



Cu decorated multiwalled carbon nanotubes: Application to electrocatalytic oxidation and determination of 4-nitrophenol in river water samples by square-wave voltammetry

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ABSTRACT

A simple and fast electrochemical method was described and evaluated for the determination of hazardous compound, 4-nitrophenol. In this work, trace amounts of 4-nitrophenol were determined by square – wave voltammetry. A glassy carbon electrode was modified with multi-walled carbon nanotubes and copper nanoparticles. A synergistic effect was observed between Cu nanoparticles and carbon nanotubes which resulted in enhanced oxidation peak current of 4-nitrophenol. The modified electrode showed more sensitivity towards 4-nitrophenol compared to unmodified one. A wide linear concentration range from 0.2 to 298.0 μM was obtained for 4-nitrophenol with a detection limit of 0.06 μM . Reproducibility and repeatability of the method were evaluated for determination of 4-nitrophenol (0.1 mM) as 3.47% and 2.30%, respectively (relative standard deviation, RSD %), which are acceptable. The method was applied to the analysis of 4-nitrophenol (22.2 μM) in spiked river water samples, successfully. Simplicity, sensitivity, selectivity and high efficiency of the proposed method can be used in routine analysis of trace amounts of 4-nitrophenol in polluted waters.

1. Introduction

Nitrophenols are required in manufacturing of pesticides, colors, and pharmaceuticals. They are classified as environmental pollutants due to their biorefractory nature [1-3]. 4-Nitrophenol (4-NP, *p*-nitrophenol) is one of the most abundant nitrophenols, and is a dangerous substance that causes considerable harm to the environment as well as living systems. Severe ingestion or inhalation of 4-NP can cause headaches, sleepiness, vomiting, and cyanosis. It can be found in wastewater and agricultural run-off due to biodegradation of parathion and methyl parathion [4]. Detoxification of 4-NP polluted water is a hard process due to chemical stability and resistance to microbial disintegration [5]. 4-NP was entered in the list of pollutants of US Environmental Protection Agency (EPA), which fixed the allowed limit of 4-NP in drinking water at 0.43 μM [6]. So, the determination of small amounts of 4-NP has become necessary for environment and human safe guard.

Various analytical methods have been developed for detection of 4-NP, such as spectrophotometry [7] spectrofluorometry [8], high-performance liquid chromatography [9,10], and capillary electrophoresis [10]. However, some of these techniques are time consuming and require expensive instrumentation and pretreatment of the sample. On the other hand, electrochemical methods are excellent alternatives because they offer advantages such as easy use of techniques and equipment, inexpensive instrumentation, easy preparation of samples, and rapid response. In addition, they allow the possibility for *on-site* analysis due to the portability of new potentiostats and accessories. Therefore, several electrochemical methods have been developed for nitrophenols' analysis [11-16] It is well-known that the electrode material play critical role in the construction of electrochemical sensors. So, a variety of active materials have been utilized to the modification of electrodes for 4-NP analysis, e.g., carbon nanotubes [17] graphene oxide [18], copper oxide nanoparticles [14], poly

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(methyl orange) [12], chitosan-crafted ZnO nanoneedles [13], reduced graphene oxide [19], macroporous imprinted polymer containing Au nanoparticles [20], reduced graphene oxide/Au nanoparticle composite [21], and ordered mesoporous carbon [22]. Among them, carbon nanomaterials always are of considerable interest due to their electrical conductivity and very good detection performance for 4-NP. Carbon nanotubes, due to their interesting mechanical and electrical properties, are frequently used in design and development of electrochemical sensors [23]. Metallic nanoparticles can exhibit excellent catalytic activity, due to their high surface area-to-volume ratio and good mass transport and facility of electron transfer [24-26]. Copper nanoparticles (CuNPs), in addition to the foregoing advantages, due to availability and low price, are frequently used in different chemical forms for electrode modification [27-31]. In this work, 4-NP was determined voltammetrically by using a glassy carbon electrode modified with CuNPs and multiwalled carbon nanotubes (MWCNTs) composite. It was found that CuNPs clearly enhanced electrochemical properties of the modified electrode. Very small amounts of 4-NP were determined in river water by the proposed method, successfully.

2. Materials and methods

2.1 Reagents and materials

Copper (II) sulfate (CuSO_4), 4-nitrophenol (4-NP), disodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), monosodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), H_2SO_4 , NaOH and ethanol were of analytical reagent grade and were obtained from Merck (Darmstadt, Germany). Double distilled water was used in all experiments for preparing sample solutions. Phosphate buffer solution (PBS, 0.1 M, pH 7) was prepared and used as the supporting electrolyte.

2.2 Apparatus

Electrochemical measurements were carried out with μ -Autolab type III potentiostat/galvanostat instrument. Data acquisition was carried out using software NOVA 1.8. The system consisted of a platinum wire as counter electrode, a silver/silver chloride (Ag/AgCl , KCl 3M) as reference electrode, and copper nanoparticles/multiwalled carbon nanotubes-modified glassy carbon electrode (CuNPs/MWCNTs/GCE) as working electrode. A pH meter (Jenway, Model 140) was used with a combined glass electrode to check the pH levels of the solutions. Field emission scanning electron microscope (FE-SEM) images were obtained on an S-4800 field emission scanning electron microanalyser (Hitachi, Japan). Energy dispersive X-ray spectroscopy (EDXS) was used for elemental analysis with an electron microscope (VEGA\\TESCAN-XMU, USA).

2.3. Preparation of CuNPs/MWCNTs/GCE

CuNPs/MWCNTs/GCE was prepared according to a previously reported method [32]. Briefly, GCE was polished mechanically on Al_2O_3 slurry (mesh size: 0.05 μm) on the polishing cloth and then rinsed with double distilled water until a mirror-like surface was obtained. MWCNTs (1.0 mg) were dispersed in dimethylformamide (1 mL) and homogenized in an ultrasonic bath for 30 min., then MWCNT suspension (2.0 μL) was dropped on GCE and dried at room temperature, to obtain MWCNT-modified GCE. To prepare CuNPs/MWCNT/GCE by electrochemical deposition method, MWCNTs/GCE was treated by cyclic voltammetry in the potential range of -0.6 - 0.8 V in a solution containing CuSO_4 (10.7 μM) and H_2SO_4 (0.06 M) using a scan rate of 100 mV/s and 50 potential cycles. For comparison experiments, CuNPs was deposited on GCE (CuNPs/GCE) by placing a polished GCE in CuSO_4 (10.7 μM) and H_2SO_4 (0.06 M) solution and applying the same procedure that was described for CuNPs/MWCNTs/GCE.

2.4. Analytical procedure

A certain volume of 4-NP solution (0.01 M) and PBS (10 mL, 0.1 M, pH 7) was transferred into an electrochemical cell, while the three electrode system was immersed in it. Cyclic voltammograms were recorded from 0 V to 1.2 V at scan rate of 100 mV/s. Square wave voltammograms were recorded from 0.7 V to 1.2 V. The same procedure was carried out for the river sample analysis.

3. Results and discussion

3.1. Characterization of CuNPs/MWCNTs/GCE

CuNPs/MWCNTs/GCE was characterized by cyclic voltammetry in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution (Figure 1). For comparison, the voltammograms also were recorded on bare GCE (curve a) and MWCNTs/GCE (curve b). Higher redox peak currents can be obtained at CuNPs/MWCNTs/GCE, without shift in peak potential (curve c), suggesting that the electrochemical active sites of GCE increased by both CuNPs and MWCNTs. This can be attributed to the highly conducting CuNPs acting as electron-transfer channels, which further improved the conductivity of MWCNTs. The behavior for CuNPs/MWCNTs composition was observed in earlier reports [33,34]. SEM images in Figure.2 show the string lattice structure of MWCNTs and uniform distribution of CuNPs on MWCNTs with different magnifications. The presence of Cu atoms electrodeposited on the electrode surface was confirmed by EDXS analysis (Figure. 3).

3.2. Electrocatalytic oxidation of 4-NP

4-NP contains two redox active groups, nitro and hydroxyl functional groups. Nitro group is reducible, while OH group is oxidizable. Both functional groups have been used in electrochemical determination of NPs, but in the case of -

NO_2 reduction, dissolved oxygen should be removed from the experimental solution. In this work, irreversible oxidation of OH group (Eq. 1) was followed for determination of 4-NP at different electrodes. In the absence of 4-NP, no oxidation peak appeared in cyclic voltammograms (CVs) in the applied potential range (Figure 3A). In the presence of 4-NP, an oxidation peak was observed at the surface of different electrodes (Figure 3B). But the bare GCE showed a weak response to 4-NP (curve a). The peak current increased at CuNPs/GCE, MWCNTs/GCE, and CuNPs/MWCNTs/GCE (curves b, c, and d). The response at CuNPs/MWCNTs/GCE was characterized by the highest peak current of 4-NP and negative potential shift, showed its effective catalytic ability for 4-NP oxidation. The reason may be the π - π interaction between MWCNTs and aromatic ring of 4-NP [35] which accumulates more target compound to the electrode surface. Excellent conductivity and electrocatalysis of CuNPs were also involved in current enhancement of 4-NP at the surface of CuNPs/MWCNTs/GCE. Enhanced peak current may be partially due to complex formation between phenolic group of 4-NP and CuNPs at the interphase [36].

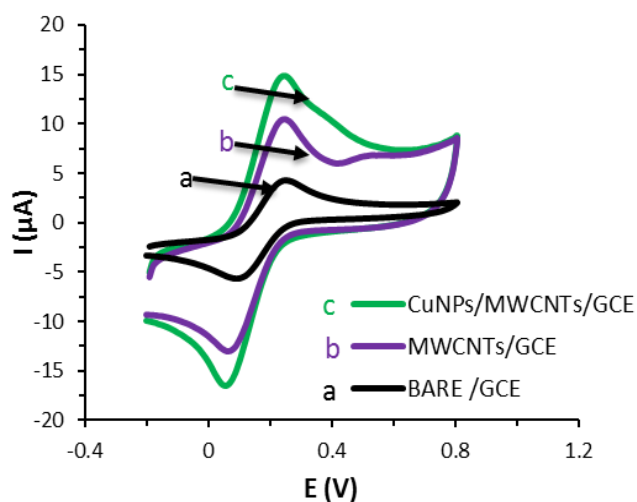
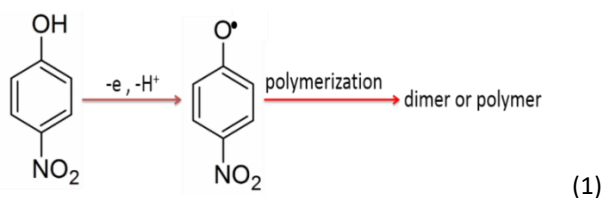


Fig. 1. Cyclic voltammograms of bare GCE (a) MWCNTs/GCE (b) and CuNPs/MWCNTs/GCE (c) in 1 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution. The scan rate was 100 mV/S

3.3. Effect of scan rate on electrochemical response of 4-NP

As the kinetic and thermodynamics of electron transfer depends of potential scan rate (ν) [37], its influence on the oxidation of 4-NP on CuNPs/MWCNTs/GCE was investigated by using cyclic voltammetry (Figure 4). It was found that the increase in ν lead to small shift of oxidation peak potential towards negative values and the increase of peak current. A linear dependence between peaks current and $\nu^{1/2}$ was obtained in the range of 20–400 mV/s, which refers to a diffusion-controlled process. The obviously nonlinear plot of peak current against ν also confirms the non-adsorptive current flow [37] at CuNPs/MWCNTs/GCE.

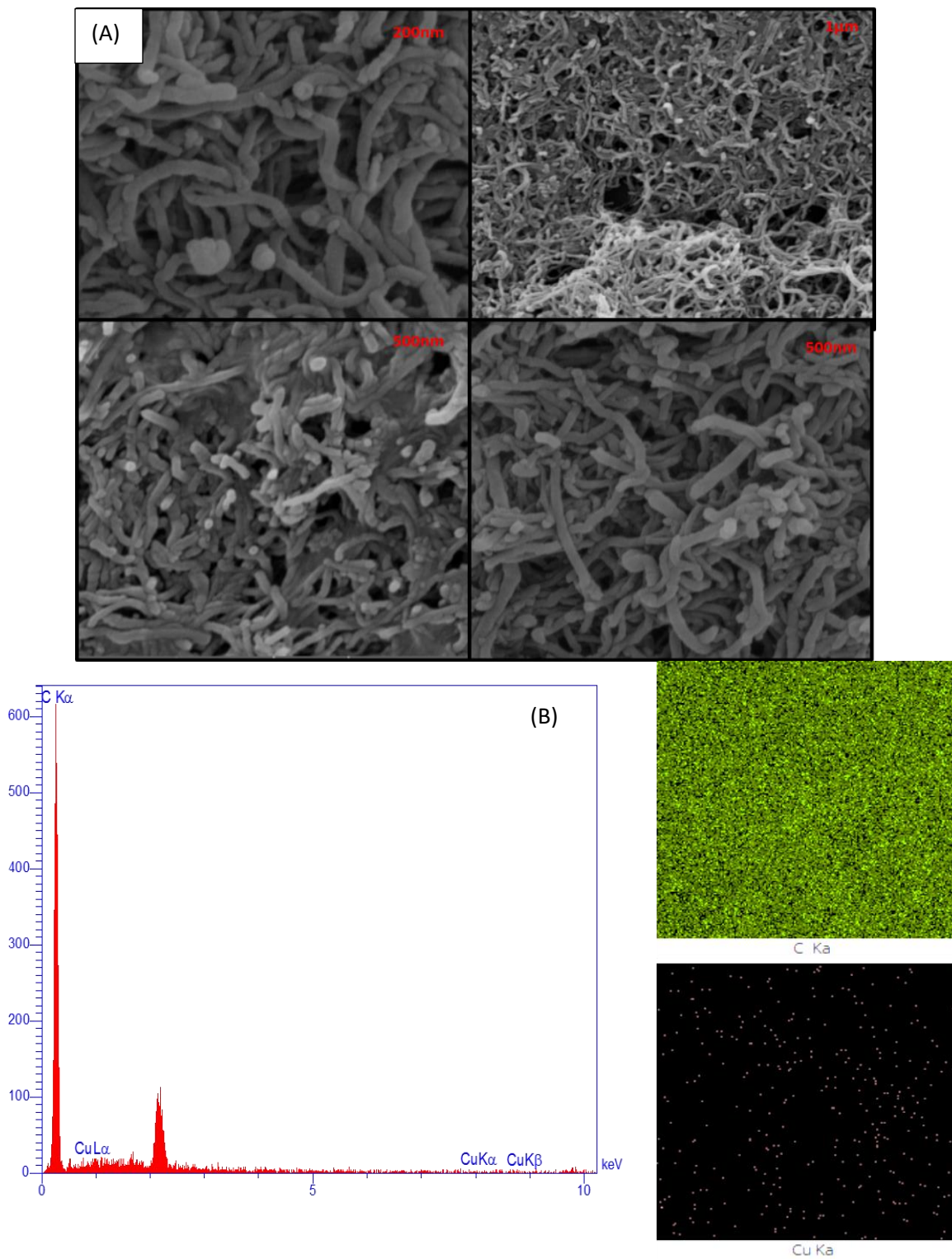


Fig. 2. (A) SEM images with different magnifications of CuNPs/MWCNTs/GCE. (B) EDXS analysis of CuNPs/MWCNTs/GCE.

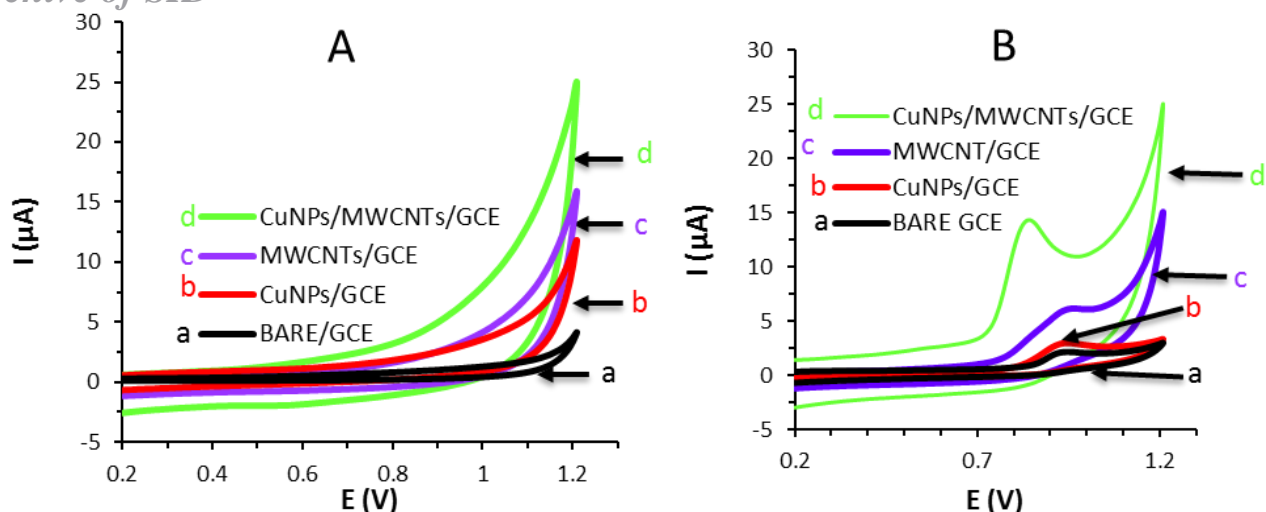


Fig. 3. CVs obtained at bare (a), CuNPs /GCE (b), MWCNTs/GCE (c) and CuNPs/MWCNTs/GCE (d) in the absence (A) and presence (B) of 0.1 mM 4-NP. Scan rate=100 mV/S

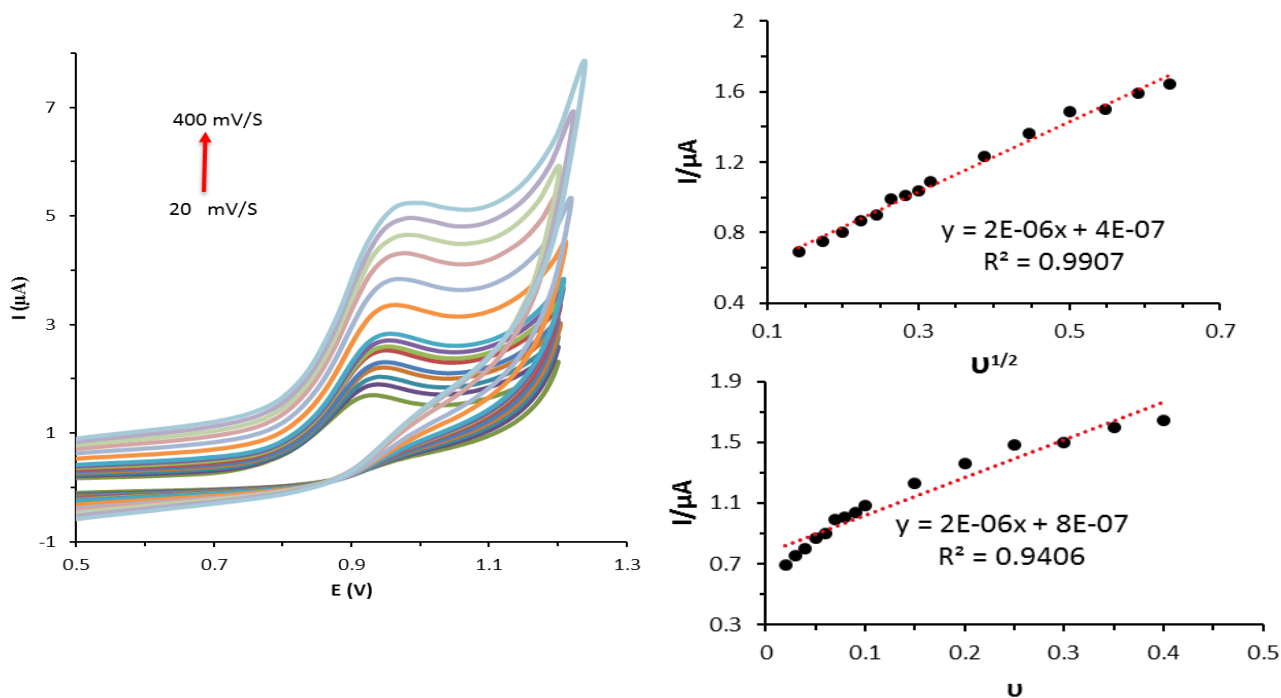


Fig. 4. Cyclic voltammograms of 4-NP (0.1 mM) on CuNPs/MWCNTs/GCE at various scan rates (20–400 mV/s)

3.4. Effect of pH

Effect of pH on the oxidation peak current of 4-NP (0.1 mM) was studied by cyclic voltammetry (Figure 5A) in the pH range of 2 –8 by using PBS (0.1 M). The oxidation peak current of 4-NP increased gradually with increasing pH up to 7.0 (Figure 5B). The peak potential was decreased at increasing pH values; a linear dependence was observed

with a slope of -0.0608 mV (Figure 5B). From the slope (very close to Nernstian slope, 0.059 V), it could be concluded that an equal number of electrons and protons are involved in the electrooxidation of 4-NP, as was reported previously (Eq. 1) [38].

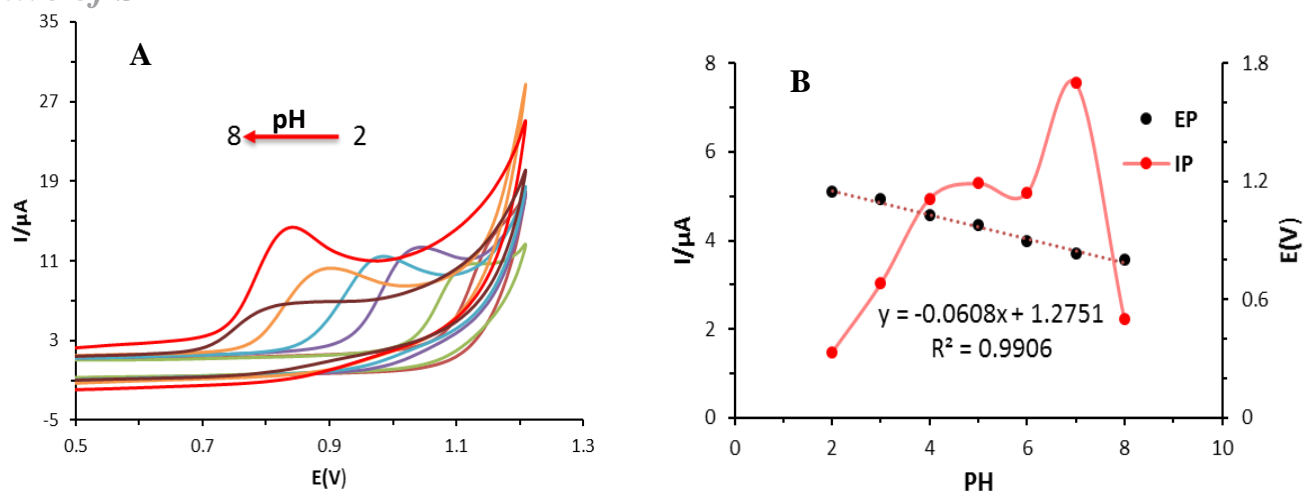


Fig. 5. (A) Effect of pH on cyclic voltammograms of 4-NP (0.1 mM) at CuNPs/MWCNTs/GCE. (B) Variation of peak current (IP) and peak potential (EP) against pH.

3.5. Calibration curve and detection limit

In order to increase the sensitivity of determination, square wave voltammetry (SWV) was used to obtain the calibration curve of 4-NP on CuNPs/MWCNTs/GCE (Figure 6). A linear

calibration curve was obtained in the concentration range of 0.2 to 298 μM of 4-NP. The calibration curve contained two linear segments: from 0.2 to 12.3 μM , and from 12.3 up to 298 μM (inset). The detection limit (LOD) was estimated to be 0.06 μM based on $S/N = 3$.

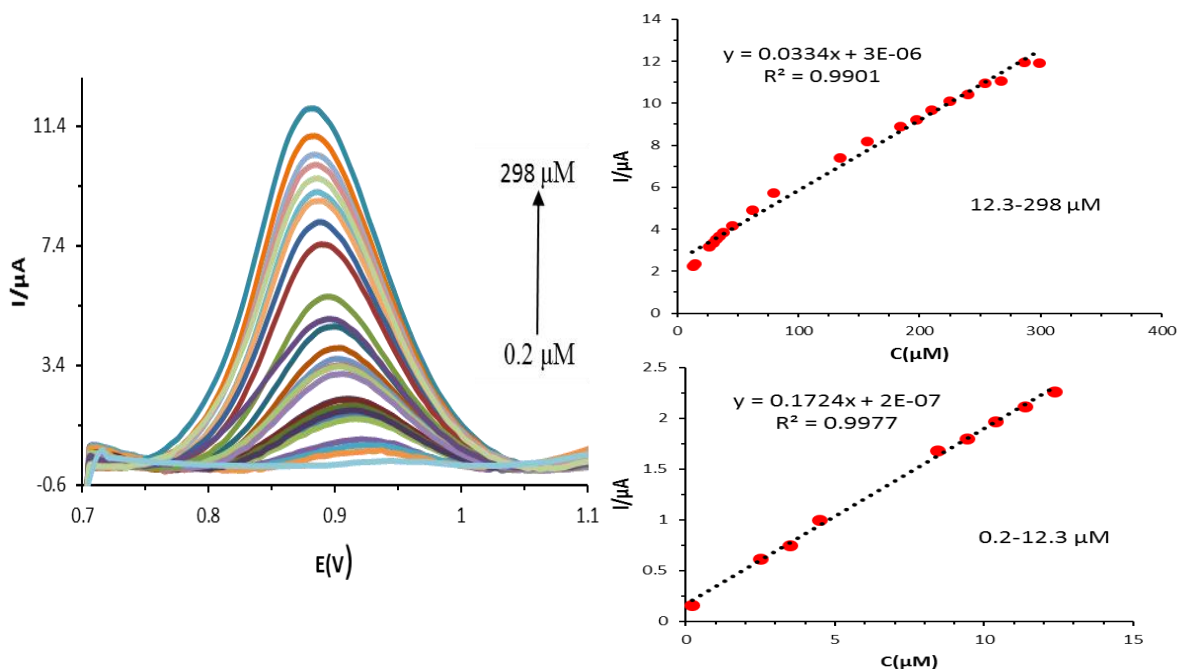


Fig. 6. Square wave voltammograms recorded at CuNPs/MWCNTs/GCE in PBS (0.1 M, pH 7). Inset: calibration curves

3.6. Reproducibility and stability

The reproducibility and repeatability of the method was studied on CuNPs/MWCNTs/GCE. In a group of 3 modified electrodes, all prepared with the same procedure, the oxidation current of 4-NP (0.1 mM) resulted in RSD% value of 3.47% as reproducibility. Furthermore, repeatability of the method was evaluated by 5 determinations of 4-NP (0.1

mM) on the same electrode which resulted in RSD% of 2.30%. It was concluded that the procedure has acceptable accuracy and precision to be used in 4-NP analysis. The analytical performance of the suggested method was compared with some previously reported electrochemical methods (Table 1). The results exhibited superior, in some cases, or comparable analytical performance of

CuNPs/MWCNTs/GCE against other methods reported in literature.

3.7. Effect of interfering compounds

In order to evaluate the selectivity of the prepared sensor, the effect of various possible interfering species in real samples was investigated on the determination of 4-NP (Table 2). It was observed that inorganic cations and anions usually present in aqueous solutions showed negligible interference even when present 100 times in excess. Furthermore 4-amino benzoic acid (1 mM) also showed no significant interference in the presence of 4-NP (0.01 mM). The influence of several phenol derivatives was also examined. The experimental results showed that 2-nitrophenol, 3-nitrophenol, 2, 4- dinitrophenol and catachol had no significant effect when present in 10 times excess. These results confirmed the acceptable selectivity of the method for the analysis of 4-NP in the presence of other isomers and structurally similar compounds.

3.8. Application of the proposed method to real samples

To evaluate the suitability of the developed sensor for environmental applications, CuNPs/MWCNTs/GCE was used to detect 4-NP in river water samples which were collected from Qarasu River (Kermanshah, Iran) without any pretreatment prior to determination, unless filtration of the initial sample to separate the solid content. The sample (1.0 mL) was pipetted into PBS (10 mL, 0.1 M, pH 7) and 4-NP was determined by SWV on the modified electrode. No peak current for 4-NP was observed, which may be attributed to the absence of the analyte or the presence of 4-NP in concentrations lower than LOD of the proposed method. Thus, the standard addition method was applied to samples spiked with 4-NP at a certain concentration (22.2 μ M), the recovery was obtained by using the proposed method (99.29 \pm 2.08% for 3 replications), which was quite satisfactory.

Table 1. Comparison of proposed sensor with other previously reported sensors

Modifier	Method	Linear range (μ M)	LOD (μ M)	References
rGOa /GCE	DPV	50 - 800	42	[39]
NMP/GS ^b	DPV	0.2–20	0.04	[40]
Mg(Ni)FeO	DPVs	2.0~200	0.2	[41]
Graphite Nanoflake	CV	1–10,10–300,300–6000	0.7	[42]
Poly(p-ABSA) ^c	SDeV	3–700	0.3	[43]
PFFF ^d	DPV	0.75–100	0.04	[44]
PDDA-Gr ^e	LSV	0.06–2, 10–110	0.02	[45]
Electrochemical reduced graphene oxide	DPV	8.3-79.8	2.13	[46]
PMB ^f	DPV	0.015–0.25	0.09	[47]
CuNPs/MWCNTs/GCE	swv	0.2 - 12.3, 12.3-298	0.06	in this work

^a reduced graphene oxide; ^b (N-methyl-2-pyrrolidone-exfoliated graphene nanosheets); ^c p-aminobenzene sulfonic acid; ^d polyfurfural film; ^e polyelectrolyte-functionalized graphene; ^f poly(methylene blue)

Table 2. Influence of interfering species on the determination of 4-NP (0.01 mM) by the proposed method

Interferent	Concentration (mM)	Deviation (%)
Mg ²⁺	1	-3.11
Ca ²⁺	1	-2.1
Al ³⁺	1	-3.33
Zn ²⁺	1	-1.7
Fe ³⁺	1	-3.6
Pb ²⁺	1	-4.45
NO ₃ ⁻	1	-4.83
SO ₄ ²⁻	1	-0.17
Br ⁻	1	-1.89
4- Amino benzoic acid	1	-2.19
Catechol	0.01	1.56
	0.1	-4.76
2-Nitrophenol	0.01	0.32
	0.1	4.52
3-Nitrophenol	0.01	-1.22
	0.1	5.5
2,4- Dinitrophenol	0.01	0.75
	0.1	6.53

4. Conclusions

A simple and fast electrochemical method was described and evaluated for the determination of hazardous compound, 4-nitrophenol. Cu nanoparticles were deposited on multiwalled carbon nanotube – modified electrode and used as a sensitive electrochemical sensor in 4- nitrophenol analysis. In studying the electrode material, the presence of both ingredients was necessary for enhancing the current response of the sensor. Several experiments were designed to study the stability, precision and accuracy of the proposed method. The electrode was quite stable for more than 3 months, along with acceptable repeatability (RDS=2.30%) and reproducibility (RSD% = 3.47%). Square wave voltammetry was selected as a sensitive voltammetric technique, which resulted in a linear dependence between oxidation peak current of 4-NP and its concentration in a range of 0.2 to 298.0 μM with a detection limit of 0.06 μM . After studying the potential interference of structurally-similar compounds, river water was selected as the real sample. Application of the proposed method resulted in satisfactory results for recovery calculations of 4-NP spiked to the river samples ($99.29 \pm 2.08\%$ for 3 replications).

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