

Electrochemical Detection of Hydroquinone by Square Wave Voltammetry using a Zn Layered Hydroxide-Ferulate (ZLH-F) Modified MWCNT Paste Electrode

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In this paper, a multiwall carbon nanotubes (MWCNT) paste electrode modified by a Zn layered hydroxide-ferulate (ZLH-F) was used for detection of hydroquinone (HQ). The morphology and characteristic of the ZLH-F/MWCNT was investigated by scanning electron microscope (SEM), transmission electron microscope (TEM) and square wave voltammetry (SWV). Under optimal conditions, the SWV response showed linear plot for HQ concentration in the range of 1.0×10^{-5} M – 1.0×10^{-3} M. The detection limit was found to be 5.7×10^{-6} M and correlation coefficient of 0.9957. The glucose, fructose, sucrose, bisphenol A, acetaminophen, lysine, NO_3^- , Cl^- and SO_4^{2-} did not interfere the HQ response. This modified electrode can be used to determine HQ content in wastewater and cosmetic cream with range of recovery 97.8% - 103.0%.

Keywords: 1,4-dihydroxybenzene, hydroquinone, multiwall carbon nanotubes, square wave voltammetry.

1. INTRODUCTION

1,4-dihydroxybenzene or commonly known as hydroquinone (HQ) is often used in organic reducing agents, especially in cosmetics, pesticides, pharmaceutical, photographic developers, the production of polymerization inhibitors, rubber, and food antioxidants [1-3]. Overexposure to HQ can cause fatigue, kidney damage, headache and tachycardia [4,5]. The United States Environmental Protection Agency (US EPA) classified HQ as environmental pollutants because of the low degradability and high toxicity to both environment and human even at very low concentrations and

also was banned from the European cosmetic market by European Union (EU) legislation [6,7]. In China, the emission concentration of dihydroxybenzene should be less than 4.45×10^{-3} M [8]. Consequently, development of materials in determination of HQ is important and necessary.

Currently, several analytical approaches such as high performance liquid chromatography (HPLC) [9,10], spectrophotometry [11], gas chromatography (GC) [12] and electrochemiluminescence [13,14] have been used to determine the concentration of HQ. However, these methods are still restricted by many disadvantages such as high cost instruments, time-consuming sample pre-treatment and complicated pre-separation step [15,16]. Because of all these factors, it is strongly demanded to develop cheap, efficient, simple operation, highly selective and sensitive methods for the determination of HQ such as electrochemical methods that satisfy all of these criteria [17,18].

Carbon nanotubes (CNT) were firstly discovered by Iijima in 1991. Numerous novel application of carbon nanotubes have been investigated due to their unique chemical, mechanical and electronic properties [19]. Until present, many researchers give more effort to develop the CNTs electrode to determine its inherent properties. Bu [20] fabricated a multiwall carbon nanotubes (MWCNT) modified with ionic liquid, while Qi and Zhang [21] developed a glassy carbon electrode modified with MWCNT for simultaneously determination of HQ and catechol. Saidin [22,23] reported the determination of nickel and copper(II) by using MWCNT modified with chloropalladium(II) complex and tetracarbonylmolybdenum(0), respectively.

In this work, the ZLH-F/MWCNT paste electrode performance for HQ determination using SWV has been studied. In order to obtain the best performance response, parameters such as pH, percentage composition, pulse, step size and frequency were optimized.

2. EXPERIMENTAL

2.1. Reagents and chemicals

MWCNT (Timesnano, China), paraffin oil, barium chloride, copper(II) sulphate, potassium iodide, potassium nitrate, glucose, fructose, sucrose, disodium hydrogen phosphate, sodium dihydrogen phosphate (Merck, Germany) and supporting electrolyte salts such as sodium acetate and chloride salts of all cations (Sigma-Aldrich, USA) were used as received. All reagents used were analytical grade. Stock solutions of hydroquinone were freshly prepared by dissolving appropriate amount of hydroquinone in deionized water.

2.2. Apparatus

Square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS) were performed with a Potentiostat Series-G750 (USA) and Potentiostat/Galvanostat model Ref 3000 (USA), respectively. Three electrode system consisting of the ZLH-F/MWCNT paste electrode as the working electrode, a platinum wire as the counter or auxiliary electrode and an Ag/AgCl electrode

MF-2052 (Bioanalytical system, USA) with a fiber junction as the reference electrode, were used. The surface morphology of the ZLH-F/MWCNT was characterized by FESEM model SU8020 UHR (Hitachi, Japan).

2.3. Synthesis of ZLH-F

ZLH-F nanocomposites were synthesised using ZnO as starting material, by a direct method similar to those previously described [24]. 0.025 M, 0.05 M and 0.10 M solutions of F were prepared by dissolving the required amount of F in 50 ml of 99.8 % methanol. 0.50 g of ZnO powder was suspended in 20 ml of water. Then, the prepared of F solution was added into the ZnO suspension and magnetically stirred for 2 ½ hours at room temperature. The resulting slurry was aged in an oil bath shaker at 70 °C for 24 hours. Next, the precipitate was centrifuged, thoroughly washed by deionized water and dried in an oven at 60 °C overnight. It was ground and kept in a sample bottle for further use and characterisation

2.4. Preparation of the electrode

The ZLH-F/MWCNT paste electrode was prepared by hand mixing 5 mg of the ZLH-F and 100 mg of MWCNT in a mortar and pestle. Then, 3 drops of paraffin oil was added to the above mixture and mixed until a homogenized paste was obtained. The paste was then packed firmly into Teflon tubing (i.d. 2.0 mm and 3 cm long) and the electrical contact was established through copper wire to the end of the paste. The surface at the other end of the paste was polished by smoothing on a soft paper just before use. The unmodified MWCNT paste electrode was also prepared in the same way without the ZLH-F added.

2.5. Measurement procedure

Voltammetry was performed in 0.1 M PBS as supporting electrolyte containing HQ at a desired concentration and pH 7.0. The HQ solutions were deoxygenated for 15 minutes with N₂ prior to electrodeposition. The determination of HQ was carried out using SWV between -0.1 V to +0.7 V and the conditions were as follows: frequency, 150 Hz; pulse height, 60.0 mV and step increment, 6.0 mV. All the experiments were conducted at ambient temperature of 25 ± 1 °C.

3. RESULT AND DISCUSSION

3.1. Studies of surface morphology

The morphology of ZLH-F and fabricated ZLH-F/MWCNT were characterized by SEM and TEM. Fig. 1A shows the layer of rod of ZLH-F. Fig. 1B indicates that the transparent tube of MWCNT

was covered by ZLH-F with the size of 40 – 60 nm and the thickness of several nanometres. These results clearly reveal the existence of ZLH-F along with MWCNT.

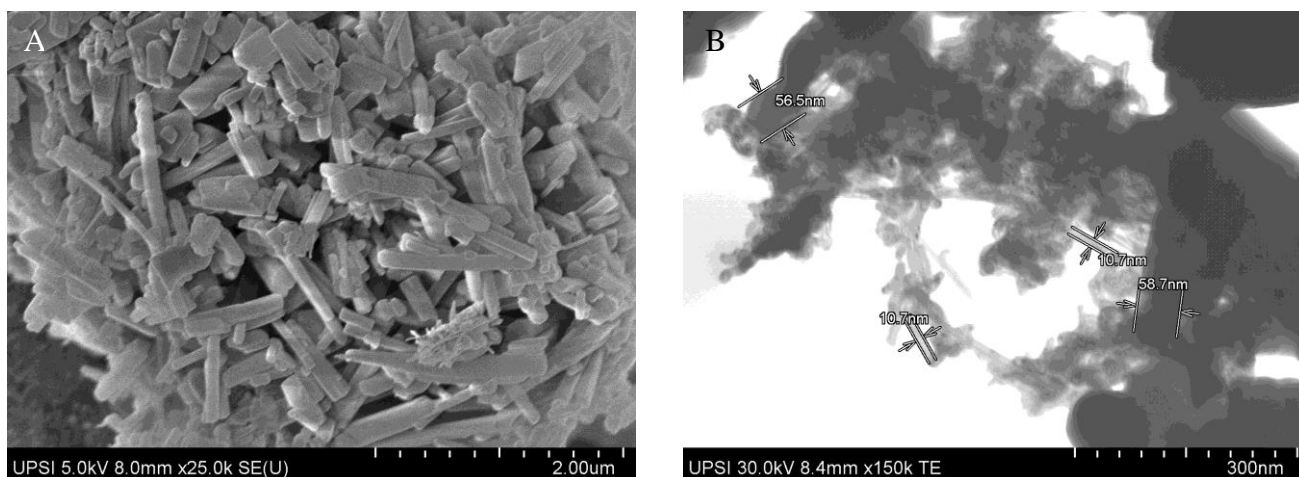


Figure 1. (A) SEM image of ZLH-F and (B) TEM image of ZLH-F/MWCNT.

3.2. Electrochemical characterization of the ZLH-F/MWCNT paste electrode

Fig. 2 shows cyclic voltammogram (CV) of the unmodified MWCNT and the ZLH-F/MWCNT paste electrodes in 4.0 mM $K_3[Fe(CN)_6]$ containing 0.1 M KCl. Unmodified MWCNT paste electrode shows redox peak current at $I_{pa} = 9.908 \mu A$, $I_{pc} = 7.620 \mu A$ and a peak-to-peak separation, $\Delta E_p = 350.8 \text{ mV}$. However, the redox peak current of the ZLH-F/MWCNT increased to $I_{pa} = 17.10 \mu A$, $I_{pc} = 15.46 \mu A$, while the ΔE_p decreased to 179.9 mV. Thus, the use of the ZLH-F as modifier has improved the performance of conductivity and the electron transfer rate on the electrode surface.

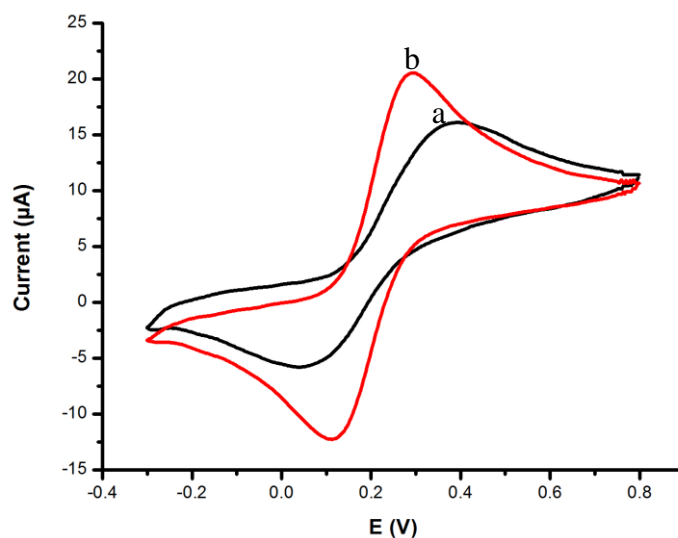


Figure 2. CV of the (a) unmodified MWCNT and (b) ZLH-F/MWCNT in 4.0 mM $K_3[Fe(CN)_6]$ containing 0.1 M KCl at scan rate 100 mVs^{-1} .

EIS is commonly used to investigate the interfacial properties of the electrode. In the Nyquist plots, diameter of the semicircle represents the charge transfer resistance, R_{ct} at the electrode surface while the straight line indicates the diffusion process [25]. Fig. 3 illustrates the EIS result for unmodified MWCNT and the ZLH-F/MWCNT paste electrode. By fitting the Randles equivalent electrical circuit (Fig. 3 inset), the R_{ct} values for unmodified MWCNT and the ZLH-F/MWCNT paste electrode were 4.649 k Ω and 1.072 k Ω , respectively. The ZLH-F/MWCNT displayed smaller diameter size of semicircle indicating minimal charge transfer resistance within the interfacial layer. The electron transfer apparent rate constant, k_{app} on the unmodified MWCNT and the ZLH-F/MWCNT paste electrode was calculated according to the equation (1):

$$k_{app} = RT/F^2 R_{ct} C$$

where R = gas constant, T = temperature, F = Faraday's constant and C = concentration of the $K_3[Fe(CN)_6]$ solution. The electron transfer apparent rate constant, k_{app} for unmodified MWCNT and the ZLH-F/MWCNT paste electrode were $1.43 \times 10^{-5} \text{ cms}^{-1}$ and $6.21 \times 10^{-5} \text{ cms}^{-1}$, respectively. The low R_{ct} and high k_{app} values for the ZLH-F/MWCNT paste electrode showed faster electron transfer process compared to the unmodified MWCNT.

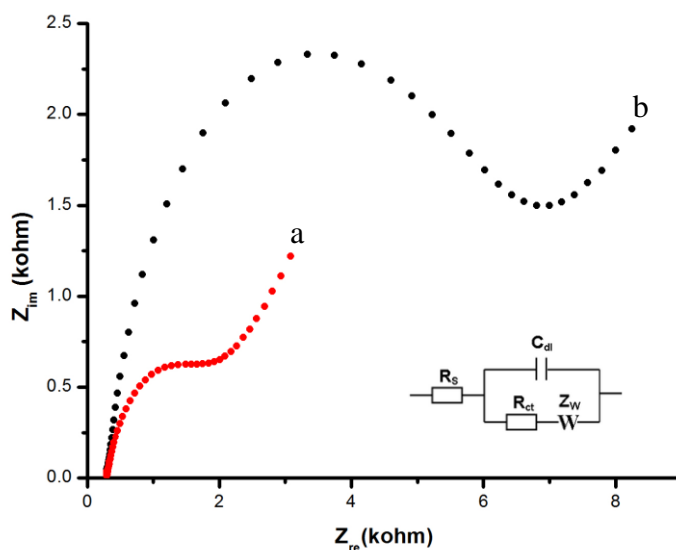


Figure 3. Nyquist plot of the (a) unmodified MWCNT and (b) ZLH-F/MWCNT in 4.0 mM $K_3[Fe(CN)_6]$ containing 0.1 M KCl. Inset: Randle's equivalent electrical circuit system.

3.3. Electrochemistry of HQ on the ZLH-F/MWCNT paste electrode

SWV of 0.1 mM HQ in 0.1 M PBS at pH 7.0 on unmodified MWCNT and the ZLH-F/MWCNT paste electrode were studied. Fig. 4 shows that the anodic peak current, I_{pa} of the ZLH-F/MWCNT paste electrode is higher than the unmodified MWCNT paste electrode. The ZLH-F offers larger active sites and facilitate electron transfer during the electrochemical reactions [26,27]. Thus, the modification of MWCNT by adding the ZLH-F has increased the performance of paste electrode in determination of HQ.

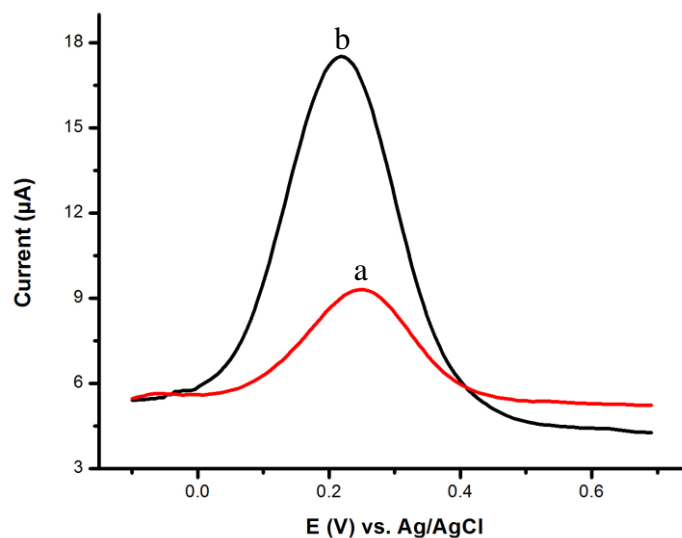


Figure 4. SWV of the (a) unmodified MWCNT and (b) ZLH-F/MWCNT towards 0.1 mM HQ in 0.1 M PBS at pH 7.0.

3.4. Optimization of the experimental conditions

3.4.1. The effect of pH

The effect of pH values on the peak potentials and the peak currents of HQ at the ZLH-F/MWCNT were examined by SWV over a pH range of 5.5 – 8.0 as shown in Fig. 5A. From pH 5.5 to 7.0, it can be seen that the peak current increased up to 12.78 μA as the pH increased and when pH was higher than 7.0, the peak current decreased, which could be caused by the shortage of protons at higher pH value [8]. The effect of pH on peak currents of HQ may result from electrochemical oxidation processes of HQ and their adsorption on the ZLH-F/MWCNT paste electrode. In order to obtain a high sensitivity, pH 7.0 was chosen in this work.

3.4.2. The effect of square wave parameters

According to the calculations performed by Osteryoung, characteristic of SW voltammogram is linearly dependent on some electroanalytical parameters used [28]. Hence, the effect of different square wave parameters such as frequency, step size and pulse size were studied to get peak currents at high scan speed with better sensitivity. The effect of frequency was examined by increasing the frequency from 30 Hz to 150 Hz. As shown in Fig. 5B, the peak current increased linearly as increasing of frequency. The step size was varied in the range of 1 mV to 6 mV at fixed frequency, 150 Hz and the result shows the increasing of peak current of HQ with the increasing of step size (Fig. 5C). A similar behaviour can be seen when pulse size varied from 10 mV to 60 mV at fixed frequency, 150 Hz and fixed step size, 6 mV as shown in Fig. 5D. Therefore, the optimal SWV parameters chosen for the subsequent determination of HQ were frequency = 150 Hz, step size = 6 mV and pulse size = 60 mV.

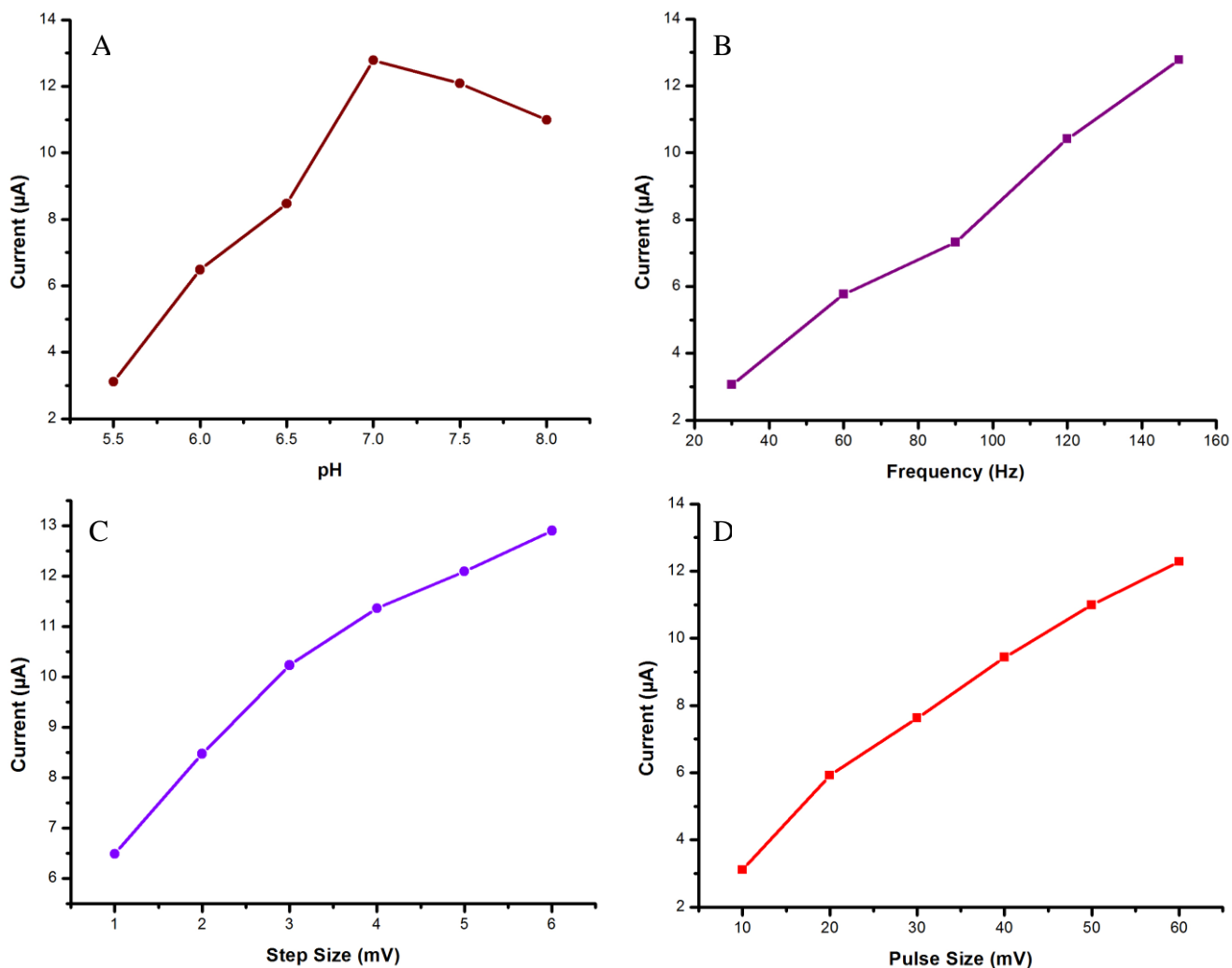


Figure 5. Effect of the (A) pH, (B) frequency, (C) step size and (D) pulse size on the peak current of 0.1 mM HQ

3.5. Calibration curve

Under optimal conditions, the response of the ZLH-F/MWCNT paste electrode towards different concentrations of HQ in 0.1 M PBS (pH 7.0) was investigated. As can be seen in Fig. 6, the peak current, I_{pa} increased with the increasing of HQ concentration from 1.0×10^{-5} M to 1.0×10^{-3} M. The calibration curve shows good linearity with the correlation coefficients, $R^2 = 0.9957$ and limit of detection (LOD) = 5.7×10^{-6} M. The LOD was calculated according to the equation (2):

$$\text{LOD} = 3\sigma/m$$

where σ = standard deviation of signal obtain from the blank and m = slope of the calibration curve. Table 1 shows a comparison of the proposed method with other modified electrodes. It can be seen that the ZLH-F/MWCNT displays quite good sensitivity if it was not better than previously reported HQ detector.

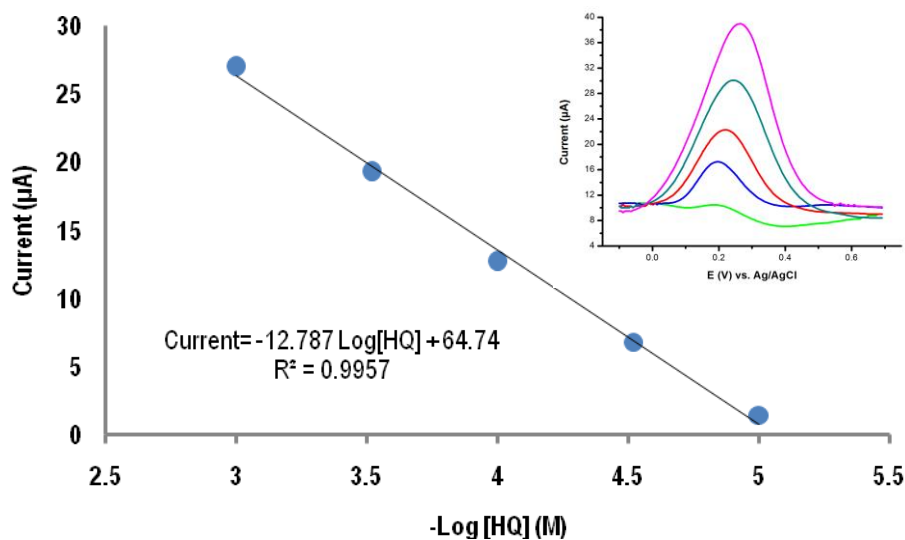


Figure 6. Calibration plot of HQ (inset: SWV responses to various concentration of HQ).

3.6. Reproducibility and stability

Table 1. Performance comparison of the fabricated electrode for HQ determination.

Modifier/Electrode	Method	Calibration curve (M)	LOD (M)	Ref
Zucchini crude extract-palladium/GCE ^a	CV ^b	$6.2 \times 10^{-5} - 8.9 \times 10^{-3}$	8.3×10^{-6}	[2]
Zn/Al layered double hydroxide film/GCE	DPV ^c	$1.2 \times 10^{-5} - 8.0 \times 10^{-4}$	9.0×10^{-6}	[29]
Pt-graphene hybride/GCE	DPV	$2.0 \times 10^{-5} - 1.5 \times 10^{-4}$	6.0×10^{-6}	[30]
1-octyl-3-methylimidazolium hexafluorophosphate/ CPE ^d	CV	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	8.1×10^{-7}	[31]
<i>Solanum gilo</i> extract in chitosan biopolymer	SWV ^e	$2.5 \times 10^{-4} - 5.5 \times 10^{-3}$	2.0×10^{-6}	[32]
Polyaniline-poly(3-methylthiophene-poly(3,3'-diaminobenzidine	Amp ^f	$4.37 \times 10^{-7} - 9.5 \times 10^{-2}$	1.31×10^{-7}	[33]
Zn layered hydroxide-ferulate (ZLH-F)/MWCNT ^g	SWV	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	5.7×10^{-6}	This work

^a Glassy carbon electrode

^b Cyclic voltammetry

^c Differential pulse voltammetry

^d Carbon paste electrode

^e Square wave voltammetry;

^f Amperometry

^g Multiwall carbon nanotubes

Under the optimized conditions, the relative standard deviation (RSD) for ten measurements with the same ZLH-F/MWCNT paste electrode was 3.72%. Three ZLH-F/MWCNT paste electrodes were fabricated under the same conditions showed an acceptable reproducibility with the 3.48% RSD.

Lastly, the peak currents slightly decreased to 92.7% from their initial values after the electrode is stored at room temperature for two weeks. These results proved a good stability and reproducibility of the ZLH-F/MWCNT paste electrode for determination of HQ.

3.7. Interference study

The interference from various substances such as glucose, fructose, sucrose, bisphenol A (BPA), acetaminophen (AC), lysine, NO₃⁻, Cl⁻ and SO₄²⁻ were studied. Under optimal conditions, the interference substances were added to 10-fold and 100-fold into 100 μM HQ. Fig. 7 shows that the presence of interference substances at 10- and 100-fold did not interfere to the selectivity of electrode with signal deviations below than 10% which indicates that this method has suitability of HQ detection in the mixture of these interference substances.

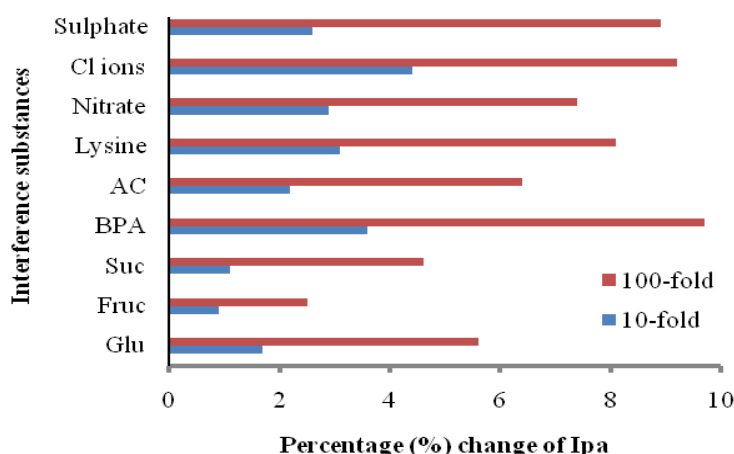


Figure 7. The effect of interference substances to 0.1 mM HQ.

3.8. Analytical application to real samples

Table 2. Recovery results for HQ determination in water samples and cosmetic cream.

Samples	HQ added (M)	HQ found (M)	Recovery (%)	RSD (%)
Tap water	3.0×10^{-5}	2.96×10^{-5}	98.7	2.7
	5.0×10^{-4}	4.89×10^{-4}	97.8	2.5
Mineral water	3.0×10^{-5}	3.02×10^{-5}	100.7	2.9
	5.0×10^{-4}	4.90×10^{-4}	98.0	3.4
Lake water	3.0×10^{-5}	2.95×10^{-5}	98.3	3.3
	5.0×10^{-4}	5.12×10^{-4}	102.4	4.1
Cosmetic Cream	3.0×10^{-5}	3.09×10^{-5}	103.0	3.8
	5.0×10^{-4}	5.13×10^{-4}	102.6	3.5

The ZLH-F/MWCNT paste electrode was tested to the determination of HQ in water samples and cosmetic cream. The recovery was measured by spiking with known concentration of the HQ into

the samples. The SWV results are summarized in Table 2. The recovery was between 97.6% - 101.4% which reveals the feasibility of this method to the HQ determination.

4. CONCLUSION

This work demonstrated the application of the ZLH-F/MWCNT paste electrode as mediator in determination of HQ by SWV. Under optimal conditions, this electrode showed a linear working concentration range with correlation coefficient of 0.9957 and LOD = 5.7×10^{-6} M. In addition, the results proved that the ZLH-F/MWCNT paste electrode had high reproducibility and good stability for HQ detection. Consequently, the developed method is found to be simple and rapid.

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