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Original scientific paper

Surfactant modified carbon nanotube paste electrode for the sensitive determination of mitoxantrone anticancer drug

Jamballi G. Manjunatha

Department of Chemistry, FMKMC College, Madikeri, Mangalore University Constituent College, Karnataka, India; E-mail: manju1853@gmail.com; Tel.: +91-08272228334

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Abstract

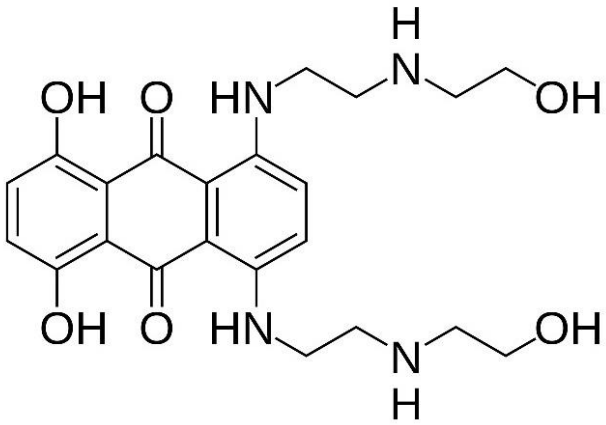
Surfactant modified carbon nanotube paste electrode is prepared as electrochemical sensor with high sensitivity responding to mitoxantrone (MTX). Electrochemical oxidation of MTX is investigated in buffered solution by cyclic voltammetry that is found very sensitive method for detection of MTX. It is shown that the sodium dodecyl sulfate modified carbon nanotube paste electrode (SDSMCNTPE) gives enhanced current response for MTX compared to the bare carbon nanotube paste electrode (BCNTPE). Different parameters were tested to optimize the conditions for MTX determination. The effects of different surfactant and surfactant concentration, pH, scan rate, and concentration of MTX on the oxidation peak current values were determined. Excellent results were obtained by cyclic voltammetry using SDSMCNTPE, where two MTX oxidation peaks appeared around 370 and 600 mV vs. *SCE. Detailed analysis of the second voltammetric peak showed the linear dependence on concentration between* 2×10^{-7} *and* 7×10^{-6} *M MTX with the slope of the corelation coefficient of 0.99271. LOD and LOQ were determined as* 3.5×10^{-8} *M and* 11×10^{-8} *M, respectively. The SDSMCNTPE showed very good reproducibility, high stability in its voltammetric response, high electrochemical sensitivity and low detection limit for MTX.*

Keywords

Electrochemical sensors; MTX determination; carbon nanotubes; surfactant modified electrodes

Introduction

Mitoxantrone (MTX) is one of the important drugs that has extensively been used for the treatment of leukemia, breast cancer, non-small cell lung cancer and lymphoma and thereby its analytical determination is considered very valuable [1]. MTX is the anthraquinone derivative (Scheme 1) and has usually been determined by means of spectrophotometry [2], chromategraphic methods [3,4], electrochemical assays [5,6], flow injection analysis [7,8] and radioimmunoassay [9,10].



Scheme 1. *Structure of mitoxantrone*

Electrochemical determination of MTX is very rare [11] mainly due to the low sensitivity and relatively expensive equipment. After inventions of many new materials, a need has been expressed for developing of stable, simple and efficient materials as sensors for highly sensitive MTX determination by electrochemical methods. At present, there is the whole area of research occupied with developing of new materials and fabrication of new biosensors with controlled features on a nanometer scale. Carbon nanotubes (CNTs) with their very good electronic properties, great chemical resistivity and mechanical stability, have frequently been used for preparation of biosensors [12–14]. CNTs behave electrically as a metal or semiconductor. The electronic properties suggest that CNTs have the capability to promote charge-transfer reactions when used as an electrode [15]. The modification of traditional electrode materials with carbon nanotubes for use in analytical sensing is well evidenced and characterized by lower detection limits, increased sensitivities, reduced overpotentials and increased resistance to surface fouling. Therefore, CNTs have usually been applied as electrochemical sensors [16].

Surfactants are amphiphilic molecules with hydrophilic and lipophilic properties, which through adsorption at the electrode surface are capable to change the electrode/solution interface and electrochemical process carried out there [17]. Michaelis *et al.* [18] have prepared crystalline ZnO films by cathodic electrodeposition from aqueous solution in the presence of sodium laurylsulfate and obtained films of remarkably different morphologies. Rusling *et al.* [19] immobilized hemoglobin on the electrode by incorporating it into surfactant film and realized direct electrochemistry of hemoglobin. Chen and Chzo [20] have found that simultaneous determination of dopamine and ascorbic acid can be made using didodecyldimethylammonium bromide film-modified electrodes. Our group has already reported [21–23] determination of several biomolecules and showed remarkably enhanced electrochemical responses of analytes in the presence of surfactants. Surfactants also have potential applicability for suppressing electrode fouling from products of the electrochemical reaction [24]. Due to their unique molecular structure, surfactants have been widely used in the area of electrochemistry [17,25] and for other purposes. It has already been shown that adsorption of surfactant aggregates on the electrode surface increases the peak current, changes the redox potential and charge transfer or diffusion coefficients.

With the intention to propose an effective, quick and inexpensive method for determination of MTX, fabrication of various surfactant modified CNT paste electrodes by an easy immobilisation method is described in this paper. All prepared electrodes are tested for the presence of MTX using cycling voltammetry experiments. The electrode showing the highest sensitivity, the sodium dodecyl sulfate modified carbon paste electrode (SDSMCNTPE), is analysed for all relevant details.

Experimental

Reagents

MTX was received from Biovision Inc, USA. Spectroscopically pure multiwalled CNTs were obtained from Sigma Aldrich. Silicone oil and sodium dodecyl sulfate (SDS) were purchased from Nice Chemicals, India. Cetyltrimethylammonium bromide (CTAB) was purchased from Molychem, India, while Triton X-100 (TX-100) was purchased from Himedia, India. All chemicals were of analytical grade and used without further purification. Stock solutions of 25×10^{-4} M MTX and 25×10^{-3} M SDS, CTAB and TX-100 were prepared by dissolving in double distilled water. The supporting electrolyte was the phosphate buffer solution, 0.2 M PBS, pH 7.0. PBSs of other pH values (5.5-8.0) were prepared by mixing the corresponding volumes of standard 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solutions.

Apparatus

Voltammetric measurements were executed using a model-201 electrochemical analyzer and conventional three-electrode system. The following electrodes were used as the working electrodes: graphite (carbon) paste electrode (CPE), bare carbon nanotube paste electrode (BCNTPE), SDS modified carbon paste electrode (SDSMCPE), SDS modified carbon nanotube paste electrode (SDSMCNTPE), cetyltrimethylammonium bromide modified carbon nanotube electrode (CTABMCNTPE) and TX-100 modified carbon nanotube electrode (TX-100MCNTPE). The counter electrode was a platinum wire, while the saturated calomel electrode (SCE) served as the reference electrode. All potential values are referred to the SCE.

Preparation of electrochemical sensor electrodes

The BCNTPE was prepared by mixing CNTs and silicone oil (60.0 % w/w CNTs and 40.0 % w/w silicone oil) in a mortar [26]. The paste was then packed into the cavity (3 mm diameter) of a home-made electrode and smoothed out by a tissue paper. The CPE was prepared by grinding 70 % of graphite powder (particle size 150 mesh) and 30 % of silicone oil to produce a homogeneous carbon paste electrode. The paste was then filled into the cavity of a homemade electrode and smoothed out by a tissue paper. SDSMCPE, SDSMCNTPE, CTABMCNTPE and TX-100MCNTPE were prepared by immobilizing 20 μL of SDS, CTAB and TX-100 surfactants on the electrode surfaces for 5 min.

Electrochemical and microscopic measurements

Determination of MTX was carried out in a voltammetric cell with 0.2 M PBS, pH 7.0 supporting solution at room temperature. Cyclic voltammograms and differential pulse voltammograms were usually recorded by changing potentials from 0 to 1000 mV and 0 to 750 mV, respectively, with potential scan rate, ν =100 mV s^{-1}. Between two oxidation peaks appearing around 370 and 600 mV, the peak at 600 mV was chosen for detailed analysis in this study. Prior each MTX measurement, the electrode surface was renewed.

Microscopic studies were made by using Field emission scanning electron microscopy (FESEM) and Energy-dispersive X-ray spectroscopy (EDX).

Results and discussion

Microscopic study of CNT, BCNTPE and SDSMCNTPE

Fig. 1 illustrates the FESEM images of CNT (Fig. 1a) BCNTPE (Fig. 1b) and SDSMCNTPE (Fig. 1c) surfaces. The surface of the BCNTPE looks rougher than CNT, whereas in the case of the

SDSMCNTPE, the deposition of SDS with some large groups is observed with FESEM. It is well known that surfactants adsorb or cluster into supramolecular structures at the surface of the electrode, influencing thus electrochemical processes taking place.

The BCNTPE and SDSMCNTPE structures were examined by EDX measurement, giving spectra shown in Fig. 2. EDX spectrum of BCNTPE indicates the presence of C, O, and Si (Fig. 2A), while for SDSMCNTPE, presence of C, O, Na, Si and S elements is indicated in the spectrum (Fig. 2B) suggesting thus successful modification of the electrode surface by SDS.

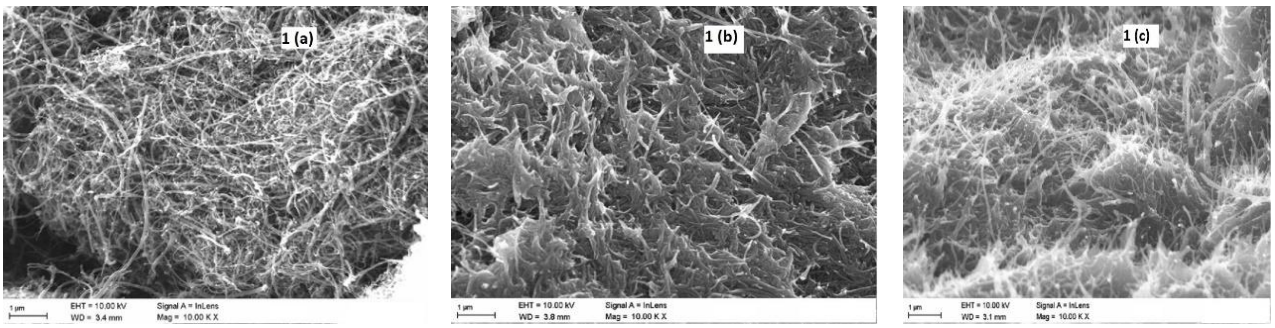


Figure 1. *FESEM images of (a) CNT (b) BCNTPE (c) SDSMCNTPE*

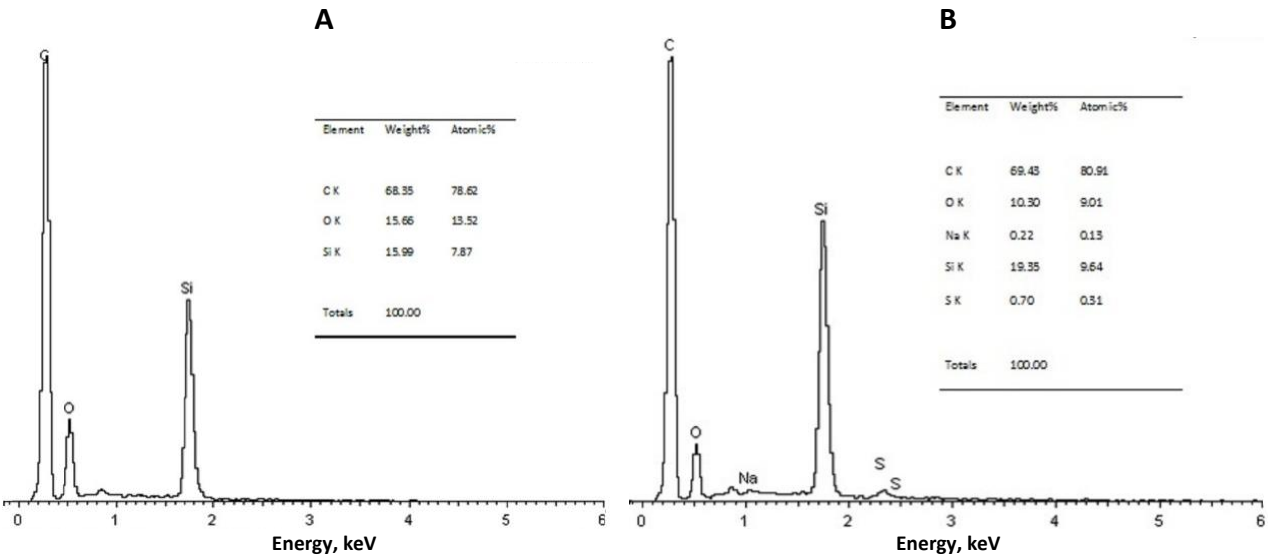


Figure 2. *EDX spectra of **A** -BCNTPE and **B** - SDSMCNTPE*

Optimization for the amount of SDS surfactant

In this part, the effect of amount of SDS (20–50 μL) on the MTX oxidation peak current is studied by cyclic voltammetry experiments. The peak current increased gradually with the increase of SDS amount at first and then tended to be stable for the amount realized by 20 μL. This is probably due to the excessive compactness of the SDS monolayer and non-negligible electrostatic interaction between adsorbed substrates. Further increase of SDS amount resulted in the decrease of peak current, what is presented in Fig. 3. This effect may be due to the micellar effect of surfactant that causes abrupt change of oxidation current of MTX around the critical micelles concentration (CMC) of SDS. Therefore, 20 μL SDS was adopted as the optimum in this work.

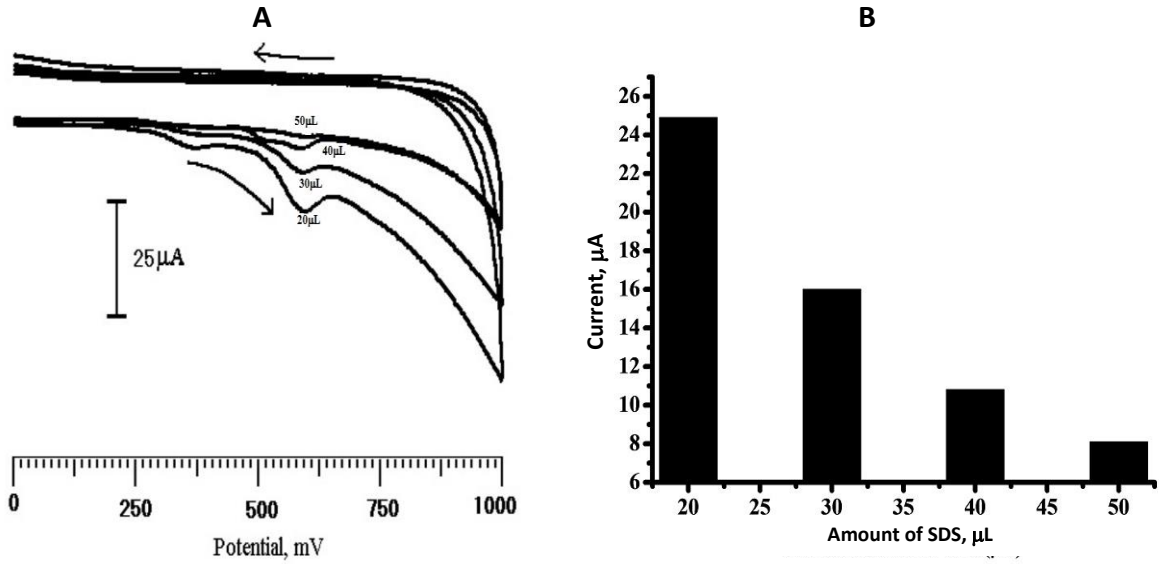


Figure 3. A *- Cyclic voltammograms (ν = 100 mV/s) of MTX (1×10^{-4} M) oxidation at DSMCNTPE in 0.2M PBS, pH 7.0, for different amounts of SDS (20 µl–50 µl);* ***B*** *- Peak current values* vs. *amount of SDS*

Reproducibility and stability of the electrode.

The reproducibility of the electrode response was measured by five times utilization of the same electrode for determination of MTX by cyclic voltammetry experiments under optimized conditions. For SDSMCNTPE, the relative standard deviation (RSD) of five measurements was 4.93 %, which indicated good reproducibility in the electrochemical response for this electrode. The stability of the electrode was tested by measuring the current response of MTX during one month period. It was found that after 30 days, the SDSMCNTPE maintained 94 % of its original activity, suggesting thus good stability of this sensor.

Electrochemical response of MTX at CTABMCNTPE and TX-100MCNTPE

Electrochemical responses of MTX oxidation at BCNTPE and at the same electrode with very small amount of either TX-100 or CTAB surfactants are compared in Fig. 4. It is obvious that the voltammetric response is apparently improved in the presence of 20 µL of CTAB (Fig. 4A) and TX-100 surfactants (Fig. 4B) in immobilized forms.

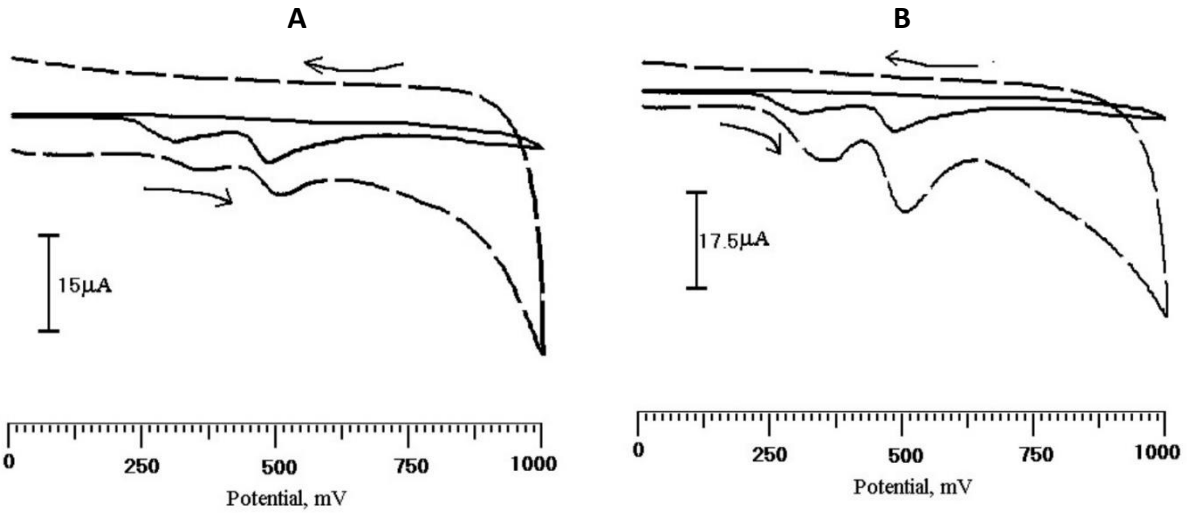


Figure 4. *Cyclic voltammograms (ν = 100 mV s^{-1}) of MTX (1×10^{-4} M) oxidation in 0.2 M PBS, pH 7.0 at:*
A *- BCNTPE (solid line) and CTABMCNTPE (dashed line);*
B *- BCNTPE (solid line) and TX-100MCNTPE (dashed line)*

When either anionic surfactant SDS, cationic surfactant CTAB or non-ionic surfactant TX-100 was applied, the peak current values increased, and the highest increase is observed for the SDSMCNTPE. Therefore, the SDSMCNTPE has been selected for the further study.

Electrochemistry of MTX at SDSMCNTPE

Fig. 5 exhibits cyclic voltammograms of MTX (10^{-4} M) electro-oxidation on SDSMCNTPE in PBS (0.2 M, pH 7.0). No significant peak is observed for the blank solution, while after addition of MTX, the current enhancement and formation of the peak at 600 mV become completely evident. These results suggest that the SDSMCNTPE increased electroactive surface area enhancing the electrocatalytic activity for MTX oxidation.

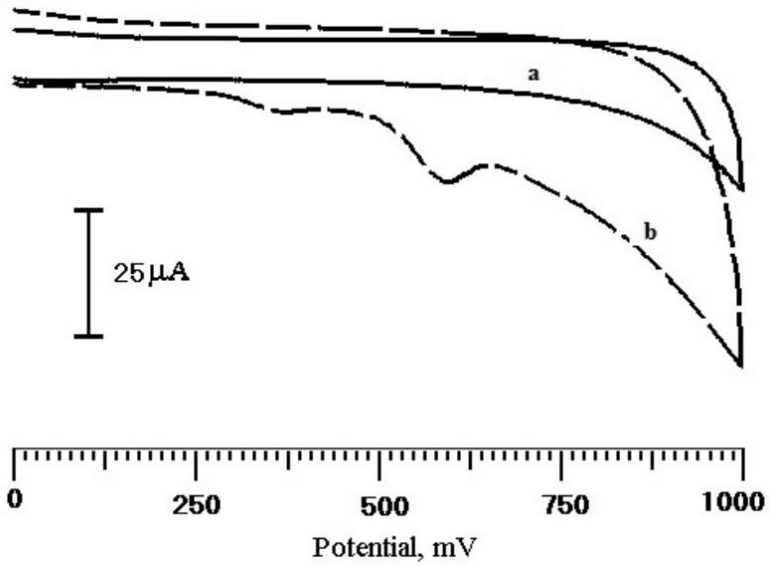


Figure 5. *Cyclic voltammograms (ν = 100 mV s^{-1}) of SDSMCNTPE in 0.2 M PBS, pH 7.0: Blank solution (curve a) and MTX (1×10^{-4} M) (curve b)*

Electrochemical behavior of MTX at SDSMCNTPE

The redox nature of MTX (10^{-4} M) at BCNTPE and SDSMCNTPE in 0.2 M PBS, pH 7.0 is compared in Fig. 6. At BCNTPE, two redox peaks appeared at 310 and 490 mV. At SDSMCNTPE, however, two redox peaks are observed at 370 and 600 mV, respectively. The peak currents at the SDSMCNTPE increased by 61 % and 70 % compared to BCNTPE, indicating the catalytic oxidation of MTX at the surfactant modified electrode. Also, the peak potentials were shifted in a positive direction, *i.e.* from 310, 490 mV (BCNTPE) to 370, 600 mV (SDSMCNTPE). Thus, presence of SDS as a modifier facilitates the rate of the charge transfer and increases the over potential of MTX oxidation.

The electrochemical responses of (1×10^{-4} M) MTX at SDSMCPE and SDSMCNTPE were studied in 0.2 M PBS, pH 7 and the resulted cyclic voltammograms are displayed in Fig. 7. The peak potential of MTX at the SDSMCPE were observed at 405 mV and 600 mV, while at the SDSMCNTPE, the same peaks were observed at 370 mV and 600 mV. At the same time, peak current values at the SDSMCNTPE are higher compared to those at the SDSMCPE. These results proved that the SDSMCNTPE enhanced the sensitivity for MTX determination. It is possible that the bulky pore volume of carbon nanotubes provides a big specific area, leading to the increased peak current values.

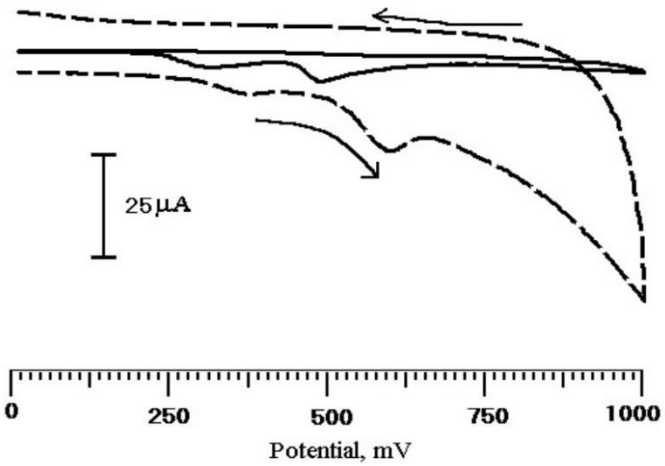


Figure 6. *Cyclic voltammograms (ν = 100 mV s^{-1}) of MTX (1×10^{-4} M) in 0.2 M PBS, pH 7.0 at BCNTPE (solid line) and SDSMCNTPE (dashed line)*

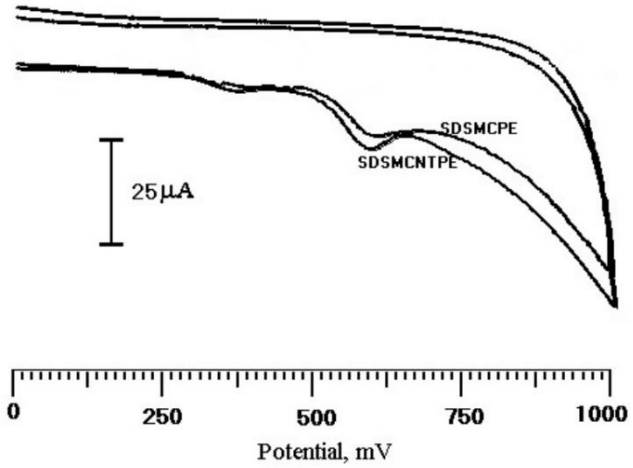


Figure 7. *Cyclic voltammograms (ν = 100 mV s^{-1}) of MTX (1×10^{-4} M) in 0.2 M PBS, pH 7.0 at SDSMCPE and SDSMCNTPE*

Differential voltammetric study of MTX at SDSMCNTPE

Differential voltammograms, DPVs, were recorded at 30 mV/s scan rate in the potential range from 0 to 750 mV for MTX (1×10^{-4} M) in 0.2 M PBS, pH 7.0 solution. For the BCNTPE, Fig. 8 shows a pair of MTX oxidation peaks at 264 and 470 mV, respectively. For the SDSMCNTPE, however, peaks are located at 320 and 480 mV and showed strongly increased peak current values.

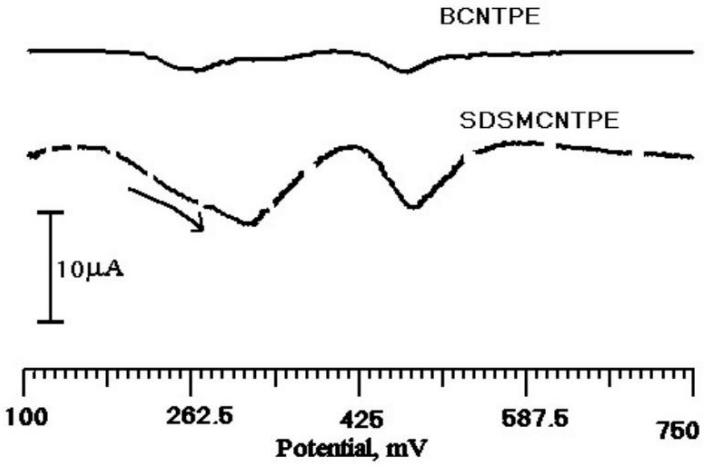


Figure 8. *DPVs of BCNTPE (solid line) and SDSMCNTPE (dashed line) in 0.2 M PBS, pH 7.0 and MTX (1×10^{-4} M)*

Influence of scan rate

The scan rate dependence of the peak current values of MTX oxidation at the SDSMCNTPE is shown in Fig. 9. Cyclic voltammograms of the SDSMCNTPE in MTX (1×10^{-4} M), 0.2 M PBS, pH 7.0 measured at the scan rates between 100 and 500 mV s^{-1} are shown in Fig. 9a. Fig. 9b shows that the peak current values increased linearly with the scan rate. The linear regression equation was determined as I_{pa} / μA = 4.08 + 0.092 ν / mV s^{-1} (R = 0.99194) [27], what suggests that the adsorption controlled electrochemical oxidation reaction of MTX is taking place on this electrode.

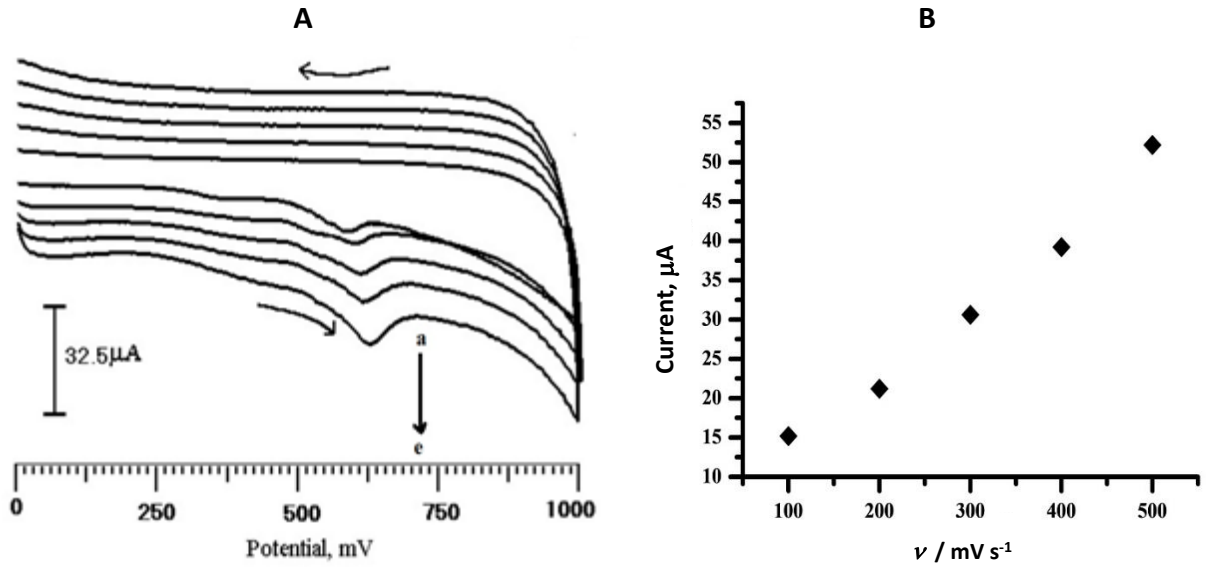


Figure 9. A *- Cyclic voltammograms of the SDSMCNTPE in 0.2 M PBS, pH 7.0 and MTX (1×10^{-4} M) at various ν = a) 100, b) 200, c) 300, d) 400 and e) 500 mVs^{-1}*
B *- Plot of the peak current value as a function of ν*

Relationship between pH, peak potential and peak current values

The effects of pH changes were investigated by measuring CVs of SDSMCNTPE in solutions containing MTX and PBS of different pH in the range 5.5 – 8 and these results are shown in Fig. 10A. As shown in Fig 10A and Fig. 10B, the topmost peak current value of MTX oxidation is obtained at pH 7.0, while at all other (lower and higher) pH, peak current values are lower. This, together with the fact that the physiological pH value is about 7 was the main reason why pH 7.0 is chosen as the supporting electrolyte in electrochemical determination of MTX. Fig. 10c shows the relationship between the peak potential of MTX oxidation and pH of the solution. The linear regression equation for anodic peak potentials, E_{pa}, and pH could be depict as E_{pa} / V = 1038 − 63.6 pH (R =0.9973). The anodic peak potential of MTX is shifted negatively with the increase of the pH value, indicating reactions accompanied by proton transfer. The slopes of 63.6 mV/pH for MTX oxidation is nearby to the theoretical value of 59 mV/pH and pointed out toward two protons and two electrons involved in the oxidation process [28–30].

Calibration plot and limit of detection for MTX

Fig. 11 depicts the calibration plot, *i.e.* the peak oxidation currents of CVs recorded at the SDSMCNTPE in 0.2 M PBS, pH 7.0 for different concentrations of MTX in the range between 2×10^{-7} and 7×10^{-6} M. The oxidation peak current values increased linearly with increase of MTX concentration. The linear regression equation for the given range of concentration, *C*, is expressed as i_{pa} / A = 5.92×10^{-5} + 3.06575 *C* (M) with the R= 0.99271.

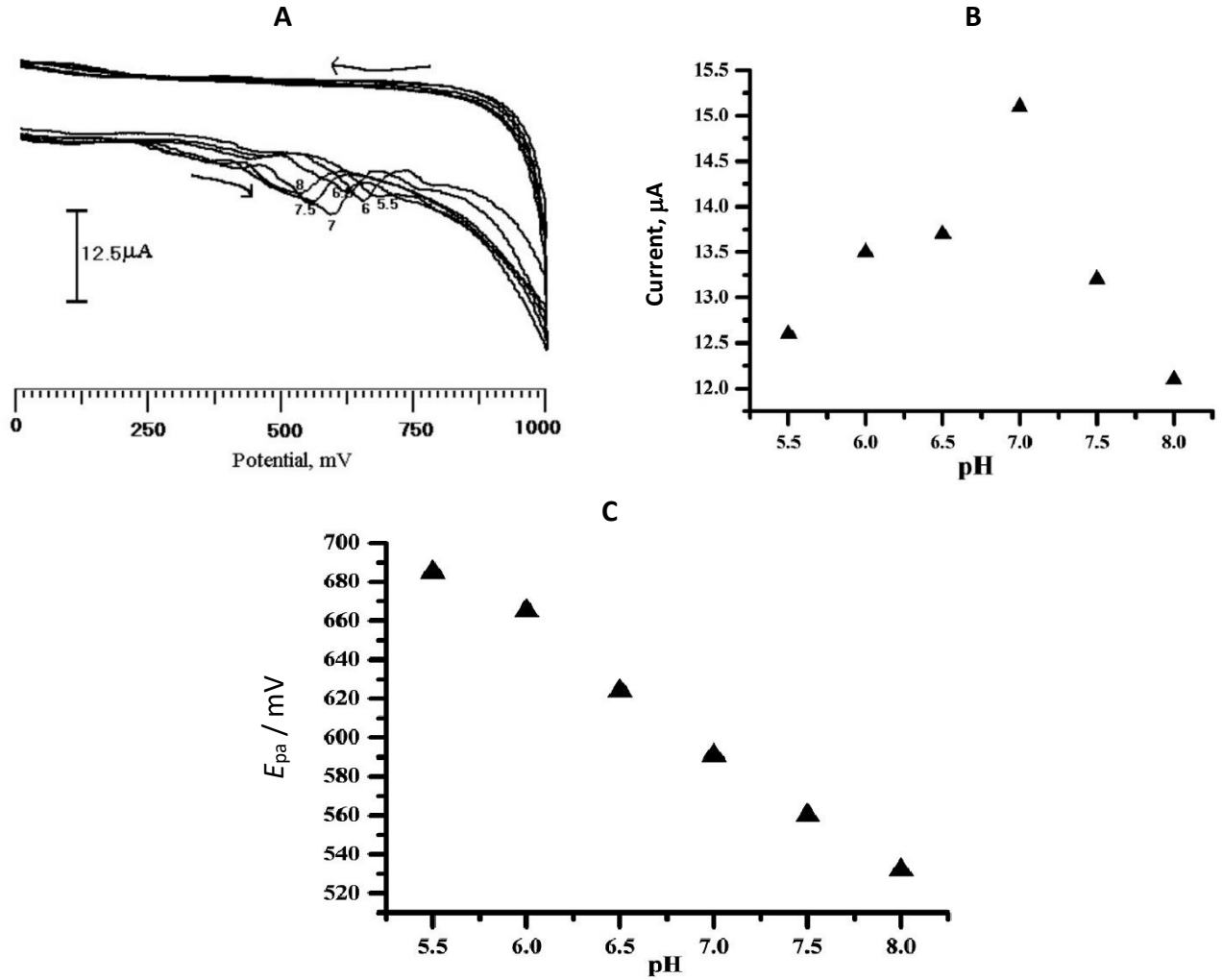


***Figure 10. A** - Cyclic voltammograms (ν = 100 mV s^{-1}) of SDSMCNTPE for MTX (1×10^{-4} M) in 0.2 M PBS, pH 5.5, 6, 6.5, 7, 7.5 and 8; **B** - Plot of anodic peak current vs. pH (5.5–8.0); **C** - Plot of peak potential, E_{pa} vs. pH (5.5–8.0)*

The detection limit (LOD) was estimated by applying the standard formula of LOD = $3s_b/m$ [31], where m is the slope of the calibration curve and s_b is the standard deviation of the peak currents of the blank solution (five replicates). The detection limit for determination of MTX at SDSMCNTPE was evaluated as 3.5×10^{-8} and limit of quantification as 11×10^{-8}. Table 2 presents the linear range and detection limits for MTX determination at SDSMCNTPE obtained in the present study and also for some other carbon modified electrodes taken from the literature. Data in Table 2 show that the linear range, as well as detection limit for MTX at SDSMCNTPE is better than for other sensors [32,33]. In addition, the sensor described in the present work is less expensive and simpler to use than other ones.

***Table 1.** Detection limits for determination of MTX at some modified carbon electrodes*

Electrode	Detection limit, M	Method	Reference
CS-dispersed graphene film coated/GCE	2×10^{-10}	DPV	[40]
dsDNA/CPE	5.62 × 10^{-8}	DPV	[11]
DNA/GCE	10^{-7}	SWV	[41]
SDSMCNTPE	3.5 ×10^{-8}	CV	This work

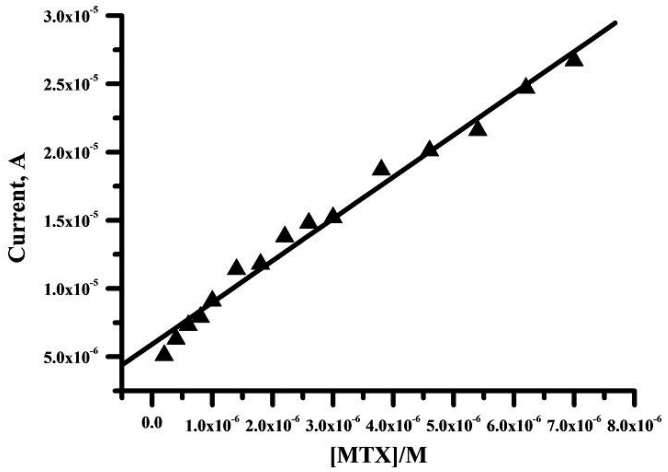


Figure 11. *Calibration plot for determination of MTX at the SDSMCNTPE in 0.2 M PBS, pH 7.0*

Analytical application

Suitability of here described CV method using the SDSMCNTPE for determination of MTX in real samples was tested by analysis of MTX in a commercial injection. The injection was dissolved in 0.2 M PBS, pH 7.0 and the standard addition method was applied by adding the known concentration of MTX into the test solution. The recovery for determination of MTX was in the range of 99.2-111 % for three samples. The recovery and RSD were acceptable, expressing thus good accuracy of the prepared sensor.

Conclusions

Excellent sensors based on carbon nanotubes modified by different surfactants were prepared and tested for determination of MTX by cyclic voltammetry experiments. The prepared electrodes were characterized using CV, DPV, FESEM and EDX. The catalytic activity of SDSMCNTPE electrode toward electrooxidation of MTX was investigated and compared with BCNTPE, CTABMCNTPE, TX-100MCNTPE and SDSMCPE. The results showed that the SDSMCNTPE demonstrated excellent electrocatalytic activity for the oxidation of MTX. Wide linear range, low detection limit, good repeatability and reproducibility, distant term stability and acceptable sensitivity and recovery values of the SDSMCNTPE suggest that this electrode can be applied as a sensor for estimation of MTX in real samples. Better properties of the SDSMCNTPE were also observed in comparison with few other electrodes which have already been developed for electrochemical determination of MTX.–The capability of other modified CNT electrodes for determination of MTX and possible analysis of other bioactive molecules will be the subject of further research.

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