

# Determination of hydroquinone in food and pharmaceutical samples using a voltammetric based sensor employing NiO nanoparticle and ionic liquids



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## ABSTRACT

A sensitive modified carbon paste electrode (MCPE) employing NiO nanoparticle (NiO/NPs) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMITFB) ionic liquid was used for trace level analysis of hydroquinone (HQ) in aqueous solution. Compared to bare electrode, the electro-oxidation signal of HQ was greatly improved. The obtained result shows that, the electro-oxidation signal was increased to about 2.5 times at the surface of (NiO/NPs/BMITFB/MCPE) compared to CPE. The linear response range and detection limit were found to be 0.1–500  $\mu\text{M}$  and 0.05  $\mu\text{M}$  by square wave voltammetry (SWV), respectively. NiO/NPs/BMITFB/MCPE was effectively applied for the determination of HQ in real samples such as Liposomes carrier containing HQ and water sample.

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## 1. Introduction

Hydroquinone (HQ, 1,4-dihydroxybenzene) is an isomer of phenolic compounds which extensively used in several fields such as cosmetics, medicines, dye, photostabilizer, plastic, petroleum refinery, antioxidant, pesticides, and photography [1–3]. HQ works by inhibiting the enzyme tyrosinase, which is essential in the production of the pigment melanin and lead to bleaching of the skin [4]. Hydroquinone blocks a step in a specific enzymatic pathway that involves tyrosinase as an enzyme in the procedure of converting dopamine to melanin [5]. HQ is used as a topical application for skin whitening for reducing the color of the skin. However, numerous studies revealed that if HQ taken orally may cause exogenous ochronosis, a disfiguring disease in which blue-black pigments are deposited onto the skin [6]. HQ is difficult to degrade in the ecological environment and highly toxic to human health even at low concentrations [7,8]. High concentration of HQ can lead to acute myeloid leukemia, tinnitus, headache, fatigue, dizziness, nausea, edema of internal organs, skin irritation and cause kidney damage in humans [9–11]. HQ considered as an environmental pollutant by the US Environmental Protection Agency (EPA) and the European Union (EU) [12]. Therefore, development of sensitive and reliable analytical methods with high accuracy has been greatly demanded in the field of environmental pollutant analysis.

So far, numerous analytical procedures including high performance liquid chromatography [13,14], fluorescence [15,16], chemiluminescence [17,18], spectrophotometry [19,20] and electrochemical methods [21–23] has been reported for determination of HQ in various matrices. Electrochemical methods in comparison to other strategies received more interest because the mentioned techniques mostly involve expensive instruments, lengthy sample preparation and complicated analysis procedures which has limited their application in the rapid and quantitative analysis of electroactive compounds [24–28]. On the other hand, electrochemical sensors as an efficient approach offering advantages such as low cost, fast analysis, high sensitivity and selectivity in compare to instrumental analysis [29–31].

Room temperature ionic liquids (RTILs) which composed entirely of ions received increasing interest over the last decade due to their characteristics of negligible vapor pressure and good solubility and chemical stability. RTILs due to their unique electrochemical properties such as considerable high ionic conductivity, broad electrochemical window and fast ion mobility have been applied in various fields such as electrolytes in batteries, binder, electrochemical cells, and electroplating. As a new green medium, RTILs have also been newly used in construction of electrochemical modified sensors. The obtained results revealed that the use of RTILs could increase the sensitivity of electrochemical response and facilitate efficient direct electron transfer of various biological, environmental and pharmaceutical compounds [32–34]. Nanomaterials and especially metal oxide nanoparticles of a variety of shapes, sizes and compositions benefited the electrochemical measurement of electroactive materials because of their unique electrical, thermal, chemical and physical properties [35–40]. This kind of materials

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can be improved sensitivity and selectivity voltammetric sensors in analysis filed [41–43]. Metal oxide nanoparticles with high surface area show valuable electrocatalytic activity and high conductivity to modify the surface of electrodes. Metal oxide nanoparticles due to their good biocompatibility are remarkably applied in preparation of biosensors [44–46]. It can be concluded that combination of metal oxide nanomaterials and RTILs could reveal awesome and novel features in preparation of new electrochemical sensors for pharmaceutical, biological and environmental compound analysis.

## 2. Materials and methods

### 2.1. Chemical and reagents

Hydroquinone, 1-butyl-3-methylimidazolium tetrafluoroborate were purchased from Sigma-Aldrich. Lecithins, NaOH, cholesterol, mineral oil, and methanol and graphite powder were obtained from Merck. Phosphate buffer solution (PBS) with various pH was prepared by mixing the stock solution of 0.1 M  $H_3PO_4$ . The doubly distilled water was used in all solution preparations. All of the other chemicals were purchased in analytical grade from Merck.

### 2.2. Apparatus

Voltammetric measurements were performed on a Sama-500 electrochemical workstation (Isfahan, Iran). A three-electrode system was employed with a modified or unmodified carbon paste electrode as working electrode, a Pt wire as counter electrode, and a Ag/AgCl/KCl<sub>saturated</sub> electrode as reference electrode.

Microstructure and surface morphology of nanoparticles were identified by a scanning electron microscope (SEM, Philips).

### 2.3. Preparation of BMITB/NiO/NPs/CPE

NiO/NPs/BMITFB/MCPE was prepared by mixing 0.2 g of BMITFB, 0.8 g of paraffin, 0.1 g of nanoparticles and 0.9 g of graphite powder. Then the mixture was mixed well for 1 h until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into a glass tube as described above to prepare NiO/NPs/BMITFB/MCPE. When necessary, a new surface of NiO/NPs/BMITFB/MCPE was obtained by pushing an excess of the paste out of the tube and polishing it on a white paper.

### 2.4. Recommended procedure

NiO/NPs/BMITFB/MCPE was polished with a white and clean paper. To prepare a blank solution, 10.0 mL of the buffer solution (PBS, pH 7.0) was transferred into an electrochemical cell. The initial and final potentials were adjusted to  $-0.4$  and  $0.8$  V vs. Ag/AgCl, respectively. Cyclic voltammogram was recorded with a scan rate of 100 mV/s to record the electrochemical signal at pH = 7.0.

### 2.5. Real sample preparation

Liposomes containing HQ were prepared using film hydration method. Lecithin and cholesterol were dissolved in chloroform solvent with three different compositions of 50:50, 60:40 and 70:30, respectively. Rotary evaporator was used to evaporate the solvent, until an oily concentrated mixture was obtained and then a known amount of HQ which is dissolved in di-water, was added to the mixture and for 30 min rotary evaporating process was continued until milky color suspensions containing liposomes were formed. To prevent the oxidation of lecithin the procedure was carried out under inert atmosphere. To determine the amount of HQ loading in all formulations, the non-entrapped compounds were separated from encapsulated ones by centrifuge. The supernatant phase which contains the non-trapped HQ was separated.

Standard addition method was used to determine the percentage of non-trapped HQ using proposed sensor.

Water sample was used without any pretreatment for spike HQ analysis as a real sample.

## 3. Results and discussion

### 3.1. SEM investigation for used nanoparticles

Surface morphology of NiO nanoparticles was characterized by SEM method (Fig. 1). The dark spots correspond to NiO nanoparticles, which were only synthesized in our synthesis condition. Nanoparticles with near-spherical shapes were synthesized.

### 3.2. Electrochemical analysis

According to previous published paper, the electro-oxidation signal of HQ is closely related to the pH value of buffer solution [47]. According to the mentioned paper, optimization of pH is a very important factor for trace analysis of it in real samples. The obtained results show that the electro-oxidation current increased gradually from pH 6.0 to 7.0, and then the oxidation signal conversely decreased when the pH value increased from 7.0 to 9.0 (Fig. 2). So pH 7.0 was selected as a best condition in analytical procedure in further steps. The relationship between the electro-oxidation potential and pH was also investigated. A linear shift of  $E_{pa}$  towards negative potential with an increasing pH can be obtained, which indicates that protons are directly involved in the oxidation of HQ (Fig. 3). A slope of 0.064 V/pH suggests that the number of electron transfer is equal to the proton number involved in the electrode reaction.

The current density for oxidation signal of HQ derived from the cyclic voltammogram responses of 500  $\mu$ M HQ (pH 7.0) at the surface of different electrodes is shown in Fig. 4 (inset).

The cyclic voltammograms of HQ at NiO/NPs/BMITFB/MCPE are also compared with that at bare carbon paste electrode (CPE), NiO/NPs/MCPE and BMITFB/MCPE at a scan rate of 100 mV/s in 0.1 M PBS (pH 7.0) (Fig. 4). At the bare electrode, the electro-oxidation of HQ

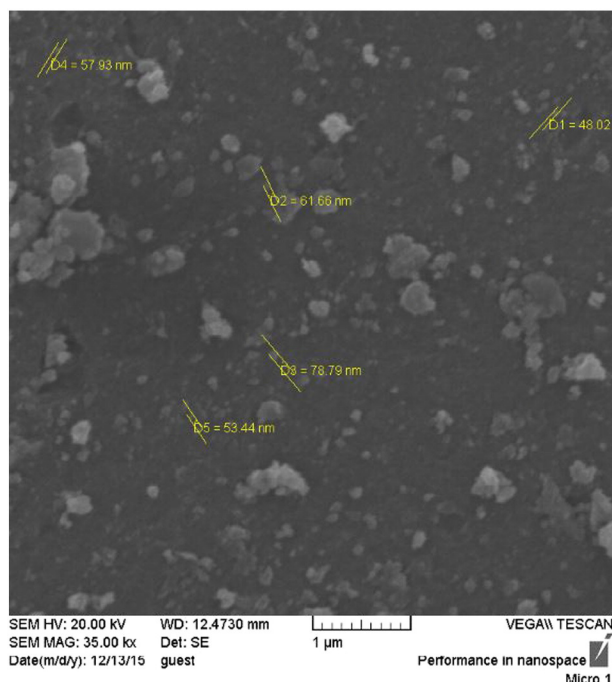
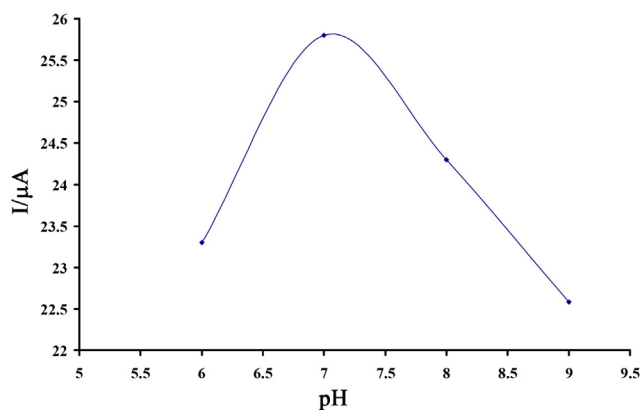


Fig. 1. SEM image of synthesized NiO nanoparticles.

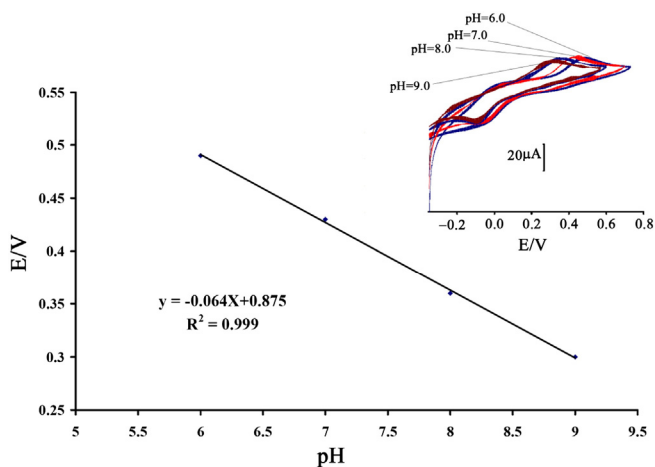


**Fig. 2.** Current–pH curve for electrooxidation of 500  $\mu\text{M}$  HQ at NiO/NPs/BMITFB/MCPE. Inset) influence of pH on cyclic voltammograms of HQ at the surface of the modified electrode, (pH 6.0, 7.0, 8.0 and 9.0, respectively).

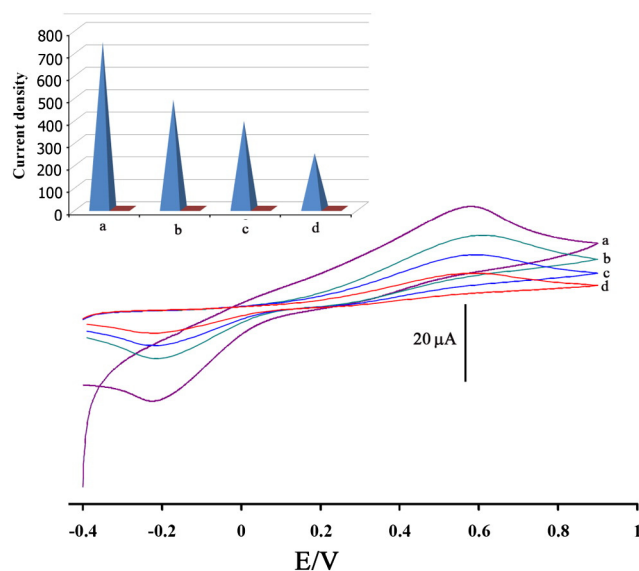
has a low current with high overvoltage. After modification with NiO/NPs or BMITFB ionic liquid oxidation signal for HQ improved and overvoltage reduce for it. Therefore, we found that NiO/NPs and BMITFB are two conductive compounds and can be used as a mediator for carbon paste modification. Fig. 4 (curve a) shows better condition for electro-oxidation of HQ. The result confirms that modification of electrode with NiO/NPs or BMITFB is increasing quality of sensor for trace analysis of HQ. So, we selected NiO/NPs/BMITFB/MCPE as a suitable sensor in this work.

Electrochemical mechanisms and kinetic characteristics of an electroactive compound (HQ in this case) can be investigated by scan rate study of it. Fig. 5 insets showed the cyclic voltammograms of HQ on NiO/NPs/BMITFB/MCPE between  $-0.3$  and  $0.60$  V at various scan rates. Fig. 5 shows the electro-oxidation peak currents ( $I_p$ ) increased linearly vs.  $v^{1/2}$  from 300 to 800 mV/s indicating that the electro-oxidation of HQ on NiO/NPs/BMITFB/MCPE was a diffusion controlled process.

Chronoamperometric analysis of HQ at NiO/NPs/BMITFB/MCPE was carried out by setting the working electrode potential at 900 mV for the 100  $\mu\text{M}$ , 200  $\mu\text{M}$ , 300  $\mu\text{M}$ , 400  $\mu\text{M}$  and 500  $\mu\text{M}$  of HQ in buffered aqueous solutions (pH 7.0) (Fig. 6A). Experimental plots of  $I$  vs.  $t^{-1/2}$  were employed, with the best fits for different concentrations of HQ (Fig. 6B). The slopes of the resulting straight lines were then plotted vs. HQ concentration. From the resulting slope and Cottrell equation the mean value of the  $D$  was found to be  $4.14 \times 10^{-5}$   $\text{cm}^2/\text{s}$ .



**Fig. 3.** Plot of potential,  $E$ , vs. pH for the electro-oxidation of 500  $\mu\text{M}$  HQ at a surface of NiO/NPs/BMITFB/MCPE. Inset: influence of pH on cyclic voltammograms of HQ at a surface of the modified electrode (pH 6–9, respectively).



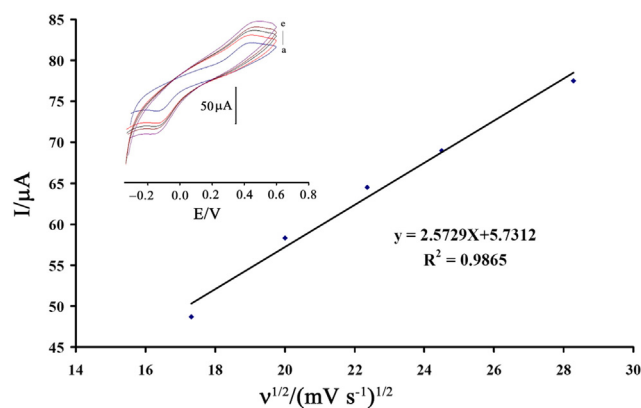
**Fig. 4.** Cyclic voltammograms of (a) NiO/NPs/BMITFB/MCPE, (b) BMITFB/MCPE, (c) NiO/NPs/CPE and (d) BCPE in the presence of 500  $\mu\text{M}$  HQ pH 7.0, respectively.

### 3.3. Interference of coexisting substances

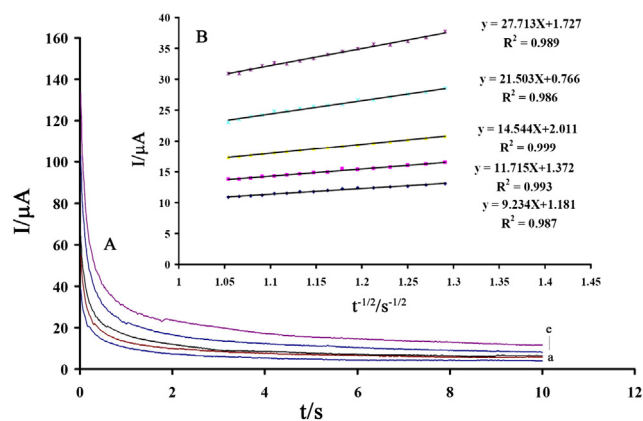
The influence of some compounds on the determination of 50.0  $\mu\text{M}$  HQ was also studied. It was found that 100-fold concentration of fructose, lactose, glucose, urea, thiourea, sucrose, phenol, and  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{Ni}^{+2}$  and 75 fold concentration of histidine, methionine, cysteine, lysine, phenyl alanine, and glycine do not affect the determination of HQ (signal change  $\leq 5\%$  in current and potential).

### 3.4. Dynamic range

Square wave voltammetry curves showed that as the concentration of HQ increased, the current signal gradually increased. During the HQ concentration range 0.1–500  $\mu\text{M}$ , the concentration and the current response of HQ exhibited a linear relationship with equation:  $I = 0.3425 C_{\text{HQ}} + 1.9640$ ;  $R^2 = 0.9913$ , where  $C$  is  $\mu\text{M}$  concentration of HQ and  $I_p$  is the peak current. The detection limit was determined at 0.05  $\mu\text{M}$  HQ according to the definition of  $Y_{\text{LOD}} = Y_B + 3\sigma$ .



**Fig. 5.** Plot of  $I_{\text{pa}}$  versus  $v^{1/2}$  for the oxidation of HQ at NiO/NPs/BMITFB/MCPE. Inset shows cyclic voltammograms of HQ at NiO/NPs/BMITFB/MCPE at different scan rates of (a) 300, (b) 400, (c) 500, (d) 600 and (e) 800 mV/s in 0.1 M phosphate buffer, pH 7.0.



**Fig. 6.** (A) Chronoamperograms obtained at NiO/NPs/BMITFB/MCPE in the presence of (a) 100; (b) 200; (c) 300; (d) 400 and (e) 500  $\mu\text{M}$  HQ in the buffer solution (pH 7.0). (B) Cottrell's plot for the data from the chronoamperograms.

### 3.5. Stability and reproducibility

The reproducibility of the NiO/NPs/BMITFB/MCPE was evaluated by determination of HQ with four sensors prepared using the same procedure. The relative standard deviation (RSD) is 1.9% for HQ, which indicated the suitable reproducibility of the fabricated sensor.

The stability of the novel modified electrode is also a major issue for the practical implementation of electrochemical analysis. Therefore, the stability of the NiO/NPs/BMITFB/MCPE was studied over 65 days. The proposed sensor was stored dry at room temperature for 10 days and still retained about 97.0% of its original response for HQ, revealing that the as-prepared electrode had excellent stability.

### 3.6. Real sample analysis

In order to assess the ability of the NiO/NPs/BMITFB/MCPE as a novel sensor, it used for direct analysis of HQ in real samples such as tap water and waste water. The results are listed in Table 1 and shows feasibility of the NiO/NPs/BMITFB/MCPE in the direct analysis of HQ in real samples.

Moreover, the encapsulation efficiency of formed liposome containing HQ was calculated by determination of the non-entrapped HQ which is remaining in supernatant phase by proposed fabricated sensor. According to the obtained results using standard addition method, the composition of 70:30 (Lecithin:cholesterol) liposome revealed the best encapsulation efficiency of 76.7% in compare to the other prepared composition.

## 4. Conclusion

This work demonstrated the application of a NiO/NPs and 1-butyl-3-methylimidazolium tetrafluoroborate as a modifier in carbon paste matrix for the determination of HQ. The proposed sensor showed good electrocatalytic activity towards the electro-oxidation response of HQ with the enhancement of the electro-oxidation signal. Under the optimum conditions in cyclic voltammetric investigation, the peak current was proportional to the HQ concentration in the range of 0.1–500  $\mu\text{M}$

with the detection limit of 0.05  $\mu\text{M}$ . The excellent properties of the NiO/NPs/BMITFB/MCPE make them promising for application to real sample analysis.

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**Table 1**  
Determination of HQ in real samples.

Sample	HQ		Recovery %	RSD
	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )		
Tap water	10.00	9.87 $\pm$ 0.45	98.7	2.2
	20.00	20.55 $\pm$ 0.75	102.8	2.8
Waste water	50.00	50.85 $\pm$ 1.11	101.7	3.2
	80.00	79.45 $\pm$ 1.32	99.3	3.8



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