Arabian Journal of Chemistry (2012) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Voltammetric determination of resorcinol on the surface of a glassy carbon electrode modified with multi-walled carbon nanotube

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Received 7 February 2011; accepted 18 April 2012

KEYWORDS

Multi-walled carbon nanotubes;
Resorcinol;
Glassy carbon electrode;
Voltammetry;
Determination

Abstract A multi-walled carbon nanotubes (MWCNTs) film coated glassy carbon electrode (GCE) was fabricated, and the electrochemical oxidation of resorcinol (RS) was studied in Britton–Robinson (BR) buffer (pH 6.0) using cyclic, square wave, and differential pulse voltammetry (CV, SWV, and DPV). The results revealed that the modified electrode shows an electrocatalytic activity toward the oxidation of RS by a marked enhancement in the current response in buffered solution. The oxidation of RS at this nano-structured film coated electrode was irreversible and diffusion-controlled. Under the optimum conditions, the anodic peak current showed a linear relation versus RS concentration in the range of 1.2×10^{-6} to 1.9×10^{-4} M with detection limits of 4.9×10^{-7} and 1.1×10^{-6} M (signal-to-noise = 3) for SWV and DPV, respectively. Moreover, the modified electrode demonstrated good reproducibility (RSD = 2.4%, n = 10) and long-term stability. This method has been applied to the determination of RS in wastewater, and the recoveries were from 93% to 104%.

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Peer review under responsibility of King Saud University.
http://dx.doi.org/10.1016/j.arabjc.2012.04.009

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1. Introduction

Phenolic compounds are highly toxic environmental pollutants, and seriously threaten human's health. They are widely used in many fields, such as tanning, cosmetic, dye, chemical and pharmaceutical industries (Wang et al., 2007). Phenolic compounds in environment come from different sources, including industrial wastewater, solid castoff of coal tar, coking factory, gasworks, paper mill, chemical plants and pharmaceutical industry (Ware, 1992). Some of the phenolic compounds have been listed as control targets because of their toxicities in many countries. Phenolic compounds are also poisonous organic

Please cite this article in press as: Ghoreishi, S.M. et al., Voltammetric determination of resorcinol on the surface of a glassy carbon electrode modified with multi-walled carbon nanotube. Arabian Journal of Chemistry (2012), http://dx.doi.org/10.1016/j.arabjc.2012.04.009

pollutants. Therefore, many governments have spent a lot of effort in their detection and control.

Resorcinol (RS) is one kind of phenolic compounds with high toxicity. It can be easily absorbed through the gastric tract and human skin, which can cause dermatitis, catarrh, convulsion, cyanopathy, and even death (Guardia et al., 1995). At present, various methods have been employed for RS determination, including spectrophotometric (Kang et al., 2000), high-performance liquid chromatography with diode array detection (Yang et al., 2006), microchip capillary electrophoresis with end channel amperometric detection (Wu and Lin, 2006), quartz crystal microbalance (Mirmohseni and Oladegaragoze, 2004), flow injection chemiluminescence (Du et al., 2001), surface plasmon resonance (Wright et al., 1998), fluorescence (del Olmo et al., 2000; Pistonesi et al., 2006) and spectrofluorimetric (Fan et al., 2007; Wenxiang and Dan, 2007).

Electrochemistry has always provided analytical techniques characterized by instrumental simplicity, moderate cost, and portability. These techniques have introduced the most promising methods for specific applications (Goyal et al., 2006, 2007a, 2009a; Gupta et al., 2010, 2011a). But these methods normally have low sensitivity at conventional electrodes. However, low sensitivity and poor selectivity of electrochemical methods can be overcome by electrode modification (Goyal et al., 2005, 2007b, 2007c, 2008a, 2008b; Gupta et al., 2011b).

Carbon nanotubes (CNTs) are a novel nanoscale material, mainly consisting of SWCNTs and MWCNTs (Bethune et al., 1993; Fernandez-Abedul and Costa-Garcia, 2008). These nanoscale materials have attracted considerable interest owing to their extraordinary mechanical and unique electrochemical properties (Goyal et al., 2008c). The subtle electronic behavior of CNTs demonstrates that they have the ability to promote electron-transfer reactions when used as electrode materials (Nugent et al., 2001). Several types of CNT electrodes have been reported, including CNT paste electrodes (Davis et al., 1997; Valentini et al., 2003), CNT film-coated electrodes (Luo et al., 2001; Guo et al., 2004), CNT powder microelectrodes (Zhao et al., 2002) and CNT paper electrodes (Barisci et al., 2000). CNT-modified GCEs provide a stable and sensitive electrochemical response for phenols (Wang et al., 2003), NADH (Musameh et al., 2002), estrogenic phenolic compounds (Vega et al., 2007a,b; Agui et al., 2007), ascorbic acid, dopamine (Wu and Hu, 2004), uric acid (Wu and Hu, 2004) and tetracycline (Vega et al., 2007a).

The main objective of this work was to develop a simple and sensitive electrochemical sensor for the determination of RS. Based on the good electrocatalytic activity of MWCNT modified GCE toward the electrochemical oxidation of RS, a sensitive electrochemical method has been proposed for the determination of RS.

2. Experimental

2.1. Chemicals and reagents

Resorcinol was purchased from the MERCK Company. BR buffer solution was made up of phosphoric acid (MERCK), boric acid (MERCK), and ice acetic acid from the MERCK and its pH value was adjusted with NaOH (MERCK). MWCNTs with purity of >95% (40–60 nm in diameter) were obtained from the Chinese Academy of Sciences. Generally, pristine MWCNTs contained 3% amorphous carbon, SWCNTs, and graphite requiring some purification pre-treatments before electro-analytical characterization. MWCNTs refluxed under stirring for 5 h in concentrated nitric acid. It has been reported that this treatment could purify the CNTs and cause carboxylation at their termini (Tsang et al., 1994; Hiura et al., 1995). A 1.0×10^{-3} M RS standard solution was simply prepared by dissolving RS in deionized water. Working solutions were prepared with this standard solution and using suitable dilution with a 0.1 M BR buffer solution. BR buffer solution was also used as the supporting electrolyte.

2.2. Apparatus

Electrochemical measurements were carried out on a M273 electrochemical workstation (EG&G Corporation, USA) with a conventional three-electrode system. This equipment was equipped with a platinum plate (Metrohm) as the counter electrode, a saturated calomel electrode (SCE) from Metrohm as the reference electrode and a MWCNT/GCE as the working electrode. Solution pH values were determined using a 691 pH meter (Metrohm Swiss made) combined with glass electrode (Metrohm). Deionized water was formed with an ultrapure water system (smart 2 pure, TKA, Germany). MWCNT was dispersed with an ultrasonic bath (SONOREX DIGITAL, 10P, BANDELIN). Data were collected at room temperature.

2.3. Fabrication of the modified electrode

Using ultrasonic agitation, 0.5 mg of purified MWCNTs was dispersed into 5 ml of redistilled water for 30 min. Prior to modification, the GCE was polished with 0.05 mm alumina slurry and then cleaned ultrasonically in double-distilled water. Subsequently, the GCE was coated with 20 μL of MWCNT suspension and the solvent was evaporated in air.

2.4. Analytical procedure

Twenty milliliters of 0.1 M BR buffer solution (pH 6.0) containing a specific amount of standard solution of RS was added to an electrochemical cell. Electrochemical measurements were carried out by CV and recorded in the potential range of 0.1–1.0 V at a scan rate of 20 mV s^{-1}. DPV employed the following parameters: $E_{initial}$ = 0.3 V, E_{final} = 0.9 V, scan rate = 20 mV s^{-1}. SWV was recorded from 0.3 to 0.9 V and the current peak at 0.6 V was measured. The SWV parameters were as follows: SWV frequency = 80 Hz, pulse height = 100 mV, amplitude = 10 mV.

3. Results and discussion

3.1. Voltammetric behavior of RS at MWCNT/GCE

Fig. 1 shows the cyclic voltammograms (CVs) of 5.0×10^{-5} M RS on a bare GCE and MWCNT–GCE in 0.1 M BR buffer solution (pH 6.0). Compared to the bare electrode, the anodic peak current of RS increased significantly at the modified electrode. Also, the oxidation peak potential shifted to the negative values (Fig. 1a) in contrast to those at the bare electrode (Fig. 1b), which indicated that the modified electrode has a catalytic effect on the oxidation of RS. The following reasons might explain the electrocatalytic response of RS on

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