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Electrochemical Analysis of 2-chlorophenol Using a Multi-Walled Carbon Nanotube-Ionic Liquid Composite Modified Electrode

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A multi-walled carbon nanotube-ionic liquid composite modified glassy carbon electrode was fabricated. The modified electrode showed highly catalytic ability towards the oxidation of 2-chlorophenol. Square wave voltammetry was used for the determination of 2-chlorophenol. The oxidation peak currents were linearly with the concentrations of 2-chlorophenol in the range of 0.5 to 12.0 μM, with a detection limit of 0.1 μM. The proposed method was successfully applied for the determination of 2-chlorophenol in water samples with satisfactory recoveries.

Keywords: 2-chlorophenol; Modified electrode; Multi-walled carbon nanotube; Ionic liquid

1. INTRODUCTION

Chlorophenols are widely used in the industry, such as paper and pesticides production [1]. They are well-known pollutants in environmental waters and soils due to the effluent discharges from factories. The chlorophenols are chemicals with high toxicity including estrogenic, mutagenic and carcinogenic effects (e.g. 2-chlorophenol) [2]. Thus, chlorophenols are listed as the priority pollutants by the U.S. Environmental Protection Agency (EPA, Toxic Substance Control Act, Washington, DC 1979). Monitoring of chlorophenols is of great importance in environmental control, remediation and safety. Many methods have been developed for the determination of chlorophenols, such as spectrophotometry [3], gas chromatography-mass spectrometry [4], high performance liquid chromatography [5], fluorescence [6], enzyme linked immuno-assay [7] and electrochemical methods

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[8–14]. Among these methods, electrochemical method has been proved to be a promising method due to its high sensitivity, simple operation and low cost.

With the rapid development of nanotechnology, a great number of nanomaterials have been developed as electrode materials. Carbon nanotubes (CNT) have been widely used in electrochemical field for their unique properties of large specific surface area, good electrocatalytic activities and high electronic conductivity [15-17]. Ionic liquid (IL) is a salt in the liquid state, which is largely made of ions and ion pairs. It has been widely used as powerful solvents and electrolytes in electrochemistry due to its unique properties such as good ionic conductivity, high viscosity, high chemical and thermal stabilities [18]. Therefore, the functional composite of IL and CNT could be used as a kind of promising electrode material.

In this work, multi-walled carbon nanotubes (MWCNT) -ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim]BF_4) composite modified glassy carbon electrode (MWCNT-IL/GCE) was fabricated. Electrochemical measurements showed the obvious electrocatalytic activity of MWCNT-IL/GCE towards the oxidation of 2-chlorophenol. Based on this, a sensitive analytical method was established for the determination of 2-chlorophenol. The analytical performance of the proposed method for the determination of 2-chlorophenol in river water samples was evaluated and satisfactory recoveries of 92.9% to 95.3% were obtained. The proposed method represents a new platform for the determination of environmental pollutants.

2. EXPERIMENTAL

2.1 Reagents and instrumentation

Multi-walled carbon nanotubes (MWCNT) was obtained from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China) with a typical diameter of 10–20 nm. The purity was more than 97%. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) was purchased from Lanzhou Centre for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). 2-chlorophenol, 4-chlorophenol, nitrophenol, aminophenol were purchased from Sinopharm Chemical Reagent Co., Ltd. China. All other chemical reagents (AR grade) were obtained from Nanjing Chemical Reagent Company (Nanjing China). Stock solution of 5.0×10^{-4} mol L^{-1} 2-chlorophenol was prepared by dissolving 2-chlorophenol into ethanol, and then diluted to working solution at desired concentration. All solutions were prepared with double-distilled water.

All electrochemical experiments were carried out on a CS350 Electrochemical Workstation (Wuhan Corrtest Instruments CO., LTD, Wuhan, China). A conventional three-electrode cell configuration was employed for the electrochemical measurements. A modified glassy carbon electrode (disc diameter of 3 mm) was used as the working electrode. The saturated calomel electrode (Saturated KCl) and platinum wire were employed as the reference and the counter electrode, respectively.

2.2 Preparation of MWCNT-IL composite and fabrication of the modified electrode

The preparation process of MWCNT-IL composite was according to the previous work[19]. Briefly, a total of 4 mg of the MWCNT was dispersed in 5 ml of [Bmim]BF_4 by ultrasonic agitation for about 1 h. The suspension was then centrifuged at 6000 rpm for 20 min. The MWCNT-IL composite was finally collected by removing the supernatant.

For the fabrication of MWCNT-IL/GCE, 2 mg of MWCNT-IL composite was dispersed in 1 ml of methanol forming the composite suspension, a total of 10 μl of the suspension was dropped on the clean GC electrode surface and then the solvent was evaporated in air. For the fabrication of MWCNT/GCE,, MWCNT was dispersed in methanol with the aid of ultrasonic agitation to prepare 2 mg ml^{-1} MWCNT suspension. Then 10 μl of the suspension were dropped onto the clean GC electrode surface and the solvent was evaporated in air.

2.3 Experimental procedures

A certain volume of 2-chlorophenol working solution and 10 mL of 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 5.0) were added into an electrochemical cell, and then the three electrode system was installed in it. The cyclic voltammograms were recorded from 0 to 0.8 V at scan rate of 0.1 Vs^{-1}, the square-wave voltammograms were recorded from 0.3 to 0.9 V with a step increment of 4 mV, amplitude of 25 mV and frequency of 15 Hz.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of 2-chlorophenol at different electrodes

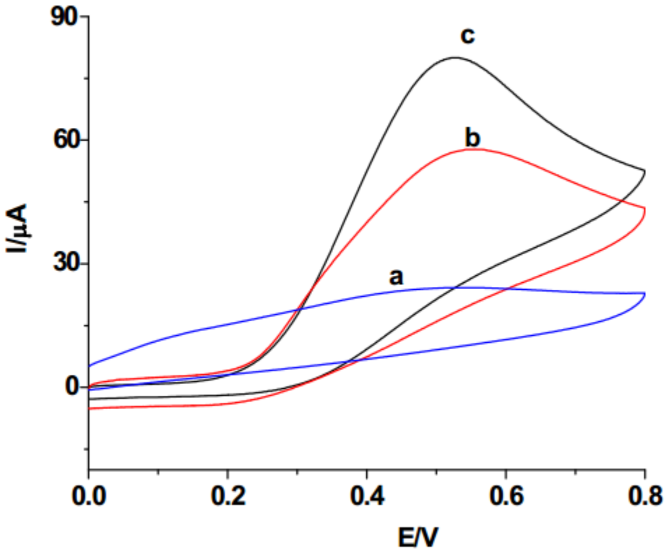

Figure 1. CVs of bare GCE (a), MWCNT/GCE (b) and MWCNT-IL/GCE (c) in 0.1mol L^{-1} PBS containing 50 μM of 2-chlorophenol. Scan rate: 0.1 V s^{-1}.

Fig. 1 shows the cyclic voltammograms(CVs) of 50 μM of 2-chlorophenol at bare GCE (a), MWCNT/GCE (b) and MWCNT-IL/GCE (c) in 0.1 mol L^{-1} PBS. As can be seen, no obvious peak is found for bare GCE. It suggests that 2-chlorophenol could not be oxidized on the GCE surface. An obvious oxidation peak (*E*pa, 0.55V) is observed on curve b, which corresponding to the oxidation of 2-chlorophenol on the MWCNT/GCE. This may be attributed to the large specific surface area and fast electron transfer rate of MWCNT. From curve c, we can see that the current response of 2-chlorophenol at the MWCNT-IL/GCE is much higher than that of MWCNT/GCE. Moreover, the peak potential shifts to 0.52 V. This means that the MWCNT-IL/GCE has higher electrocatalytic activity towards the oxidation of 2-chlorophenol. It suggests that the presence of IL could enhance the peak current and decrease the oxidation peak potential, which is related to the synergic effect of IL and MWCNT. From all the curves, no reduction peak is found in the reverse scan, indicating that the electrode reaction of 2-chlorophenol is a totally irreversible electrode process.

3.2 Effect of supporting electrolyte and pH

Supporting electrolyte is an important factor affecting the performance of MWCNT-IL/GCE to the oxidation of 2-chlorophenol. The effect of supporting electrolytes including phosphate buffer solution (PBS), Britton–Robinson buffer solution (B-R), acetate buffer solution (AB) and Na_2SO_4 on the current response was shown in Fig. 2A. The best peak current of 2-chlorophenol was obtained with PBS.

The pH effect of the PBS was investigated in the range of 3.0 –7.0. As can be seen from Fig. 2B, the oxidation peak current increased with increasing the pH of the buffer solution and reached the maximum at around pH 5.0. At higher pH values, the peak current decreased. Therefore, pH 5.0 was selected in the following voltammetric determinations.

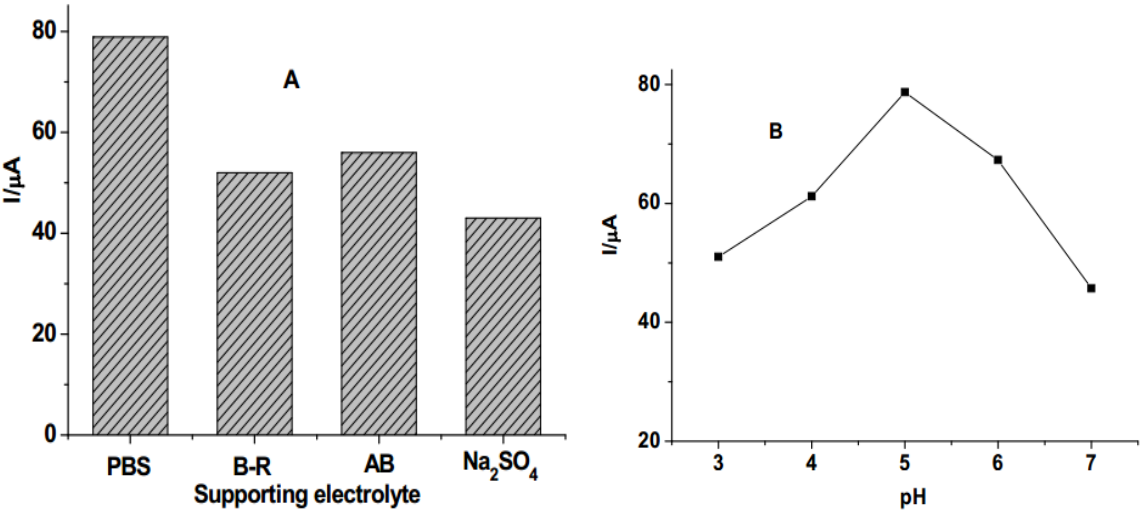

Figure 2. Effect of supporting electrolyte (A) and pH (B) on the oxidation peak current of 50 μM 2-chlorophenol.

3.3 Determination of 2-chlorophenol

For the determination of 2-chlorophenol, square wave voltammetry (SWV) was used due to its higher current sensitivity and better resolution than cyclic voltammetry. Fig. 3A shows the SWVs of MWCNT-IL/GCE in PBS solution containing different concentrations of 2-chlorophenol. It can be seen that the oxidation peak current increase with the increasing 2-chlorophenol concentrations. Fig. 3B shows that the oxidation peak currents of 2-chlorophenol are proportional to their concentrations in the range from 0.5 to 12.0 μM, with a detection limit of 0.1 μM. The linear regression equation can be expressed as I_{pa} (μA) = 3.72 + 4.49c (μM), with a correlation coefficient $r = 0.9987$.

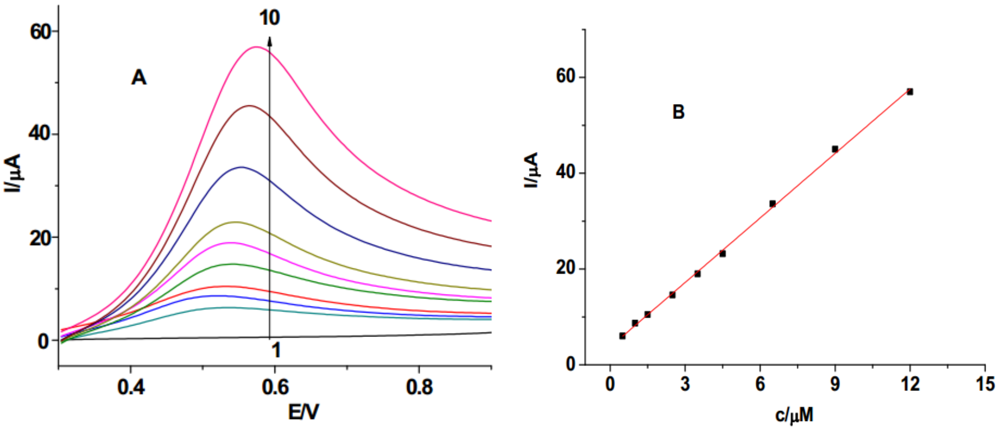

Figure 3. SWVs of MWCNT-IL/GCE in PBS containing different concentrations of 2-chlorophenol, from 1-10: 0, 0.5, 1.0, 1.5, 2.5, 3.5, 4.5, 6.5, 9.0, 12.0 μM (A) and plot of peak current versus 2-chlorophenol concentration (B).

For comparison, the determination performance of the proposed method was compared with other electrochemical methods. As shown in Table 1, it is can be seen that the proposed method has a wide linear range and a low detection limit, which makes it suitable for the determination of 2-chlorophenol.

Table 1. The determination performance comparison with other electrochemical methods.

Modified electrode	Linear range (μM)	LOD(μM)	References
Myoglobin- agarose /GCE	12.5–208	2.06	[10]
Tyrosinase/MCWNT/GCE	2.0–100	0.66	[20]
Horseradish peroxidase/MCWNT/GCE	1.0 –100	0.38	[21]
MWCNT-IL/GCE	0.5 – 12.0	0.1	this work

3.4 Reproducibility and stability

To investigate the reproducibility of the proposed method, a series of four modified electrodes prepared in the same manner were tested for the determination of 2.5 μM 2-chlorophenol and the RSD was 4.7%. The stability of the modified electrode was also studied, when the modified electrode was stored at room temperature after ten days, the peak current response retained 94% of its initial response.

3.5 Selectivity study

The interference of some foreign species on the determination of 2-chlorophenol was studied. The oxidation peak current of 2.5 μM 2-chlorophenol in the absence and presence of various concentrations of foreign species was measured, and the peak current change can be obtained. When the peak current change exceeds 5%, it is considered that this substance causes interference, and the corresponding concentration was defined as tolerance level. It is found that 30 μM nitrophenol, 20 μM aminophenol, 4.0 μM phenol and 4- chlorophenol, almost do not interfere with the oxidation peak current of 2-chlorophenol. Moreover, the effect of several ions on the determination of 2-chlorophenol was also studied. The results showed that 200-fold concentration of Na^+, K^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Cl^-, NO_3^- , SO_4^{2-} have no interference on the determination of 2-chlorophenol.

3.6 Real water sample analysis

The proposed method was used for the determination of 2-chlorophenol in local river water samples. The data were listed in Table 2. As can be seen, no 2-chlorophenol was detected for the water samples. It is assumed that there is no 2-chlorophenol in the water sample or the concentration of 2-chlorophenol is too low to be detected. Thus, the recovery experiments were performed by adding known concentrations of 2-chlorophenol. The recoveries of 92.9% to 95.3% were obtained, which indicates the applicability and reliability of the proposed method.

Table 2. Determination of 2-chlorophenol in river water samples.

River water	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Sample 1	0	Not detected	-	-
	1.5	1.43	95.3	4.5
	4.5	4.18	92.9	4.1
Sample 2	0	Not detected	-	-
	1.5	1.41	94.0	3.9
	4.5	4.26	94.7	4.3

4. CONCLUSION

In this study, multi-walled carbon nanotube-ionic liquid composite was prepared and a modified glassy carbon electrode was fabricated. The modified electrode showed highly catalytic ability towards the oxidation of 2-chlorophenol. Square wave voltammetry was used for the determination of 2-chlorophenol. The modified electrode showed high sensitivity, wide linear range and low detection limit, which makes it a good method for the detection of 2-chlorophenol. The applicability of the proposed method for the determination of 2-chlorophenol in river water samples was performed with good recoveries.

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