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Original Research article

A New Electrochemical Approach for the Determination of Phenylhydrazine in Water and Wastewater Samples using Amplified Carbon Paste Electrode



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ABSTRACT

An electroanalytical sensor amplified with NiO-SWCNTs nanocomposite and 1-hexyl-3-methylimidazolium chloride (HMC) was fabricated and used for determination of phenylhydrazine as a water contaminant. The NiO/SWCNTs nanocomposite was synthesized by a simple and one-pot method (chemical precipitation in this case) and characterized by FESEM and EDS methods. In continuous, NiO-SWCNTs/HMC/CPE was used as working electrode for investigation electrochemical behavior of phenylhydrazine. In compare to unmodified electrode, oxidation signal of phenylhydrazine was improved about 6.8 times and results confirm a linear dynamic range between $3.0 \text{ nM} - 350 \mu\text{M}$ with detection limit 0.8 nM using differential pulse votammetric method (DPV). The ability of NiO-SWCNTs/HMC/CPE as an analytical tool was check for determination of phenylhydrazine in water samples and results confirm powerful ability of suggested sensor for this goal with recovery data 97.8% - 104.35%.

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Graphical Abstract



Introduction

Measurement of pollutant compounds in aquatic environments is one of the most important issues in the study of surface and groundwater quality [1-5]. Due to the role of surface and groundwater in human health and the quality of agricultural products, various techniques have been reported for the analysis of various types of water pollutants [6-8]. Meanwhile, hydazine and its derivatives, such as phenylhydrazine, have many adverse effects on the body, especially the eyes and skin, and are introduced into the surface and groundwater by some industrial factories [9-11]. Therefore, design of new analytical approach with fast response and good limit of detection for analysis of phenylhydrazine is very necessary [11].

In between of analytical approach, electrochemical systems are very attractive for analytical researchers due to low cost, simple fabrication of sensor, easy handling and high sensitivity [12-25]. Therefore, for electroactive compounds such as phenylhydrazine, the electrochemical sensors are very attractive methods [26]. On the other hand, electrochemical methods could be modified with conductive mediators for creating highly sensitive with good selectivity in analysis procedure [27-40].

Application of nanomaterials in different science increased in recent years [41-45]. This point is relative to unique properties of nanostructure based materials [46-52]. Electrochemical sensors is one of branch of science that showed more attractive to application of nanomaterials [53-55]. Nanomaterials with good electrical conductivity such as carbon nanotubes and metal nanoparticle showed more application in this issue [56-65].

Ionic liquids with positive/negative structure showed good electrical conductivity and good choice for amplification of electroanalytical sensors in determination of biological, environmental compounds [66-70].

In this research, NiO-SWCNTs/HMC/CPE was introduced and used for electroanalytical determination of phenylhydrazine in the dynamic range 3.0 nM – 350 μ M with detection limit 0.8 nM. The proposed sensor showed good catalytic activity and reduce oxidation over potential of phenylhydrazine about 40 mV compare to CPE.

Experimental

Materials and instruments

Phenylhydrazine hydrochloride, 1-hexyl-3-methylimidazolium chloride, graphite powder, sodium hydroxide, nickel nitrate hexahydrate, SWCNTs were purchased from Sigma-Aldrich. Stock solution of phenylhydrazine hydrochloride was prepared by dissolving 0.0144 g in 100 mL distilled water solution and used for next investigation. The electrochemical signals was recorded by an Ivium-Vertex instrument connect with Ag/AgCl/KCl_{sat} as references electrode.

Synthesis of NiO-SWCNTs nanocomposite

29.08 g nickel nitrate hexahydrate and 2 g SWCNT-COOH was dispersed in 100 mL distilled water and stirred for 45 min. In next step, 100 mL sodium hydroxide 2.0 was added in solution stirring continued for 2 h. The black sample was filtered and dried for 16 h at 120 °C. In final step, the powder was calcinate at 450 °C for 3 h [35].

Preparation of NiO-SWCNTs/HMC/CPE

60 mg NiO-SWCNTs + 940 mg graphite powder was dissolved in mortar and pestle in the presence 10 mL ethanol. After evaporation of ethanol, HMC (13.3% v:v) + paraffin oil was drop wise to powder. The resulting paste was input in end of glass tube.

Water and wastewater preparation as real sample

The drinking water, tap water, well water and urban effluent was prepared from Mashhad, Iran. The samples centrifuged (3000 rpm for 30 min) and the filtered. The obtained sample was used for real sample analysis.

Result and discussion

Characterization of nanocomposite

Figure 1a. showed FESEM image of synthesized NiO-SWCNTs nanocomposite. As can be seen, the nanotubes are presence in this Figure and loaded by spherical NiO nanoparticle. The EDS analysis data is presence in Figure 1b. and confirm presence of Ni, O and C elements with good purity.



Figure 1. A) FESEM and B) EDS analysis data of NiO-SWCNTs nanocomposite

Electrochemical behavior of phenylhydrazine using NiO-SWCNTs/HMC/CPE

According to Scheme 1, electrochemical behavior of phenylhydrazine is depended to concentration of proton in the solution. Therefore, cyclic voltammograms of 1.0 mM phenylhydrazine was recorded in pH range 5.0-10.0 (Figure 2 inset).



Scheme 1. Electro-oxidation mechanism for phenylhydrazine



Figure 2. Plot of potential-pH for electro-oxidation of phenylhydrazine at surface of NiO-SWCNTs/HMC/CPE (n=4). Inset, relative cyclic voltammograms in different pH value

As can be seen, the oxidation potential of phenylhydrazine was decreased to negative value with increasing of pH solution with equation of E = -0.0669 pH + 0.7848 (R² = 0.9986). This slope confirm suggested electro-oxidation mechanism in Scheme 1. According to cyclic voltammograms signals, the pH=7.0 was selected for next investigation as an optimum condition. The cyclic voltammograms of 2.0 mM phenylhydrazine was recorded at surface of CPE (Figure 3 curve a), NiO-SWCNTs/CPE (Figure 3 curve b), HMC/CPE (Figure 3 curve c) and NiO-SWCNTs/HMC/CPE (Figure 3 curve d).



Figure 3. Cyclic voltammograms 2.0 mM phenylhydrazine at surface of CPE (a), NiO-SWCNTs/CPE (b), HMC/CPE (c) and NiO-SWCNTs/HMC/CPE (d). Condition; pH=7.0 and scan rate 100 mV/s.

As can be seen, oxidation current of phenylhydrazine was improved from 14.95 μ A at surface of CPE to 102.1 μ A at surface of NiO-SWCNTs/HMC/CPE. In addition, oxidation potential of phenylhydrazine was decreased about 40 mV at surface of NiO-SWCNTs/HMC/CPE compare to CPE. In addition, the active surface area of CPE, NiO-SWCNTs/CPE, HMC/CPE and NiO-SWCNTs/HMC/CPE were calculated about 0.2 cm², 0.26 cm², 0.28 cm² and 0.31 cm², respectively. The current density data are presence in Figure 3. inset and results confirm good electrical conductivity of mediators. This point confirm that presence of mediators could be improve conductivity of electrochemical sensors [68-77]

The cyclic voltammograms of 2.0 mM phenylhydrazine were recorded at surface of NiO-SWCNTs/HMC/CPE in different scan rates (Figure 4 inset). The plot of current vs. $v^{1/2}$ is presence in Figure 4. and results confirm diffusion process [78-83] for electro-oxidation of phenylhydrazine at surface of NiO-SWCNTs/HMC/CPE.



Figure 4. Current- $v^{1/2}$ curve for electro-oxidation of 2.0 mM phenylhydrazine (n=4). Inset) Cyclic voltammograms 2.0 mM phenylhydrazine at scan rates a) 10; b) 20; c) 40; d) 60 and e) 100 mV/s

The value of diffusion coefficient (D) was determined by recording chronoamperometric signal of 0.6, 0.7 and 0.8 mM phenylhydrazine at surface of NiO-SWCNTs/HMC/CPE (Figure 5a). According to obtained slopes recorded in Figure 5b, the mean value of D was calculated about 8.66×10^{-6} cm².



Figure 5. A) Chronoamperograms a) 0.6 mM, b) 0.7 mM and c) 0.8 mM phenylhydrazine at surface of NiO-SWCNTs/HMC/CPE. B) Cottrell plots relative to electro-oxidation of NiO-SWCNTs/HMC/CPE. Condition: applied potential 500 mV

Differential pulse voltammetric method was used for investigation dynamic range and detection limit of phenylhydrazine at surface of NiO-SWCNTs/HMC/CPE (Figure 6 inset). According to recorded data, the NiO-SWCNTs/HMC/CPE can be used for determination of phenylhydrazine in the concentration range $3.0 \text{ nM} - 350 \mu\text{M}$ with detection limit 0.8 nM (Figure 6).



Figure 6. Current-concentration curve for electrooxidation of phenylhydrazine in the range 3.0 nM – 350 μM (n=4). Inset) Relative differential pulse voltammograms of phenylhydrazine in the range 3.0 nM – 350 μM at surface of NiO-SWCNTs/HMC/CPE

Real sample analysis and selectivity investigation

The selectivity of NiO-SWCNTs/HMC/CPE as analytical sensor for determination of phenylhydrazine was check in the presence of some usual interference in water samples. Results are presence in Table 1. and confirm high selectivity of NiO-SWCNTs/HMC/CPE as analytical sensor for determination of phenylhydrazine. In addition, the ability of NiO-SWCNTs/HMC/CPE was checked for determination of phenylhydrazine in water and wastewater samples and results are presence in Table 2. Obtained results confirm ability of sensor for determination of phenylhydrazine.

Species	Tolerant limits (Winterference/Wphenylhydrazine)	
Al ³⁺ , NO ₃ ⁻ , F ⁻ , Na ⁺ , Li ⁺ , Mg ²⁺ , K ⁺	1000	
Hydroxylamine	600	
Sulfite, sulfide and hydrazine	200	

Table 1. The selectivity data relative to the determination of 25.0 µM phenylhydrazine using suggested sensor

Table 2. Real sample analysis data relative to phenylhydrazine using suggested sensor (n=4)				
Sample	phenylhydrazine added (µM)	phenylhydrazine expected (µM)	phenylhydrazine founded (µM)	Recovery %
Drink water			<lod< td=""><td></td></lod<>	
	10.00	10.00	9.78±0.61	97.8
Wastewater			<lod< td=""><td></td></lod<>	
	20.00	20.00	20.87±0.97	104.35
Well water			<lod< td=""><td></td></lod<>	
	15.00	15.00	15.64±0.74	104.26
Tap water			<lod< td=""><td></td></lod<>	
	5.00	5.00	4.93±0.22	98.6

Conclusion

A high quality and powerful phenylhydrazine analytical sensor was fabricated by modification of CPE by NiO-SWCNTs and HMC. The NiO-SWCNTs/HMC/CPE was improved electro-oxidation signal of phenylhydrazine and used as powerful tool for determination of this pollutant in dynamic range between 3.0 nM-350 μ M with detection limit 0.8 nM. In final step, the NiO-SWCNTs/HMC/CPE was successfully used for determination of phenylhydrazine in water and wastewater samples with recovery data 97.8% - 104.35%.

Conflict of Interest

We have no conflicts of interest to disclose.

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