ISSN 1996-5044

Research Journal of Nanoscience and Nanotechnology

Knowledgia
SCIENTIFIC
A Place to Publish Outstanding Research

http://knowledgiascientific.com

Research Journal of Nanoscience and Nanotechnology 1 (2): 75-86, 2011
ISSN 1996-5044 / DOI: 10.3923/rjnn.2011.75.86

Sensitive Voltammetric Determination of Atenolol at Multi-walled Carbon Nanotubes Modified Glassy Carbon Electrode

[1]R.N. Hegde, [2]P. Chandra and [1]S.T. Nandibewoor
[1]P.G. Department of Chemistry, Karnatak University, Dharwad-580 003, India
[2]Amity Institute of Biotechnology, Amity University Campus, A-Block Sector-125 Noida-201303 U.P, India

Corresponding Author: S.T. Nandibewoor, P.G. Department of Chemistry, Karnatak University, Dharwad-580 003, India Tel: +91 836 2770524 Fax: +91 836 2747884

ABSTRACT

This study describes the excellent electro-catalytic activity towards voltammetric oxidation of atenolol at Multi-walled carbon nanotube (MWCNT)-modified glassy carbon electrode and its determination. Compared to bare glassy carbon electrode, the MWCNT-modified glassy carbon electrode exhibited an apparent shift of the oxidation potential to the less positive direction and a marked enhancement in the current response of atenolol. The electro-catalytic behavior was further exploited as a sensitive detection scheme for the atenolol determination by differential-pulse voltammeter. Under optimized conditions, the linear range and detection limit are 2.0×10^{-7} to 6.0×10^{-6} and 2.34×10^{-8} M, respectively for atenolol. The proposed method was successfully applied to atenolol determination in pharmaceutical samples and urine, without any preliminary treatment.

Key words: Electroanalysis, atenolol, multi-walled carbon nanotube, voltammetry, electro-catalysis

INTRODUCTION

Atenolol (ATN) [4-[2-hydroxy-3-isopropylaminopropoxy]-phenylacetamide] is a hydrophillic β1-receptor blocking agent. This β-adrenoceptor blocking drug is of therapeutic value in the treatment of various cardiovascular disorders, such as angina pectoris, cardiac arrhythmia and hypertension (Maria *et al.*, 2010). With chronic treatment, it reduces mortality in hypertension and prolongs survival in patients with coronary heart disease (Wadworth *et al.*, 1991). β-Blockers are exceptionally toxic and most of them act in a narrow therapeutic range; the differences between the lowest therapeutic and the highest tolerable doses are small. Common effects associated with atenolol overdose are lethargy, disorder of respiratory drive, wheezing, sinus pause, bradycardia, congestive heart failure, hypotension, bronchospasm and hypoglycemia (Snook *et al.*, 2000). This is the reason that analysis of ATN is of great importance in pharmaceutical research. In the literature, a few methods have been reported for the determination of ATN in pharmaceutical formulations and urine. Most of them relying on the use of chromatographic techniques, like Gas Chromatography with Mass Spectrometry (GCMS) or electron capture detector (Ternes, 2001) and High Performance Liquid Chromatography (HPLC) (Leloux and Dost, 1991; Tomita *et al.*, 1991). Electrochemical determination of ATN was performed using C_{60}-modified glassy carbon electrode (Goyal and Singh, 2006) nanogold modified indium tin oxide electrode (Goyal *et al.*, 2006) at a graphite-polyurethane composite electrode (Cervini *et al.*, 2007), multi-wall carbon nanotubes modified glassy carbon electrode (Li *et al.*, 2008) and at a carbon paste electrode (Patil *et al.*, 2009).

In these studies, limits of detection such as 1.6×10^{-4} M, 1.3×10^{-7} M, 3.16×10^{-6} M, 2.0×10^{-6} M and 5.87×10^{-7} M were described, respectively. Due to the importance of ATN, it is interesting to develop a rapid screening method for its determination in pharmaceutical formulations and urine.

Although spectroscopic and chromatographic methods were widely used for the analysis of various pharmaceutical drugs (Amini-Shirazi *et al.*, 2010), most of these methods require separation and/or pretreatment steps. These methods are time consuming, solvent-usage intensive and requires expensive devices and maintenance. Electrochemical detection of analyte is a very elegant method in analytical chemistry (Hegde *et al.*, 2009a). The interest in developing electrochemical-sensing devices for use in environmental monitoring, clinical assays or process control is growing rapidly. Electrochemical sensors satisfy many of the requirements for such tasks particularly owing to their inherent specificity, rapid response, sensitivity and simplicity of preparation (Hegde *et al.*, 2009b).

Nanoparticles (Singh, 2011; Dash and Balto, 2011; Zainudin *et al.*, 2011) and nanomaterials (Pang *et al.*, 2010) have gained much attention these days in all kind of research fields. Carbon nanotubes (CNTs) continue to receive remarkable attention in electrochemistry (Merkoci, 2007; Trojanowicz, 2006). Since their discovery by Iijima (1991) using transmission electron microscopy, CNTs have been the subject of numerous investigations in chemical, physical and material areas due to their novel structural, mechanical, electronic and chemical properties (Ajayan, 1999). The subtle electronic properties suggest that CNTs have the ability to promote charge transfer reactions when used as an electrode (Nugent *et al.*, 2001). The modification of electrode substrates with multi-walled carbon nanotubes (MWCNTs) for use in analytical sensing has been documented to result in low detection limits, high sensitivities, reduction of over potentials and resistance to surface fouling. MWCNTs have been introduced as electrocatalysts (Merkoci, 2006; Hegde *et al.*, 2009a, b; Banks and Compton, 2006) and CNTs modified electrodes have been reported to give super performance in the study of a number of biological species (Zhao *et al.*, 2005).

Even though, voltammetric determination of ATN using a MWCNTs modified Glassy Carbon Electrode (GCE) has been reported (Li *et al.*, 2008), the objective of the present study is to develop a convenient and sensitive method for the determination of ATN based on the unusual properties of MWCNTs modified electrode and the obtained results have been compared with reported ones. The ability of the modified electrode for voltammetric response of selected compound was evaluated. Finally, this modified electrode was used for the analysis of ATN in pharmaceutical and urine samples using differential-pulse voltammetry. The resulted biosensor exhibits high sensitivity, rapid response, good reproducibility and freedom of other potentially interfering species.

MATERIALS AND METHODS

ATN was received as a gift sample from M/s. S.S.Antibiotics Pvt. Ltd., Aurangabad, India and used as received (October 2009). A 10.0 mM stock solution was made in double distilled water. Multi-walled carbon nanotubes were from Sigma-Aldrich (>95%, O.D: 10-15 nm, I.D: 2-6 nm, length: 0.1-10 μm). The phosphate buffers solutions were prepared in double distilled water (Goyal *et al.*, 2006). Other reagents used were of analytical or chemical grade and their solutions were prepared with doubly distilled water.

Electrochemical measurements were carried out on a CHI1110A electrochemical analyzer (CH Instrument Company, USA) coupled with a conventional three-electrode cell. A three-electrode cell was used with a Ag/AgCl as reference electrode, a Pt wire as counter electrode and a bare glassy carbon electrode with a diameter of 3 mm (modified and unmodified) were used as working electrodes, respectively. All of the used electrodes were from CHI Co. and all the potentials in this paper are given against the Ag/AgCl (3M KCl). Solution pH was measured with an Elico LI120 pH meter (Elico Ltd., India).

Multi-walled carbon nanotubes (i.e., MWCNTs) was refluxed in the mixture of concentrated H_2SO_4 and HNO_3 for 4-5 h, then washed with doubly distilled water and dried in vacuum at room temperature. The MWCNTs suspension was prepared by dispersing 2 mg of MWCNTs in 10 mL acetonitrile using ultrasonic agitation to obtain a relative stable suspension. The GCE was carefully polished with 0.30 and 0.05 μm a-alumina slurry on a polishing cloth and then washed in an ultrasonic bath of methanol and water, respectively. The cleaned GCE was coated by casting 12 μL of the black suspension of MWCNTs and dried in air. The electro-active areas of the MWCNT-modified GCE and the bare GCE were obtained by Cyclic Voltammetry (CV) using 1.0 mM $K_3Fe(CN)_6$ as a probe at different scan rates. For a reversible process, the Randles-Sevcik formula has been used:

$$i_{pa} = (2.69\times10^5)\ n^{3/2} A\ D_0^{1/2} C_0\ \mathbf{v}^{1/2} \qquad (1)$$

where, i_{pa} refers to the anodic peak current, n is the number of electrons transferred, A is the surface area of the electrode, D_0 is diffusion coefficient, **v** is the scan rate and C_0 is the concentration of $K_3Fe\ (CN)_6$. For 1.0 mM $K_3Fe\ (CN)_6$ in 0.1 M KCl electrolyte, $n = 1$, $D_0 = 7.6\times10^{-6}\ cm^2\ sec^{-1}$, then from the slope of the plot of i_{pa} vs $\mathbf{v}^{1/2}$, relation, the electro-active areas were calculated. In bare GCE, the electrode surface was found to be $4.64\times10^{-2}\ cm^2$ and for MWCNT-modified GCE, the surface was nearly 3.5-4.0 times greater.

The MWCNT-modified GCE was first activated in phosphate buffer (0.2 M, pH 8.0) by cyclic voltammetric sweeps between 0 and 1.4 V until stable cyclic voltammograms were obtained. Then electrodes were transferred into another 10 mL of phosphate buffer (0.2 M, pH 8.0) containing proper amount of ATN. After accumulating for 60 sec at open circuit under stirring and following quiet for 5 sec, potential scan was initiated and differential-pulse voltammograms were recorded between+0.7 and+.1, with a scan rate of 20 mV sec^{-1}. All measurements were carried out at room temperature of 25±0.1°C. Background subtraction treatment was done in all the measurements.

Ten pieces of ATN tablets were powdered in a mortar. A portion equivalent to a stock solution of a concentration of about 1.0 mM was accurately weighed and transferred into a 100 mL calibrated flask and completed to the volume with double distilled water. The contents of the flask were sonicated for 10 min to affect complete dissolution. Appropriate solutions were prepared by taking suitable aliquots of the clear supernatant liquid and diluting them with the phosphate buffer solutions. Each solution was transferred to the voltammetric cell and analyzed by standard addition method. The differential-pulse voltammograms were recorded between 0.70 and 1.10 V after open-circuit accumulation for 60 sec with stirring. The oxidation peak current of ATN was measured. The parameters for Differential Pulse Voltammetry (DPV) were pulse width of 0.06 sec, pulse increment of 10 mV, pulse period of 0.2 sec, pulse amplitude of 50 mV and scan rate of 20 mV sec^{-1}. To study the accuracy of the proposed method and to check the interferences from excipients used in the dosage form, recovery experiments were carried out. The concentration of ATN was calculated using calibration curve method.

RESULTS AND DISCUSSION

Cyclic voltammetric behavior of ATN: The cyclic voltammograms of ATN at a bare GCE and at MWCNT-modified GCE were shown in Fig. 1. It can be seen that the ATN oxidation peak at the bare GCE was weak and broad due to slow electron transfer while the response was considerably improved at the MWCNT-modified GCE. At the bare GCE, the peak was at about 1.06 V (Fig. 1c), but on the MWCNT-modified GCE, the peak appeared at about 0.94 V (Fig. 1a), with considerable enhancement in the peak current. This was attributed to the electro-catalytic effect caused by MWCNTs. The reason for the better performance of the MWCNT-modified GCE may be due to the nanometer dimensions of the MWCNTs, the electronic structure and the topological defects present on the MWCNTs surfaces (Britto *et al*., 1999). Meanwhile the MWCNTs increase the effective area of the electrode. The modified electrode has no electrochemical activity in phosphate buffer solution (Fig. 1b) but the background current becomes larger, which is attributed to the fact that MWCNTs can increase the surface activity remarkably.

A simple experiment was done to know whether the edge plane like sites/defects of MWCNTs or iron oxide impurities are the main function of catalytic behavior of modified electrode. We followed procedure described by Sljukic *et al*. (2006). Iron (III) oxide, Fe_2O_3, was abrasively immobilized onto a GCE by gently rubbing the electrode surface on a fine quality filter paper containing iron (III) oxide. The modified GCE was immersed in the 0.10 mM solution of atenolol and the electrochemical oxidation was explored. We compared the voltammograms of this with that obtained with MWCNTs modified GCE (Fig. 2). It is clear from the comparison that the iron oxide impurities are not playing the role in the catalytic behavior. The main reason for the electro-catalytic behavior was edge plane like sites/defects of MWCNTs, as evidenced in the literature (Banks *et al*., 2004; Banks and Compton, 2005). It also showed that no reduction peak was observed in the reverse scan, suggesting that the electrochemical reaction was a totally irreversible process.

Influence of amount of MWCNTs: Figure 3 shows that the amount of MWCNTs has influence on the peak current. At 12 µL of MWCNTs, the peak current was highest. After that amount, it decreases. This is related to the thickness of the film. If the film was too thin, the ATN amount adsorbed was small, resulting in the small peak current. When it was too thick, the film

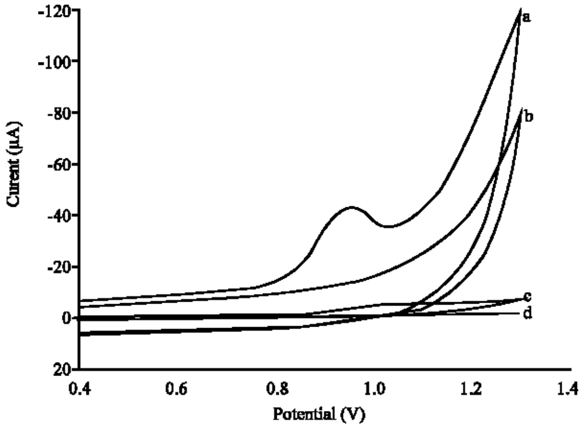

Fig. 1: Cyclic voltammograms of 0.10 mM ATN at MWCNT-modified GCE (a) and bare GCE (c). Blank CVs of MWCNT-modified GCE (b) and bare GCE (d). Scan rate: 50 mVsec^{-1}; supporting electrolyte: 0.2 Mphosphate buffer with pH 8.0; accumulation time: 60 sec (at open circuit); volume of MWCNTs suspension: 12 µL (except for c and d)

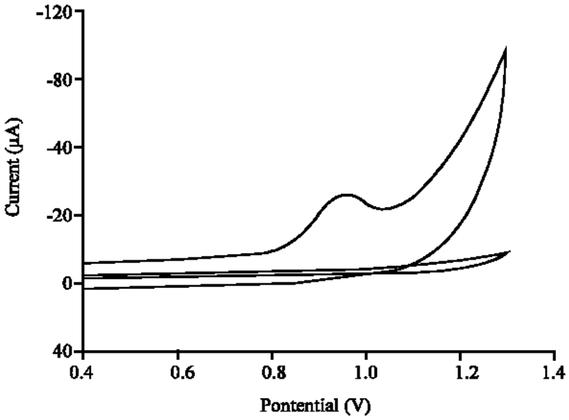

Fig. 2: Cyclic voltammograms of 0.10 mM ATN in phosphate buffer with pH 8.0 at MWCNT-modified GCE (a) and Fe (III) oxide modified GCE (b). Other conditions are as in Fig. 1

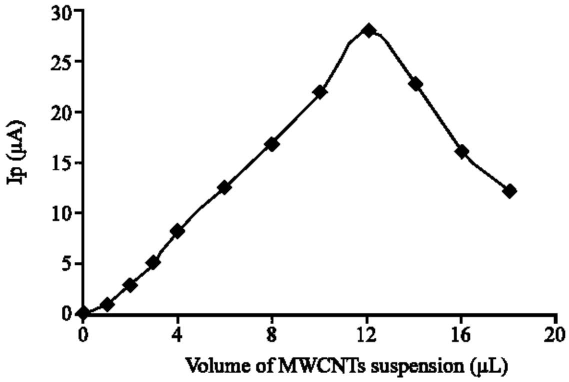

Fig. 3: Influence of MWCNTs suspension (0.2 mg mL^{-1}) volume used on the anodic peak current. Other conditions are as in Fig. 1

conductivity reduced and the film became not so stable as MWCNTs could leave off the electrode surface. Thus it blocks the electrode surface and hence the peak current decreases. Therefore, 12 µL MWCNTs suspension solution was used in the remaining studies.

Influence of accumulation potential and time: It was important to fix the accumulation potential and time when adsorption studies were undertaken. Both conditions could affect the amount of adsorption of ATN at the electrode. Bearing this in mind, the effect of accumulation potential and time on peak current response was studied by CV. The concentration of ATN used was 1.0×10^{-4} M.

When accumulation potential was varied from +0.3 to-0.3 V, the peak current changed a little. Hence, accumulation at open circuit was adopted. The peak current increased very rapidly with increasing accumulation time, which induced rapid adsorption of ATN on the surface of the modified electrode. The peak current reached the maximum after 60 sec and then being unchanged. This indicates the saturation accumulation. As too long accumulation time might reduce the stability of MWCNTs film, 60 sec was generally chosen as accumulation time.

Influence of pH: Peak potential of the oxidation peak was pH dependent and was found to shift towards less positive potentials with increasing pH (Fig. 4). The relation expressing linear dependence of Ep on pH is, Ep (V) = 1.58-0.07 pH: r = 0.992. The slope was 0.07 V/pH, which shows that equal number of protons and electrons are involved in the oxidation of ATN. The peak current was affected by the pH of the solution (Fig. 4). The current increased to a maximum value at pH 8.0 and above pH 8.0, current decreased. So, the pH 8.0 was chosen for all the further studies.

Influence of scan rate: Useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. Therefore, the electrochemical behavior of ATN at different scan rates from 25 to 250 mV sec^{-1} was also studied (Fig. 5). There is a good linear relationship between peak current and scan rate. The equation representing this was Ip (μA) = 167.62 ν (V sec^{-1}) + 18.75; r = 0.992 as shown in Fig. 5A. This indicates that the electrode process was controlled by adsorption rather than diffusion. In addition, there was a linear relation between log Ip and log ν, corresponding to the following equation: log Ip (μA) = 0.95 log ν (V sec^{-1}) + 2.03; r = 0.99. The slope of 0.95 was close to the theoretically expected value of 1.0 for an adsorption-controlled process (Gosser, 1993).

The peak potential shifted to more positive values with increasing the scan rates. The linear relation between peak potential and logarithm of scan rate can be expressed as Ep (V) = 1.15+0.06 log ν (V sec^{-1}); r = 0.995 (Fig. 5B). As for an irreversible electrode process, according to Laviron, Ep is defined by the following equation (Laviron, 1979):

$$Ep = E^{0'} + \left(\frac{2.303RT}{\alpha nF}\right)\log\left(\frac{RTK^0}{\alpha nF}\right) + \left(\frac{2.303RT}{\alpha nF}\right)\log v \qquad (2)$$

where, α is the transfer coefficient, k^0 the standard heterogeneous rate constant of the reaction, n the number of electrons transferred , ν the scan rate and $E^{0'}$ is the formal redox potential. Other symbols have their usual meanings. Thus the value of an can be easily calculated from the slope of Ep versus log ν. In this system, the slope was 0.06, taking T = 298 K, R = 8.314 J K^{-1} mol^{-1} and F = 96480 C, an was calculated to be 0.48. Generally for an irreversible process, a was assumed to be 0.5. Further, the number of electron (n) transferred in the electro-oxidation of ATN was calculated to be 1.92 ~ 2.0. The value of k^0 can be determined from the intercept of the above plot

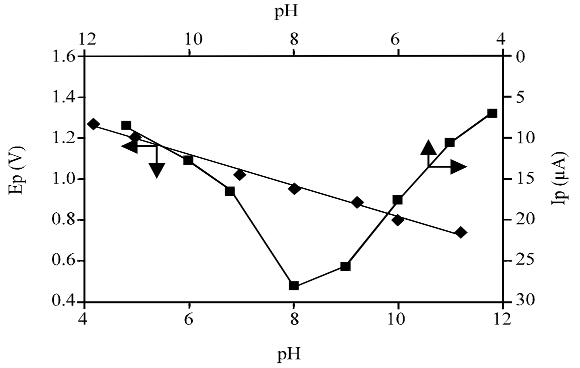

Fig. 4: Influence of pH on the peak potential and peak current of ATN. Other conditions are as in Fig. 1

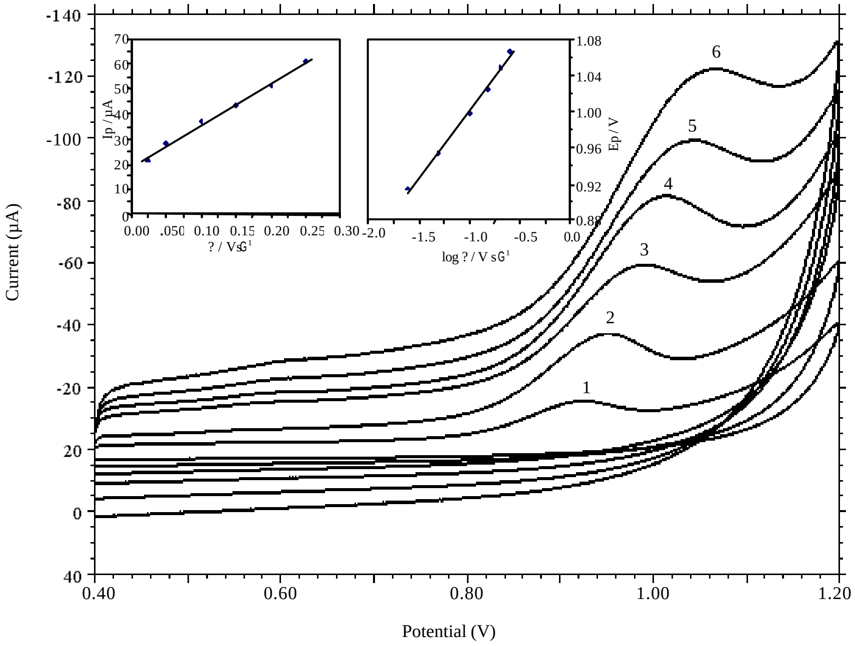

Fig. 5: Cyclic voltammograms of 0.10 mM ATN on MWCNT-modified GCE with different scan rates. (1) to (6) were 25, 50, 100, 150, 200 and 250 mVsec^{-1}, respectively. Inset: (a) Dependence of the oxidation peak current on scan rate; (b) Relationship between peak potential and logarithm of scan rates. Other conditions are as in Fig. 1

if the value of $E^{0'}$ is known. The value of $E^{0'}$ in eqn. (2) can be obtained from the intercept of Ep vs ν curve by extrapolating to the vertical axis at $\nu = 0$ (Wu *et al.*, 2004). The intercept for Ep vs log ν plot was 1.15 and $E^{0'}$ was obtained to be 0.92, the k^0 was calculated to be 3.73×10^{5}sec^{-1}. The oxidation steps are similar as reported by us in the previous works (Patil *et al.*, 2009).

Calibration curve: In order to develop a voltammetric method for determining the drug, we selected the differential-pulse voltammetric mode, because the peaks are sharper and better defined at lower concentration of ATN than those obtained by cyclic voltammetry, with a lower background current, resulting in improved resolution. According to the obtained results, it was possible to apply this technique to the quantitative analysis of ATN. The phosphate buffer solution of pH 8.0 was selected as the supporting electrolyte for the quantification as ATN gave maximum peak current at pH 8.0. The peak at about 0.90 V was considered for the analysis. Differential pulse voltammograms obtained with increasing amounts of ATN showed that the peak current increased linearly with increasing concentration, as shown in Fig. 6. Using the optimum conditions described above, linear calibration curves were obtained for ATN in the range of 2.0×10^{-7} to 6.0×10^{-6} M. The linear equation was Ip (µA) = 0.33+1.31 C (r = 0.998, C is in µM). Deviation from linearity was observed for more concentrated solutions, due to the adsorption oxidative product of ATN on the electrode surface. Related statistical data of the calibration curves were obtained from five different calibration curves. The Limit of Detection (LOD) and quantification (LOQ) were 2.34×10^{-8} M and 7.79×10^{-8} M, respectively. The LOD and LOQ were calculated using the following equations:

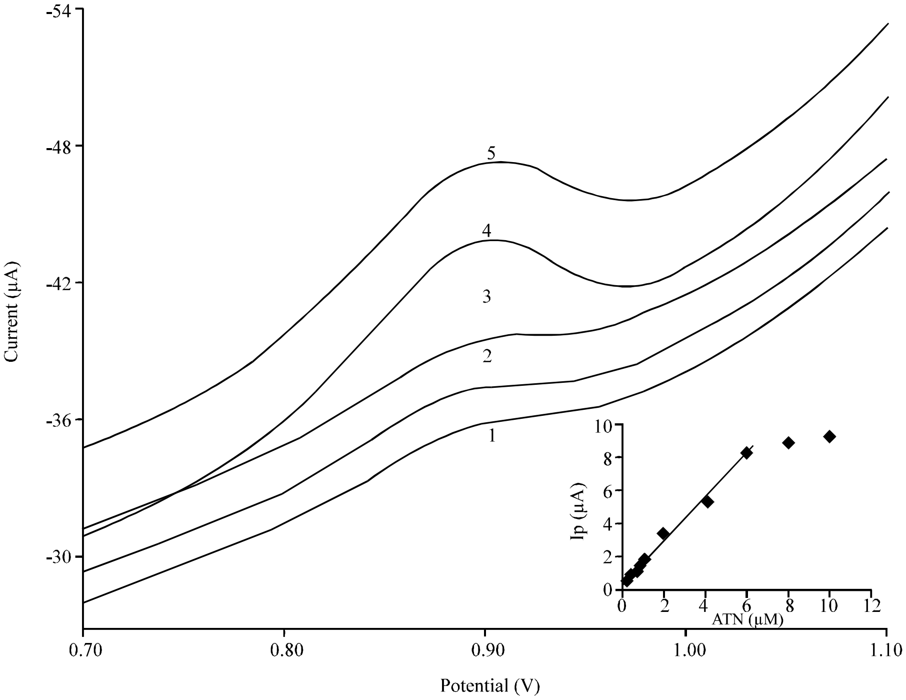

Fig. 6: Differential-pulse voltammograms of MWCNT-modified GCE in ATN solution at different concentrations: 0.2 (1), 0.4 (2), 0.6 (3), 2.0 (4) and 4.0 (5) μM. Inset: Plot of the peak current against the concentration of ATN

$$\text{LOD} = 3\ \text{s m}^{-1};\ \text{LOQ} = 10\ \text{s m}^{-1}$$

where, s is the standard deviation of the peak currents of the blank (five runs) and m is the slope of the calibration curve. The detection limits reported at different electrodes are tabulated in Table 1. This method was better as compared with other reported electrochemical methods. As compared with the reported method (Li *et al.*, 2008), our work has better sensitivity. The reason for the better sensitivity is, we have used differential-pulse voltammetry rather than cyclic voltammetry. Since differential-pulse voltammetry is more sensitive than cyclic voltammetry itself.

In order to study the reproducibility of the electrode preparation procedure, a 1.0×10^{-6} M ATN solution was measured with the same electrode (renewed every time) for every several hours within a day, the R.S.D. of the peak current was 2.16 % (number of measurements = 8). As to the between day reproducibility, it was similar to that of within a day if the temperature was kept almost unchanged. Owing to the adsorption of oxidative product of ATN on to the electrode surface, the current response of the modified electrode would decrease after successive use. In this case, the electrode should be modified again.

Tablet analysis: In order to evaluate the applicability of the proposed method in the real sample analysis, it was used to detect ATN in tablets (50 mg per tablet, supplied by Zydus Cadila Pvt. Ltd.). The procedures for the tablet analysis were followed as described in section 2.5. The results are in good agreement with the content marked in the label (Table 2). The detected content was 48.75 mg per tablet with 97.50% recovery.

Table 1: Comparison of detection limits for ATN at different electrodes

Electrodes	LR[a]($\times10^{-6}$ M)	LOD[b]($\times10^{-9}$ M)	Reference
C_{60}-modified GCE	250-1500	160000	Goyal and Singh (2006)
Nanogold modified indium tin oxide electrode	0.5-1000	130	Goyal *et al*. (2006)
Graphite-polyurethane composite electrode	4.0-10	3160	Cervini *et al*. (2007)
MWCNT-modified GCE	4.9-630	2000	Li *et al*. (2008)
Carbon paste electrode	20-100	587	Patil *et al*. (2009)
MWCNT-modified GCE	0.2-6.0	23	Present work

[a]LR: Linear range, [b]LOD: Limit of detection

Table 2: Comparative studies for ATN in tablet by proposed and literature methods and mean recoveries in spiked tablet

Parameters	GPCE*	Present method	SD±RSD (%)
Labeled claim (mg)	100.00	50.00	
Amount found (mg)[a]	95.88	48.75	0.002±1.03
Added (mg)	1.11	25.00	
Found (mg)	1.06	24.95	
Recovered (%)[b]	95.50	97.50	0.66±2.64

*Graphite-polyurethane composite electrode, [a]Each value is the mean of five experiments. [b]Recovery value is the mean of five experiments

Table 3: Influence of potential interferents on the voltammetric response of 1.0 x 10^{-6} M ATN

Interferents	Concentration ($\times10^{-3}$ M)	Signal change (%)
Glucose	0.1	-1.23
Starch	0.1	-2.61
Sucrose	0.1	-1.18
Citric acid	0.1	-8.26
Magnesium stearate	0.1	+0.21
Talk	0.1	+3.06
Gum acacia	0.1	-2.02
Ascorbic acid	0.1	+3.72
Lactic acid	0.1	-9.16
Tartaric acid	0.1	+6.79
Cystein	0.1	+4.07

The recovery test of ATN ranging from 3.0×10^{-7} to 2.0×10^{-6} M was performed using differential-pulse voltammetry. Recovery studies were carried out after the addition of known amounts of the drug to various pre-analyzed formulations of ATN. The recoveries in different samples were found to lie in the range from 98.27 to 104.81%, with R.S.D. of 2.64%.

Interference: The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than ±5% for determination of ATN. Under the optimum experimental conditions, the effects of potential interferents on the voltammetric response of 1.0×10^{-6} M ATN as a standard were evaluated (Table 3). The experimental results showed that hundred-fold excess concentration of glucose, starch, sucrose, talk, gum acacia, magnesium stearate, ascorbic acid and cystein did not interfere; however, citric acid, lactic acid and tartaric acid interfered with the voltammetric signal of ATN.

Detection of ATN in urine samples: The developed differential-pulse voltammetric method for the ATN determination was applied to urine samples. The recoveries from urine were measured by

Table 4: Determination of ATN in urine samples

Sample	Spiked ($\times10^{-6}$ M)	Found ($\times10^{-6}$ M)[a]	Recovery	S.D.±R.S.D.(%)
1	0.3	0.30	100.33	0.004±1.17
2	0.5	0.49	98.60	0.006±1.15
3	3.0	2.93	97.50	0.07±2.24
4	5.0	5.01	100.22	0.05±1.04

[a]Average of five determinations

spiking drug free urine with known amounts of ATN. The urine samples were diluted 100 times with the phosphate buffer solution before analysis without further pretreatments. A quantitative analysis can be carried out by adding the standard solution of ATN into the detect system of urine sample. The calibration graph was used for the determination of spiked ATN in urine samples. The detection results of four urine samples obtained are listed in Table 4. The recovery determined was in the range from 97.50 to 100.33% and the standard deviation and relative standard deviation are listed in Table 4.

CONCLUSION

In this study, a multi-walled carbon nanotubes modified glassy carbon electrode has been successfully developed for electrocatalytic oxidation of ATN in phosphate buffer solution. MWCNTs showed electrocatalytic action for the oxidation of ATN, characterizing by the enhancement of the peak current, which was probably due to the larger surface area and edge plane like sites/defects of MWCNTs. A suitable electrochemical oxidation mechanism for ATN was proposed. The peak at about 0.90 V was suitable for analysis and the peak current was linear to ATN concentrations over a certain range under the selected conditions. This sensor can be used for voltammetric determination of selected analyte as low as 2.34×10^{-8} M with good reproducibility. The modified electrode has been used to determine ATN in pharmaceutical samples. Also the results obtained in the analysis of ATN in spiked urine samples demonstrated the applicability of the method for real sample analysis.

REFERENCES

Ajayan, P.M., 1999. Nanotubes from carbon. Chem. Rev., 99: 1787-1800.

Amini-Shirazi, N., R. Ahmadkhaniha, S. Shadnia, M.H. Ghahremani, M. Abdollahi, A. Dadgar and A. Kebriaeezadeh, 2010. Determination of VPA and its two important metabolites in Iranian overdosed patients. Int. J. Pharmacol., 6: 854-862.

Banks, C.E., R.R. Moore, T.J. Davies and R.G. Compton, 2004. Investigation of modified basal plane pyrolytic graphite electrodes: Definitive evidence for the electrocatalytic properties of the ends of carbon nanotubes. Chem. Commun., 16: 1804-1805.

Banks, C.E. and R.G. Compton, 2005. Exploring the electrocatalytic sites of carbon nanotubes for NADH detection: An edge plane pyrolytic graphite electrode study. Analyst, 130: 1232-1239.

Banks, C.E. and R.G. Compton, 2006. New electrodes for old: From carbon nanotubes to edge plane pyrolytic graphite. Analyst, 131: 15-21.

Britto, P.J., K.S.V. Santhanam, A. Rubio, J.A. Alonso and P.M. Ajayan, 1999. Improved charge transfer at carbon nanotube electrodes. Adv. Mater., 11: 154-157.

Cervini, P., L.A. Ramos and E.T.G. Cavalheiro, 2007. Determination of atenolol at a graphite-polyurethane composite electrode. Talanta, 72: 206-209.

Dash, P.K. and Y. Balto, 2011. Generation of nano-copper particles through wire explosion method and its characterization. Res. J. Nanosci. Nanotechnol., 1: 25-33.

Gosser, D.K., 1993. Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms, VCH, New York, pp: 43.

Goyal, R.N. and S.P. Singh, 2006. Voltammetric determination of atenolol at C60-modified glassy carbon electrodes. Talanta, 69: 932-937.

Goyal, R.N., V.K. Gupta, M. Oyama and N. Bachheti, 2006. Differential pulse voltammetric determination of atenolol in pharmaceutical formulations and urine using nanogold modified indium tin oxide electrode. Electrochem. Commun., 8: 65-70.

Hegde, R.N., N.P. Shetti and S.T. Nandibewoor, 2009a. Electro-oxidation and determination of trazodone at multi-walled carbon nanotube-modified glassy carbon electrode. Talanta, 79: 361-368.

Hegde, R.N., R.R. Hosamani and S.T. Nandibewoor, 2009b. Voltammetric oxidation and determination of cinnarizine at glassy carbon electrode modified with multi-walled carbon nanotubes. Colloids Surf. B Biointer., 72: 259-265.

Iijima, S., 1991. Helical microtubules of graphitic carbon. Nature, 354: 56-58.

Laviron, E., 1979. General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems. J. Electroanal. Chem., 101: 19-28.

Leloux, M.S. and F. Dost, 1991. Doping analysis of beta-blocking drugs using high-performance liquid chromatography. Chromatographia, 32: 429-435.

Li, X.X., L.H. Shen, S. Wang and H.L. Qi, 2008. Electrochemical behavior of atenolol at multi-wall carbon nanotubes modified glassy carbon electrodes and its analytical applications. Fenxi Shiyanshi, 27: 1-4.

Maria, R., T. E. Aref, G. Fink, M. Cheurer and T.A. Ternes, 2010. Fate of beta blockers in aquatic-sediment systems: Sorption and biotransformation. Environ. Sci. Technol., 44: 962-970.

Merkoci, A., 2006. Carbon nanotubes in analytical sciences. Microchim. Acta, 152: 157-174.

Merkoci, A., 2007. Nanobiomaterials in electroanalysis. Electroanalysis, 19: 739-741.

Nugent, J.M., K.S.V. Santhanam, A. Rubio and P.M. Ajayan, 2001. Fast electron transfer kinetics on multiwalled carbon nanotube microbundle electrodes. Nano Lett., 1: 87-91.

Pang, Y.L., A.Z. Abdullah and S. Bhatia, 2010. Comparison of sonocatalytic activities on the degradation of rhodamine B in the presence of TiO2 powder and nanotubes. J. Applied Sci., 10: 1068-1075.

Patil, R.H., R.N. Hegde and S.T. Nandibewoor, 2009. Voltammetric oxidation and determination of atenolol using a carbon paste electrode. Ind. Eng. Chem. Res., 48: 10206-10210.

Singh, M., S. Manikandan and A.K. Kumaraguru, 2011. Nanoparticles: A new technology with wide applications. Res. J. Nanosci. Nanotechnol., 1: 1-11.

Sljukic, B., C.E. Banks and R.G. Compton, 2006. Iron oxide particles are the active Sites for hydrogen peroxide sensing at multiwalled carbon nanotube modified electrodes. Nano Lett., 6: 1556-1558.

Snook, C.P., K. Sigvaldaso and J. Kristinsson, 2000. Severe atenolol and diltiazem overdose. J. Toxicol. Clin. Toxicol., 38: 661-665.

Ternes, T.A., 2001. Analytical methods for the determination of pharmaceuticals in aqueous environmental samples. Trends Anal. Chem., 20: 419-434.

Tomita, M., T. Okuyama, S. Watanabe, B. Uno and S. Kawai, 1991. High performance liquid chromatographic determination of glyphosate and (aminomethyl)phosphonic acid in human serum after conversion into p-toluenesulphonyl derivatives. J. Chromatogr. Biomed. Appl., 566: 239-243.

Trojanowicz, M., 2006. Analytical applications of carbon nanotubes: A review. Trend. Anal. Chem., 25: 480-489.

Wadworth, A.N., D. Murdoch and R.N. Brodgen, 1991. Atenolol: A reappraisal of its pharmacological properties and therapeutic use in cardiovascular disorders. Drugs, 42: 468-510.

Wu, Y., X. Ji and S. Hu, 2004. Studies on electrochemical oxidation of azithromycin and its interaction with bovine serum albumin. Bioelectrochemistry, 64: 91-97.

Zainudin, S.N.F., M. Markom, H. Abdullah, R. Adami and S.M. Tasirin, 2011. Supercritical anti-solvent process for the enhancement of dye-sensitized solar cell efficiency: A review. Asian J. Applied Sci., 4: 331-342.

Zhao, G.C., Z.Z. Yin, L. Zhang and X.W. Xian, 2005. Direct electrochemistry of cytochrome c on a multi-walled carbon nanotubes modified electrode and its electrocatalytic activity for the reduction of H2O2. Electrochem. Commun., 7: 256-260.