.6	0.8	This work

^aLDHF: Zn/Al layered double hydroxide film, ^bMPE: mesoporous platinum electrode, ^cGC/CNT-RR-NF: multi-walled carbon nanotube and ruthenium red dispersed in Nafion, ^dCILE: carbon ionic liquid electrode; ^eCNx: nitrogen-doped carbon nanotubes, ^fPBS: Phosphate buffer solution, ^gABS: Acetate acid buffer solution.

Based on this Table, the detection limit of proposed method is better than those described in literature by Yin et al. [7], Li et al. [27], Pen and Gao [32], Prathap et al. [36], Dong et al. [37], Zheng [41] and Yang et al [42] and also it satisfy in comparison of literature by Foroughi et al.[33], Ma et al. [34], Zhang et al. [35], Wang et al. [38], Yan et al. [39] and Wang et al. [40]. The linear range of proposed modified electrode is satisfy in comparison of literature and also the lower concentration in calibration curve has been started from lower concentration than a lot of works [27-37 , 41, 42] and it is satisfy in comparison of works by Yin et al. [7], Wang et al. [38] and Wang et al. [40]. In summary, the figures of merit of proposed modified electrode by Pd/CuNWs-CNTs is better or comparable to similar results that were published in literature for simultaneous determination of dihydroxybenzene isomers using with different modified electrode. Also, the modified electrode preparation method is very simple and fast as well as low price. So, the proposed modified electrode can satisfy used for simultaneous determination of HQ, CC and RS in water samples.

3.7. Real Sample analysis

In order to evaluate the analytical applicability of the developed method for simultaneous determination of HQ, CC and RS, three different water samples were tested. The reliability of the method was checked by the analysis of the samples spiked with the known amount of HQ, CC and RS and are listed in Table 3.

Table 3. Determination of HQ, CC and RS in water samples using GCE/Pd/CuNWs-CNTs (n = 5).

Sample	Analyte	Detected (μM)	Added (μM)	Found (μM) ^a	Recovery (%)
City water ^b	HQ	ND ^c	33.2	32.9 \pm 0.8	99.1
			46.4	45.6 \pm 1.2	98.3
	CC	ND	33.2	33.4 \pm 0.9	100.6
			46.4	45.3 \pm 1.7	97.6
	RS	ND	33.2	32.9 \pm 1.1	99.1
			46.4	44.9 \pm 0.9	96.8
Mineral water ^d	HQ	ND	33.2	32.8 \pm 1.3	98.8
			46.4	45.8 \pm 1.0	98.7
	CC	ND	33.2	31.9 \pm 1.1	96.1
			46.4	45.0 \pm 0.9	97.0
	RS	ND	33.2	34.4 \pm 1.3	103.6
			46.4	44.6 \pm 1.1	96.1
River water	HQ	ND	33.2	32.1 \pm 0.9	96.7
			46.4	46.6 \pm 1.2	100.4
	CC	ND	33.2	33.4 \pm 1.1	100.6
			46.4	44.9 \pm 0.8	96.8
	RS	ND	33.2	32.8 \pm 1.2	98.8
			46.4	47.0 \pm 1.5	101.3

^aMean \pm standard deviation for n = 5, ^bZahedan drinking water, ^cNot detect and ^dDamavand mineral water Co., IRA

The recoveries were 96.1–103.6% for HQ, CC and RS. Therefore, a capability of the proposed electrode for the simultaneous determination of HQ, CC and RS is clear.

4. CONCLUSIONS

For the first time, GCE/Pd/CuNWs-CNTs has been used for speciation of HQ, CC and RS. Compared with the proposed electrode with literature a large peak separation between CC, HQ and RS, and the significant increase of peak current were observed at the GCE/Pd/CuNWs-CNTs. The result was shown that Pd, CuNWs and CNTs as a multifunctional catalyst could be used to enhance the kinetics of the electrooxidation of HQ, CC and RS. Finally, the GCE/Pd/CuNWs-CNTs were successfully used for separation of HQ, CC and RS in water samples with satisfactory results.

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