

A new method based on headspace adsorptive accumulation using a carboxylated multi-walled carbon nanotubes modified electrode: application for trace determination of nitrobenzene and nitrotoluene in water and wastewater

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A carboxylated multi-walled carbon nanotubes modified glassy carbon (MWCNTs-GC) electrode was fabricated *via* the drop-casting of a carboxylated carbon nanotubes suspension onto a glassy carbon electrode. A headspace adsorptive accumulation on the surface of the multi-walled carbon nanotubes modified glassy carbon electrode coupled with cyclic voltammetry has been established for analyzing nitrobenzene and 4-nitrotoluene in water samples. Factors which affect the extraction efficiency (modifier amount, pH, extraction temperature, extraction time, salt addition) have been investigated. The calibration plot for the determination of nitrobenzene and 4-nitrotoluene are linear in the wide ranges of 10–4000 ng mL⁻¹ and 20–6000 ng mL⁻¹ respectively. Under optimal extraction conditions, the detection limits (at S/N = 3) for nitrobenzene and 4-nitrotoluene were 3.0 ng mL⁻¹ and 6.0 ng mL⁻¹ respectively. The proposed method has been applied successfully for the determination of nitrobenzene and nitrotoluene in water and wastewater samples within a recovery range of *ca.* 97.5–103.33%.

Introduction

Due to the complex matrixes and low concentrations expected of the analytes in environmental and biological samples, extraction and pre-treatment is a critical step for many analytical procedures. The continuous search for sample pre-treatment procedures has led to new methods, such as solid-phase microextraction,¹ single drop microextraction,² headspace microextraction,³ dispersive liquid–liquid microextraction,⁴ *etc.*

Among the sample pre-treatment techniques, headspace solid-phase microextraction has some advantages. This technique is rapid, inexpensive, solvent-free and less polluting for the sampling site, having thus been widely used in environmental, pharmaceutical and biological analyses.³

As a result of the excellent adsorption properties for a wide range of organic and inorganic species, carbon nanotubes have been widely used for sample pre-treatment in analytical methods.^{5–8} Recently, carbon nanotubes have been used in the fabrication of solid-phase microextraction fibers. These adsorbent fibers have been used in headspace⁹ or direct immersing¹⁰ modes. However, when using carbon nanotubes in the preparation of SPME fibers, there are several problems encountered such as time consumption, fiber characterization, memory effect, desorption of analytes and fiber stability.^{9–12} Moreover, carbon

nanotubes are widely used in the preparation of modified electrodes. In general, the modification of the electrodes with multi-walled carbon nanotubes (MWCNTs) has been widely documented to result in excellent electroanalytical properties, such as wide potential windows, low detection limits, high sensitivities, reduction of over potentials and good biocompatibility.^{13,14} To achieve this purpose, the electrode surface has been covered by a thin layer of MWCNTs. The modified electrode has then been exposed to the solution for several minutes and the analyte has been accumulated on the surface of the electrode directly. The accumulated analyte has been investigated with differential pulse voltammetry, square wave voltammetry, cyclic voltammetry and other electrochemical techniques.^{13,14} There are some reports in the literature about the electrochemical determination of volatile and semi-volatile compounds in the gas-phase. For example, Toniolo *et al.* fabricated an ionic liquid based probe for the electrochemical determination of phenols in water samples.¹⁵ In another work, Wang *et al.* used an explosive preconcentrator device for collection and electrochemical determination of trinitrotoluene (TNT) in the gas phase.¹⁶ Xi and coworkers have reported an electrochemical pneumatic actuator, based on a bucky paper carbon nanotube electrode for the generation and determination of chlorine gas.¹⁷ Gas-phase electrochemical detectors are also commonly utilized in the monitoring of toxic gases, including CO, SO₂, NO_x and O₃.¹⁸

Some earlier electrochemical methods have been reported for the determination of nitrobenzene (NB) derivatives in water

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solution. These works are based on the direct immersion of modified or unmodified electrodes in the sample solutions. Zhang *et al.*, have reported the use of a glassy carbon electrode for direct determination of **NB** by differential pulse voltammetry.¹⁹ In another work, Agu *et al.* developed a direct square wave voltammetric method, based on electrochemically activated carbon-fibre electrodes, for the determination of nitroaromatic compounds including **NB**.²⁰ Li *et al.* investigated the electrochemical reduction of **NB** on a carbon nanotube modified electrode. In order to achieve this, they used a complicated packed-bed flow reactor.²¹ Also Zhao *et al.* reported a method for the direct determination of **NB** in water. They used a single-wall carbon nanotube-ionic liquid gel modified glassy carbon electrode.²² Several other methods, including gas chromatography and HPLC, have also been reported for the determination of **NB** in water.^{23,24} A new and simple method for the electrochemical determination of electroactive volatile organic compounds has been represented in this work. A multi-walled carbon nanotubes modified GC electrode was used as a sensor for preconcentration and offline electrochemical determination of **NB** and 4-nitrotoluene (**NT**), as model compounds in headspace mode.

Experimental

Chemicals and materials

Multiwalled carbon nanotubes with purity 95% (10–20 nm diameter and 10 μm length) were obtained from Research Institute of Petroleum Industry (Iran). **NB** and **NT** were obtained from Fluka. Different phosphate salts were obtained from E. Merck. These chemicals were used without any further purification. All solutions were prepared with deionized water.

Instruments and analytical conditions

All electrochemical experiments were performed by using a $\mu\text{Autolab}$ potentiostat/galvanostat type III (Eco Chemie, Netherlands), equipped with GPES 4.9 software. A three-electrode cell was also used, employing a glassy carbon (GC, 1.8 mm in diameter) electrode or modified-GC electrode, acting as the working electrode (Azar Electrode, Iran), a platinum wire was applied as the counter electrode and $\text{Ag}|\text{AgCl}|\text{KCl}$ (saturated) was used as the reference electrode (Metrohm).

Preparation of the modified electrode

Multi-walled carbon nanotubes (MWCNTs) were stirred in concentrated HNO_3 for 6 h and then refluxed in a mixture of concentrated $\text{H}_2\text{SO}_4:\text{HNO}_3$ (3 : 1) for 24 h to obtain the carboxylated multi-walled carbon nanotubes.

The MWCNTs were then washed with doubly distilled water and were dried in a vacuum at 80 $^\circ\text{C}$. The MWCNTs suspension was prepared by dispersing 10 mg of MWCNTs in 5 mL N,N'-dimethylformamide (DMF) using ultrasonic agitation to obtain a relatively stable suspension. Prior to use, the glassy carbon (GC) electrode was carefully polished with 0.05 μm alumina slurry on a polishing cloth, then it was washed in an ultrasonic bath of methanol and water, respectively. The cleaned GC electrode was coated by casting 10 μL of the black suspension of MWCNTs and dried in air.

Standards and samples

Stock solutions of 100 $\mu\text{g mL}^{-1}$ of each analyte were prepared in methanol and refrigerated at 4 $^\circ\text{C}$. The working sample solutions were prepared daily at different concentrations by the dilution of the stock standard solutions with deionized water.

Tap water and wastewater samples used for the validation of the method were collected in glass bottles from Shahid Beheshti University, Tehran, Iran. After sampling, they were filtered through a 0.45 μm membrane to remove suspended particulate matters. The bottles were completely filled to avoid evaporation of volatile compounds and were stored at 4 $^\circ\text{C}$ until analysis. No **NB** or **NT** compounds were detected in tap and wastewater samples, therefore these samples were spiked with the **NB** or **NT** compounds to assess matrix effects.

Analytical procedure

The MWCNTs-GC electrode was first activated in phosphate buffer pH 9.0 (blank solution) by cyclic voltammetric sweeps between +1.0 and -1.5 V, until stable cyclic voltammograms were obtained and then the electrodes were transferred into the extraction vial (Fig. 1). After the prescribed extraction time from the headspace of the stirred solution (10 mL) at optimal conditions (500 rpm, extraction time 15 min, extraction temperature 65 $^\circ\text{C}$), the electrode was transferred into the initial buffer solution and cyclic voltammograms were recorded between +0.25 and -1.2 , with a scan rate of 50 mV s^{-1} .

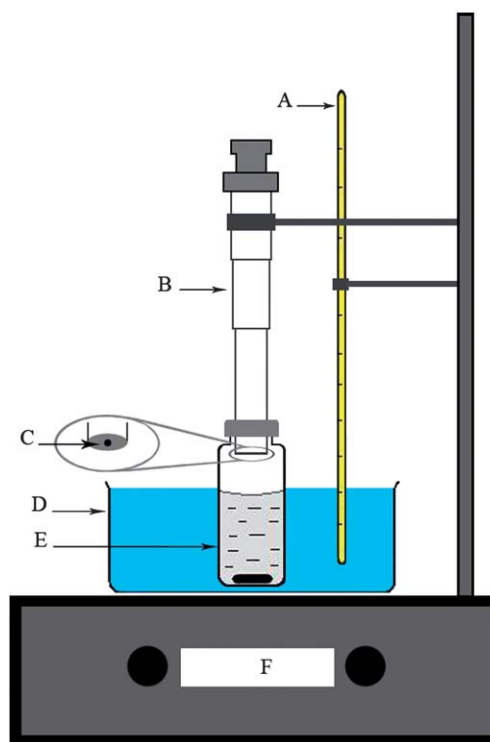


Fig. 1 Experimental setup of headspace adsorptive accumulation using MWCNTs-GC electrode as adsorbent. A: Thermometer, B: Electrode, C: Modified electrode surface (adsorbent surface), D: Water bath, E: Extraction vial, F: Magnetic stirrer.

Results and discussion

Since the electrochemical behaviors of **NB** and **NT** were the same, only the results of the studies for **NB** have been shown.

Cyclic voltammetric behavior of NB

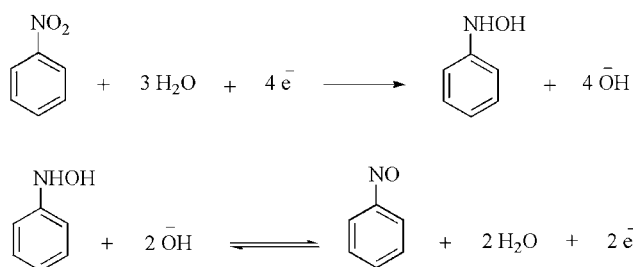
The electrochemical behavior of **NB** on the surface of different electrodes has been extensively studied.^{19–22,25} In alkaline media, **NB** is converted to phenylhydroxylamine¹⁹ and in return, phenylhydroxylamine is converted to nitrosobenzene. The overall mechanism of electrochemical behavior of **NB** in alkaline media can be shown as Scheme 1.

The cyclic voltammograms of **NB** at a bare GC electrode and at a MWCNTs-GC electrode inserted into the headspace in equilibrium with 500 ng mL⁻¹ **NB**, containing aqueous sample are shown in Fig. 2. In this figure, curve **C** is a voltammogram of **NB** at the bare GC electrode, curve **A** is a voltammogram of **NB** on the MWCNTs-GC electrode with considerable enhancement in the peak current. As shown in Fig. 2, curve **A**, at pH 9.0, **NB** has one cathodic peak at -0.80 V (**NB** to phenylhydroxylamine). It also displays an anodic peak at -0.28 V (phenylhydroxylamine to **NB**) in the return cycle. In this figure, curve **B** corresponds to the blank solution.

Optimization of headspace adsorptive accumulation

In this work, we have selected the cathodic peak current of **NB** in the cyclic voltammetry measurement as a signal and also the effect of some parameters on the height of the cathodic peak current have been investigated.

Effect of the solution pH. The effects of the pH of two mediums have been investigated on the electrochemical behavior of **NB**: electrochemical cell and extraction vial. The influence of the electrochemical cell pH on the electrochemical response of **NB** using 0.1 mol L⁻¹ phosphate buffer at pH 3.0 to 11.0 was studied (Fig. 3A). The results show that the cathodic peak current was almost constant up to pH 8.0, but when the solution pH was increased to 9.0, the current increased. A decrease in the current has been observed when the solution pH is higher than 9.0. Thus, the optimum pH for further studies was set to 9.0 (Fig. 3B). The dependence of peak potentials on the pH was also investigated. The results (Fig. 3C and 3D) show that the anodic peak (phenylhydroxylamine to nitrosobenzene) potential varies linearly with the pH. A slope of (-58 mV) per pH unit for this peak confirms the participation of equal numbers of electrons and protons in this step of the electrochemical reaction. Also the



Scheme 1 Electrochemical behavior of **NB** in alkaline media.

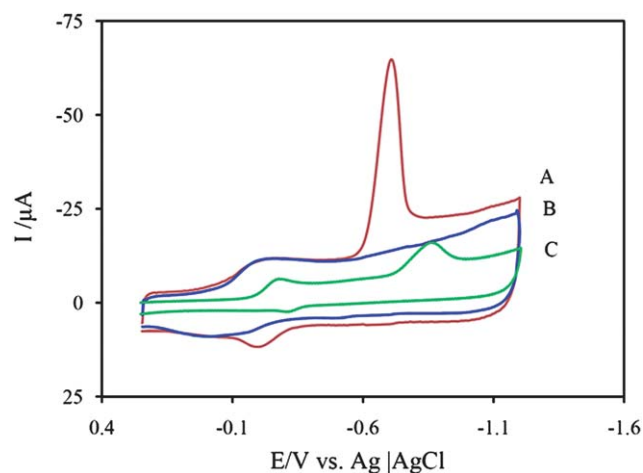


Fig. 2 Cyclic voltammograms in phosphate buffer (0.10 M, pH 9.0) at the MWCNTs-GC electrode (A, B) and the bare GC electrode (C) after HS-AA (temperature 65 °C, time 15 min, stirring rate 500 rpm) of sample solution: A and B, aqueous sample containing 500 ng mL⁻¹ **NB**; C, blank solution. Scan rate 50 mV s⁻¹.

cathodic peak potential varies with pH. In addition, the effect of the pH of the extraction vial has been investigated in the range of 3.0–11.0. In this case, the pH of the electrochemical cell was 9.0. The results show that pH of the extraction vial has no obvious effect on the HS-AA of **NB** on the surface of the MWCNTs-GC electrode. This is probably due to the chemical structure of **NB**. The nitro group can only participate in very weak hydrogen bonding and therefore the volatility of **NB** is almost pH independent.

Effect of the temperature. Extraction temperature plays a key role in the headspace microextraction technique. Higher temperatures lead to higher vapor pressure of the analyte hence its concentration in the headspace increases.²⁶ In the current

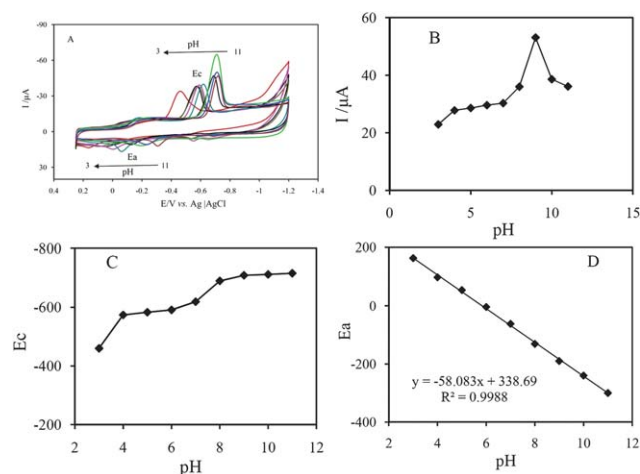


Fig. 3 (A) Cyclic voltammograms of 500 ng mL⁻¹ of **NB** on the MWCNTs-GC electrode at various pHs (3.0–11.0) of buffer solution; (B) Variation of cathodic peak current versus pH; (C) Variation of cathodic peak potential versus pH; and (D) Variation of anodic peak potential versus pH. Other conditions are as in Fig. 2.

work, the adsorption temperature varied between 45 and 75 °C. The cathodic peak height of **NB** gradually increases with the increasing of the extraction temperature, up to 65 °C, but slightly decreases at the higher temperatures. In general, higher adsorption temperatures cause a premature desorption of the analytes on the electrode surface. Thus we have selected 65 °C as the optimal temperature for headspace adsorption of **NB** on the surface of the MWCNTs-GC electrode.

Effect of the adsorption time. The adsorption time severely influences the cathodic peak current of extracted **NB**. The cathodic peak current increases significantly in the first 15 min and after that time, levels off. This may be caused by the fact that the adsorption of **NB** on the MWCNTs-modified GC electrode surface has become saturated. Thus, the headspace adsorption step in this study has been performed in 15 min.

Effect of the modifier amount. The amount of MWCNTs has effects on the electrochemical responses of the modified electrode. In this work we have investigated the effect of the modifier amount by selecting three volumes (5, 10 and 20 μL) of the modifier (2 mg mL^{-1}). In the case of 5 μL , the surface of the electrode was not covered completely and the adsorbed amount of **NB** by the modifier film was small, resulting in a small peak current (Fig. 4, curve a). In the case of 20 μL , the film of the modifier is too thick. In this case, the peak current increases slowly because of the increase in adsorbed amounts of **NB**, but the background current increases significantly. The increase in background current is related to the film conductivity. When the film is too thick, the conductivity will be reduced (Fig. 4, curve c), thus it blocks the electrode surface which leads to a small increase of the peak current.^{27,28} With higher amounts of modifier, the film became unstable and MWCNTs would leave the electrode surface. Therefore, 10 μL of MWCNTs suspension solution has been used in the remaining studies.

Effect of salt addition. The addition of salt can often improve the extraction recovery when conventional extraction methods are used. In this work, the effect of salt addition on the extraction efficiency has been studied by addition of NaCl, KCl and

Na_2SO_4 . The results showed that the addition of the salt didn't affect the efficiency of the headspace adsorption of **NB** on the surface of the MWCNTs-GC electrode. Thus, the sample solutions have been prepared without any salt.

Analytical applications

Repeatability. To ascertain the repeatability of the analysis, 5 measurements of 500 ng mL^{-1} **NB** were carried out using the MWCNTs-GC electrode at intervals of 30 min. The R.S.D. value was found to be 5.2%, which indicated that the MWCNTs-GC electrode has good repeatability.

Stability. The stability of the MWCNTs-GC electrode was tested by keeping the electrode in a phosphate buffer solution at pH 9.0 for 30 days, after this time period the CVs were recorded and compared with CVs obtained before immersion. The results indicated that peak current decreased only slightly (2–3%) for the MWCNTs-GC electrode, which indicated that MWCNTs-GC electrode has good stability. Fouling of electrochemical products on the surface of the electrode does not occur (after each analysis the electrode surface was refreshed by cleaning with acetone) and we can use each electrode for more than 30 analyses in various time periods.

Accuracy. The accuracy was calculated on the recovery of known amounts of the standard **NB** or **NT** solution spiked in various real solutions. Spiked samples were prepared at different levels. The results show that the recoveries were in the range of 97.5% to 103.33% which suggests good reproducibility and accuracy of the MWCNTs-GC electrode.

Selectivity. The interference of organic compounds, namely benzene, toluene, ethyl-benzene, aniline, 4-nitrophenol, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene were tested under the optimized experimental conditions. The results showed that these compounds did not interfere when their concentrations were 50-fold higher than the analytes (**NB** or **NT**). Benzene, toluene and ethyl-benzene did not have any oxidation or reduction peak in this potential range. Aniline and 4-nitrophenol did not extract to the headspace according to the formation of hydrogen bonding with solvent molecules. 2,4-Dinitrotoluene and

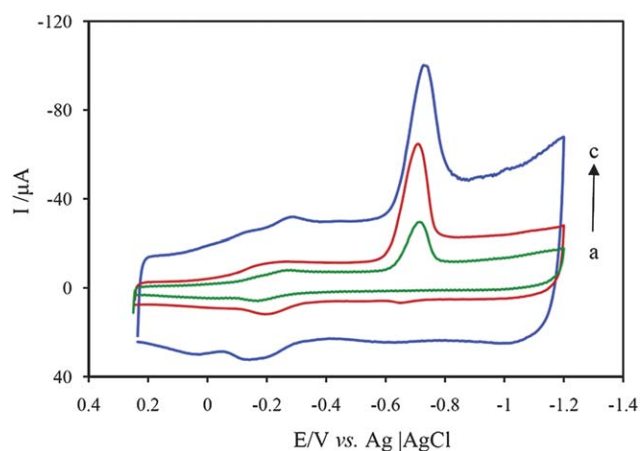


Fig. 4 Voltammograms of 500 ng mL^{-1} of **NB** at various amounts of modifier (a to c: 5, 10, 20 μL); Other conditions as in Fig. 2.

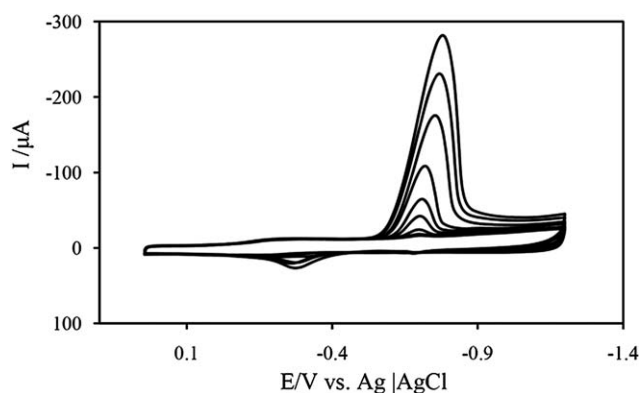


Fig. 5 Cyclic voltammograms of **NB** at various concentrations (10–4000 ng mL^{-1}); Other conditions as in Fig. 2.

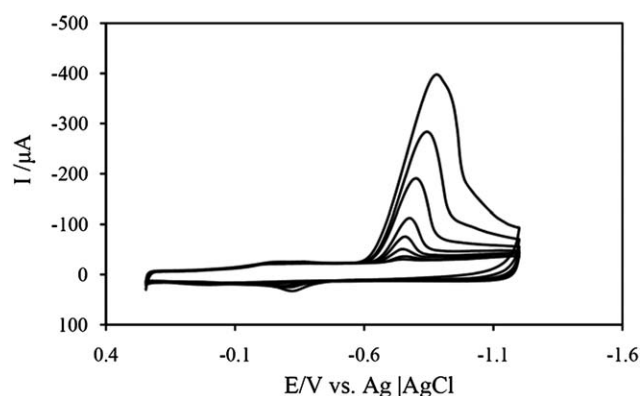


Fig. 6 Cyclic voltammograms of NT at various concentrations (20–6000 ng mL⁻¹). Other conditions as in Fig. 2.

Table 1 Determination of NB or NT in water and wastewater samples

Sample	Analyte	Added (ppb)	Found (ppb)	Recovery (%)
Tap water	NB	20	19.5	97.50
Tap water	NB	175	171.3	97.88
Wastewater	NB	1200	1187	98.92
Wastewater	NB	3000	3100	103.33
Tap water	NT	40	39.2	98.00
Tap water	NT	2500	2580	103.20
Wastewater	NB	700	692	98.86
Wastewater	NT	3400	3480	102.35

2,4,6-trinitrotoluene show negligible extraction to the headspace and it's possible that their optimization conditions are different from NB or NT according to the different boiling points for these compounds. Anions and cations did not interfere with NB determination in water samples either.

Determination of NB and NT in water and wastewater samples.

The calibration curves for NB and NT were obtained by cyclic voltammetric measurements under the optimum experimental conditions. The results (Fig. 5) show that the reduction peak currents showed a linear relationship with NB concentrations in two linear ranges of 10–500 ng mL⁻¹ ($I_p/\mu\text{A} = 0.1059C/\text{ng mL}^{-1} + 0.8374$, $R^2 = 0.9991$) and 500–4000 ng mL⁻¹ ($I_p/\mu\text{A} = 0.0648C/\text{ng mL}^{-1} + 26.323$, $R^2 = 0.9976$).

Two linear ranges of 20–1000 ng mL⁻¹ ($I_p/\mu\text{A} = 0.1651C/\text{ng mL}^{-1} + 8.4861$, $R^2 = 0.9991$) and 1000–6000 ng mL⁻¹ ($I_p/\mu\text{A} = 0.0421C/\text{ng mL}^{-1} + 129.89$, $R^2 = 0.9998$) were obtained for NT (Fig. 6).

In this section, the LOQ (low level of dynamic range) and LOD were considered as 10 S/N and 3 S/N, respectively. Therefore, LODs for NB and NT were obtained (based on LOQ) of 3.0 ng mL⁻¹ and 6.0 ng mL⁻¹ respectively.

Finally, the proposed method has been used for the determination of NB and NT in water and wastewater samples. As can be seen in Table 1, the recoveries for NB and NT are in the range of 97.50–103.33%, which confirms that the proposed method is applicable for analyzing NB and NT in water and wastewater samples.

A comparison between the analytical performance of this method and some previous electrochemical methods for the determination of NB derivatives are given in Table 2. The limits of quantifications obtained for NB and NT were the lowest by the proposed method, as shown in Table 2. In reported works in the literatures, the effect of the major interfering components such as 4-nitrophenol, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene have not been investigated on the determination of NB or NT. On the other hand, because of the headspace sampling, the proposed method has better selectivity than other reported methods. Headspace sampling also leads to increased lifetime of the electrode, applicability of the method for determination of analytes in complex matrixes and is less polluting to the sampling site and the electrode surface. Application of the proposed method for only volatile and semi-volatile compounds could be seen as a limitation for the proposed method in comparison with the aforementioned methods.

Conclusions

The proposed headspace adsorptive accumulation method coupled with cyclic voltammetry determination was shown to be useful for the analysis of NB and NT in water or wastewater samples. The optimum conditions for adsorption have been obtained by heating for 15 min at 65 °C for 10 mL of water spiked with NB or NT. Under the optimum extraction conditions for NB or NT, relatively low detection limits with good recoveries were obtained in the analysis of real water and wastewater samples.

Table 2 Comparison of the performance of the proposed method in this work with other modified electrodes reported in the literature for the detection of NB or NT

Electrode	Technique	Analyte	Calibration data (mol L ⁻¹)	LOD (mol L ⁻¹)	Ref.
OMC/DDAB CME ^a	Linear sweep voltammetry	NB	2.0×10^{-5} – 2.9×10^{-3}	1.0×10^{-5}	29
HMDE ^b	Linear sweep voltammetry	NB	1.47×10^{-5} – 1.0×10^{-3}	5.0×10^{-6}	30
C60 MCPE ^c	Semi-differential cyclic voltammetry	NB	5.0×10^{-5} – 6.0×10^{-3}	3.0×10^{-5}	31
BiF/CPE ^d	Square wave voltammetry	NB	1.0×10^{-6} – 1.0×10^{-4}	8.3×10^{-7}	32
HMDE	Differential pulse voltammetry	NB	4.06×10^{-7} – 2.44×10^{-5}	2.1×10^{-8}	33
MWCNTs-GCE ^e	Cyclic voltammetry	NB	8.1×10^{-8} – 3.25×10^{-5}	2.4×10^{-8}	This work
MWCNTs-GCE	Cyclic voltammetry	NT	1.62×10^{-7} – 4.88×10^{-5}	4.3×10^{-8}	This work

^a An ordered mesoporous carbon/didodecyldimethylammonium bromide composite modified electrode. ^b Hanging mercury drop electrode. ^c C60 modified carbon paste electrode. ^d Bismuth-film modified carbon paste electrode. ^e Multi-walled carbon nanotubes modified glassy carbon electrode.

Acknowledgements

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