**IJPSR (2021), Volume 12, Issue 12** **(Research Article)**

INTERNATIONAL JOURNAL OF PHARMACEUTICAL SCIENCES AND RESEARCH

Received on 11 January 2021; received in revised form, 08 June 2021; accepted, 13 June 2021; published 01 December 2021

# AN EFFECTIVE AND FACILE VOLTAMMETRIC STUDY OF ATRACURIUM BESILATE AT FUNCTIONALIZED MWCNTs MODIFIED GLASSY CARBON ELECTRODE

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**Keywords:**

Atracurium besilate, Stripping voltammetry, Carbon nanotubes, Glassy carbon electrode.

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**ABSTRACT:** In the present study, a modified glassy carbon electrode by a conductive film containing, i.e., functionalized multi-walled carbon nanotubes (f-MWCNTs) was selected for the determination of atracurium besilate (in short ACB), an anesthetic drug by applying the cyclic voltammetry (CV) and differential pulse anodic adsorptive stripping voltammetry (DP-AASV) techniques. Herein, nanomaterials suspension is prepared and further examined by field emission scanning electron microscopy (FESEM) analytical technique. All the effective electrochemical parameters for the detection of ACB drugs were optimized, and the oxidation peak current (Ip) of the drug was used for monitoring. The obtained results confirmed that the oxidation peak current (Ip) increased linearly by increasing in the concentration range from $1.25\times10^{-7}$ M to $7.75\times10^{-4}$ M of ACB. The limit of quantification (LOQ) and limit of detection (LOD) are 52.6 ng/mL and 1.43 ng/mL achieved, respectively. The sensor (nanomaterials modified glassy carbon electrode) revealed extreme sensitivity/sensing towards atracurium besilate (ACB) pharmaceuticals in bulk samples.

**INTRODUCTION:** Atracurium besilate (Benzenesulfonate; 5-[3-[1-[(3,4-dimethoxyphenyl) methyl ]-6,7-dimethoxy-2-methyl-3,4-dihydro-1H-isoquinolin-2-ium-2yl] propanoyloxy] pentyl-3-[1-[(3, 4-dimethoxyphenyl) methyl] -6,7-dimethoxy-2-methyl-3,4-dihydro-1H-isoquinolin- 2-ium-2-yl] propanoate) as represented in Scheme 1, is a drug used in addition to other medications to supply skeletal muscle relaxation during surgery or mechanical ventilation [1, 3]. It can also be consumed to help with endotracheal intubation, but suxamethonium (succinylcholine) is generally brought if this needs to be done quickly [4, 5]. It is given through injection into the veins. Effects are greatest at about four minutes and last for up to an h.

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**DOI:** 10.13040/IJPSR.0975-8232.12(12).6432-41

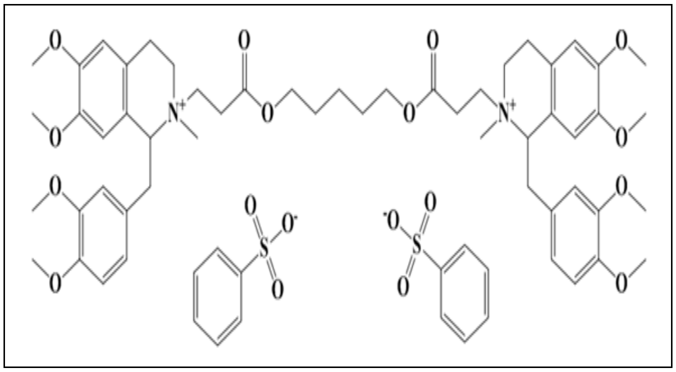
**This article can be accessed online on** www.ijpsr.com

**DOI link:** http://dx.doi.org/10.13040/IJPSR.0975-8232.12(12).6432-41

The common side-effects incorporate flushing of the skin and low blood pressure [6, 7]. While serious side-effects may include allergic reactions. However, it is not associated with malignant hyperthermia. Prolonged paralysis may occur in people with conditions like myasthenia gravis [7, 10]. Atracurium is in the neuromuscular-blocker family of medications and is of the non-depolarizing type. It works by blocking the action of acetylcholine on skeletal muscles [11, 12]. This drug is on the World Health Organization's list as essential medicines, the most effective and safe medicines needed in a health system. Atracurium is also available as a generic medication [12, 16]. The wholesale cost in the developing world is about 1.69 to 1.87 USD per dose [17, 21]. Literature survey reveals that several analytical methods have been reported for the determination of ACB in pharmaceutical combinations and some real samples, which are including high-performance chromatography (HPLC), 2,22-24 micellar electrokinetic chromatography (MEKC), liquid chromatography [25, 27]. MALDI/ionization time-of-flight mass spectrometry, capillary electrophoresis, spectrophotometric and electrochemical methods. However, these methods are often overpriced, complicated, and require lengthy procedures and tedious sample pretreatment. In some cases, low sensitivity and selectivity make them unsuitable for routine analysis.

Among the various quantification methods, electrochemical techniques appear as a simple, sensitive, inexpensive, accurate, and fast alternative for the determination of pharmaceutical compounds compared with other methods. Accompanied by sensing technology development, electrochemical sensors play an important role because of their easy, fast, low cost, and highly sensing properties. Due to low electron transfer kinetic and high over-potential and oxidation of organic compounds such as drugs at the bare solid electrodes, their modification extends the field research in analytical chemistry.

Among the wide range of electrode modifiers, acid functionalized multi-walled carbon nanotubes are exclusively considered metallic conductors because of their interesting and useful characteristics, e.g., high surface area, excellent electrical conductivity, high chemical stability, and mechanical strength, which makes them suitable for electrochemical employment. The f-MWCNTs exhibit π-conjugative structure with a highly hydrophobic surface. This unique property allows it to interact with some organic aromatic compounds through π to π electronic as well as hydrophobic interactions to form a new complex. A logical extension in the property of modifiers is related to find new combinations of the existing materials such as conductive polymer with f-MWCNTs. Widespread applications of the two components offer the possibility to observe synergetic effects, which is one of the main reasons that lead to this subject. In the past, various studies are proved that certain discrete properties of the components of conducting functionalized multi-walled carbon nanotubes are enhanced, thus validating their high suitability for some technological applications and provide the basis for the development of numerous novel sensors with high sensitivity, good selectivity, excellent environmental stability, and low power consumption. The applications of nanoparticles in electrochemical sensors are their unique abilities to alter mass transport, conductivity, and electro catalytic activity because of their miniaturized size. They provide a large specific surface area as well as mass transport enhancement. The catalytic properties of metal particles severely depend on their size and shape.



SCHEME 1: CHEMICAL STRUCTURE OF ACB

## Experimental:

**Chemicals:** Atracurium besilate liquid was used as a pharmaceutical dosage form, purchased from the local market, each tablet containing 50 mg of atracurium besilate along with some contents. To prepare the solutions of tablets, initially, the drug content of ten tablets was weighed and finely powdered. The average mass per tablet was calculated. A portion of the finely grounded material equivalent to 50 mg of atracurium besilate was accurately weighed and dissolved in 20 ml of methanol; after it, the solution was diluted with 15 ml of water and subjected to sonication for 15 min to get a homogenous solution. After dissolution, the content of the flask was centrifuged for 30 min at 1500 rpm. An aliquot of $3\times10^{-3}$ mol/L of the solution was then analyzed according to the proposed voltammetric procedure after diluting its appropriate volume with 9 ml of BR buffer in an electrochemical cell and performed determination of ACB in the liquid form by using calibration curve method. The effective concentration (E.C.) of the sample in the electrochemical cell was calculated as (concentration of analyte solution × volume of analyte solution added in the cell) total volume of solution in the cell. Where the concentration of the solution is measured in mol/L, and the volume of the solution is measured in mL. The concentration mentioned throughout this research work is in terms of effective concentrations.

**Pre-Treatment of Glassy Carbon Electrode and Voltammetric Procedure:** The GCE was polished with 0.08 μm alumina slurry and further subjected to sonication for a short duration before each measurement to remove all impurities remained onto the surface of the electrode and dried at 30 °C in oven. While for the de-oxygenation of sample solutions, a continuous stream of nitrogen gas (99% purity) was allowed to pass through the solutions before each of the voltammetric measurements.

**Instrumentation:** Electrochemical measurements were performed using a model 1230A [SR 400] electrochemical analyser (CHI Instrument, USA). The utilized electrodes were a glassy carbon electrode (GCE) as a working electrode, Ag/AgCl (3.0 mol/L KCl) as a reference electrode, and a platinum electrode as an auxiliary electrode. All the solutions examined by electrochemical techniques were purged for 10 min with purified nitrogen gas in which a continuous stream of nitrogen was passed over the solutions before each of the measurements. All pH-metric measurements were made on a CHINO-DB-1011 (Chino Scientific Instruments Mfg, Rajasthan, India) digital pH meter fitted with a glass electrode.

**Preparation of F-Mwcnts Suspension and GCE Modification:** 4 mg of MWCNTs were acidified with 4 ml of a mixture of acid ($HNO_3$: $H_2SO_4$) in the ratio of 1:3 respectively for 2 h, and acidified CNTs were washed with water until water gave pH 7.0. These activated CNTs were dried and then dispersed in the mixture of 5 mL N, N- dimethyl formamide + 0.5 mL Nafion [a conducting polymer (0.5% in ethanol)] and diluted with water followed by hot sonication for 4 h in an ultrasonic bath to get a homogeneous suspension. 10 μL of this suspension was allowed to drop onto the pre-treated bare glassy carbon electrode surface, using a micropipette, and left to dry at room temperature.

**Analytical Procedure:** 10 mL of the total solution containing BR buffer of pH 11 and the appropriate concentration of the atracurium besilate were poured in the electrochemical cell, and then a pure deoxygenated nitrogen stream was passed for 15 min to remove the oxygen gas before measurements. Electrochemical pre-treatment was always performed in the same solution in which the measurement was subsequently carried out. The electrode was carried out for a selected time while the solution was stirred at 3000 rpm. The differential pulse anodic adsorptive stripping and cyclic voltammograms were recorded after the optimization of operational parameters.

## RESULTS AND DISCUSSION:

**Characterization of f-MWCNTs/Nafion Nano-materials:** The surface morphology of f-MWCNTs was studied by field emission scanning electron microscopy (FESEM), which clearly shows the nano-sized diameter (~8 nm to 22 nm range) of nanotubes present in nanomaterials as shown in **Fig. 1**.

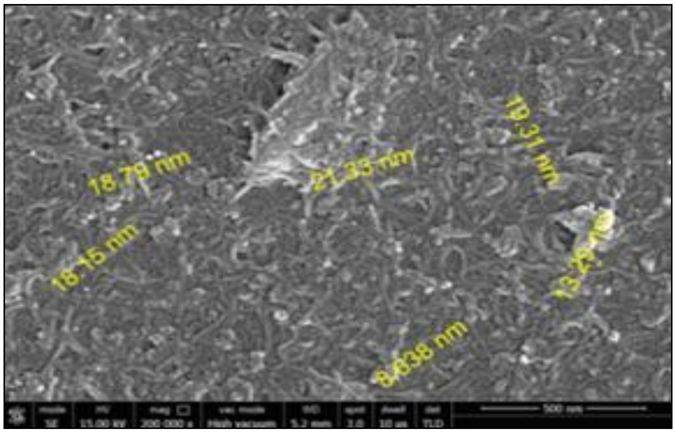


FIG. 1: THE FESEM IMAGE OF F-MWCNTS NANO-MATERIALS

**Optimization of pH:** The effect of pH on anodic peak current of $3\times10^{-4}$ mol L-1ACB was investigated by DP-AAdSV. The pH range was studied from 9 to 12. A well-defined oxidation peak and a high peak current were obtained at pH 11; thus, further studies were carried out at this pH. **Fig. 2** shows the effect of pH of supporting electrolyte on peak current. A shift of the peak potential towards a more positive direction scale was observed as the pH increased, which indicates the existence of a proton involvement 28 in the coupled reaction of the ACB oxidation process. Furthermore, the peak potential was found to be linearly dependent on pH, indicating the direct involvement of proton in the reduction process, and the corresponding regression equation was found to be Ep (V) = -0.0584 pH + 1.3218 with $r^2$ = 0.9909. The slope value 58.4 mV/pH is close to the theoretical value 59 mV/pH, indicating that the deprotonation step within the ACB is prior to the electron transfer step and the number of protons and electrons involved in the oxidation mechanism are in equal ratio.

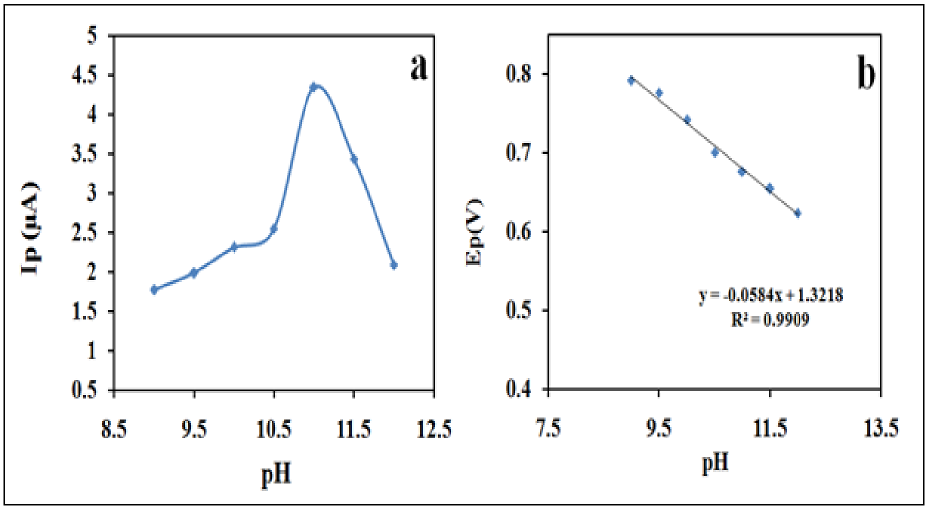


**FIG. 2: INFLUENCE OF pH ON PEAK CURRENT OF 1.8×$10^{-4}$ MOL L-1ACB IN BR BUFFER OF PH RANGE 9-12 (A), AND PLOT OF THE PEAK POTENTIAL (EP) VERSUS PH (B)**

**Electrochemical Oxidative Behavior of ACB at Modified Electrode:** The cyclic voltammograms of 1.82×$10^{-4}$ g/mL ACB in BR-buffer of pH 11 at bare GCE and f-MWCNTs/GCE exhibits a single well-defined anodic peak in the 0.0 to 0.8V. This anodic peak may be assigned to the oxidation of C-N group, which is not accompanied by a corresponding cathodic one that is indicating the irreversibility of the electrode process.

**Scan Rate Effect:** The influence of the potential scan rate on anodic peak current (Ip) and anodic peak potential (Ep) were investigated for the solution at scan rate range 20-220 $mVs^{-1}$ range as depicted in **Fig. 3**.

It was found that the peak potential (Ep) shifted towards more positive values with increasing the scan rate from 20-220 $mVs^{-1}$ which follows the criteria of irreversibility as mentioned in Nicholson theory 29 beyond this linear variation was lost.

The effect of scan rate (ν) on peak current (Ip) was examined under the above experimental conditions. As the quite promising for linearity it follows the Randles-Sevcik equation [28, 30, 31] (equation-1):

$$Ip = (2.99\times10^{5})\ n\ [\alpha n']^{1/2} A\ Co\ Do^{1/2}\ \nu^{1/2}$$

where n is the number of electrons exchanged in reduction, n' is the number of electrons involved in the rate-determining step, α is the charge transfer coefficient, A ($cm^{-2}$) is the apparent surface area of the electrode, Co (mol/L) is the concentration of the electroactive species, Ip (µA) is the anodic peak current, Do ($cm^{-2}$ $s^{-1}$) is the diffusion coefficient of the electro active species, and ν (mV $s^{-1}$) is the scan rate.

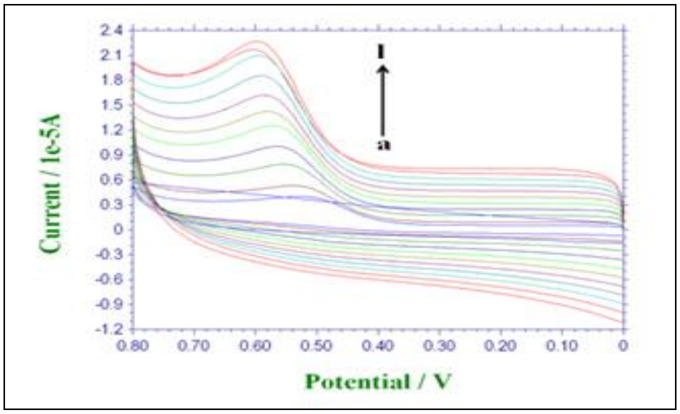


**FIG. 3: CYCLIC VOLTAMMOGRAMS OF ACB AT DIFFERENT SCAN RATES AT F-MWCNTS/GCE WITH (A) BLANK, (B) 20 MV/S, (C) 40 MV/S, (D) 60 MV/S, (E) 80 MV/S, (F) 100 MV/S, (G) 120 MV/S, (H) 140 MV/S, (I) 160 MV/S, (J) 180 MV/S, (K) 200 MV/S, AND (L) 220 MV/S IN BR-BUFFER OF PH 11 WITH ACB CONCENTRATION 1.82×$10^{-4}$ M**

Since, the linear plots of peak current (Ip) versus square root of scan rate (ν1/2) following the peak current should be linear with respect of square root of scan rate for a diffusion-controlled process, whereas the peak current should be linear with respect to scan rate for an adsorption-controlled process. Here, a plot between peak current (Ip) and the square root of scan rate ($\nu^{1/2}$) **Fig. 4**. was quite promising for linearity according to the Randles-Sevcik equation equation-2 [30, 31].

$$Ip\ (\mu A) = 16.66\ \nu^{1/2} - 28.44, r)^2 = 0.9923$$

The finding was further confirmed by plotting logIp versus logν **Fig. 4**. Where a straight line was observed, which can be express by the equation-3:

$$\log Ip\ (\mu A) = 0.473 \log\nu + 0.9434,\ r^2 = 0.982$$

The slope of this curve is 0.473, quite close to the theoretical value of 0.5 also confirms the diffusion-controlled nature of the electrode process [32, 35].

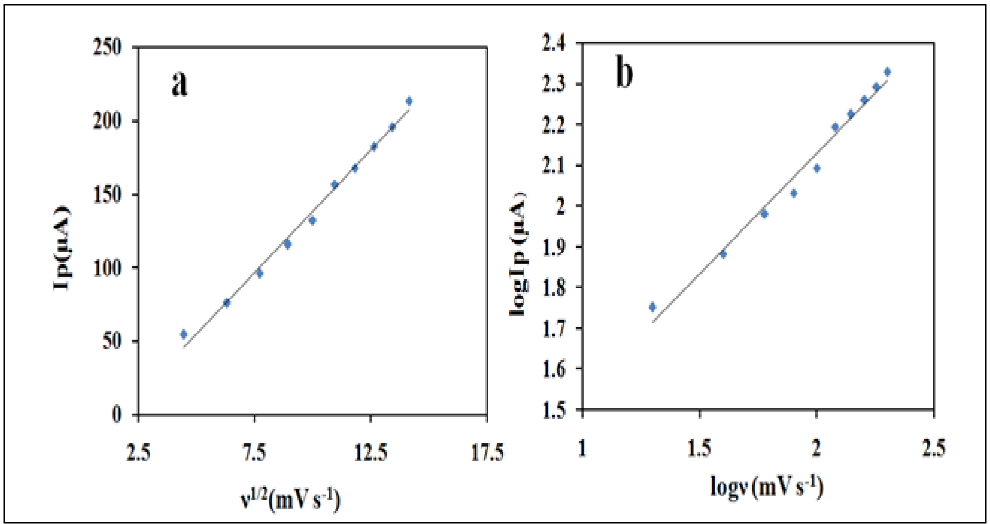


**FIG. 4: PLOT OF PEAK CURRENT (IP) VERSUS SQUARE ROOT OF SCAN RATE ($N^{1/2}$) OBTAINED BY VOLTAMMOGRAMS FIG. 3: FOR ACB IN $1.82\times10^{-4}$ M CONCENTRATION IN BR-BUFFER OF pH 11 (A) AND PLOT OF LOGARITHM OF PEAK CURRENT (LOGIP) VERSUS LOGARITHM OF SCAN RATE (LOGN) (B)**

According to Laviron [36, 37] that an irreversible electrode process Epa is defined through the given equation-4.

$$E_P = E^\circ + RT/\alpha n\, F[0.78 + 1n(D^{1/2/0}/k_s) - 0.51n\ RT/\alpha n\, F] + (RT/\alpha n\, F)1n\alpha$$

Where α is the transfer coefficient, ν the scan rate, n the number of electrons transferred, $K_s$ the standard heterogeneous rate constant of the reaction and $E_0$ is the formal redox Potential, and R, T, and F have their usual meanings. Thus, αn was easily calculated to be 0.0274 from the slope of Ep versus logν. According to Bard and Faulkner [32, 33] α can be given as equation-5.

$$\alpha = 47.7/\ (Ep - Ep/2)\ mV$$

Where Ep/2 is the potential where the current is at half the peak value. Thus, the value of α was calculated to be 0.229, and the number of electrons transferred (n) in the oxidation of atracurium brosilate 3.95 is equal to 4e. If the value of $E_0$ is known, the value of $k_0$ could be obtained from the intercept of the $E_0$ of the Laviron equation. From the intercept of $E_p$ versus log ν curve, the value of E0, namely the value of intercept in the plot between Ep and log ν is 0.728. $k_0$ values of bare GCE and f-MWCNTs/GCE are 0.172 $s^{-1}$ and 0.52 $s^{-1}$. So, the rate of reaction is ten times increase at the modified electrode than bare electrode.

**Electrochemical Oxidation of ACB at Modified Electrode:** In **Fig. 5**. The cyclic voltammograms of $1.82\times10^{-4}$ g/mL ACB in pH 11 on the surface of bare GCE (curve-b) and f-MWCNTs/GCE (curve-c). Here, at f-MWCNTs/GCE, a well-defined anodic peak is obtained for ACB at 0.625 V and compared with the bare GCE electrode. It is observed that the modification by f-MWCNTs gave a significant catalytic effect on the electrochemical oxidation of ACB, leading to a decrease of overpotential in the process, and an enhancement of the peak current is observed. The reason for the well-defined peak of the f-MWCNTs/GCE is due to nano-sized f-MWCNTs present at GCE [29, 39].

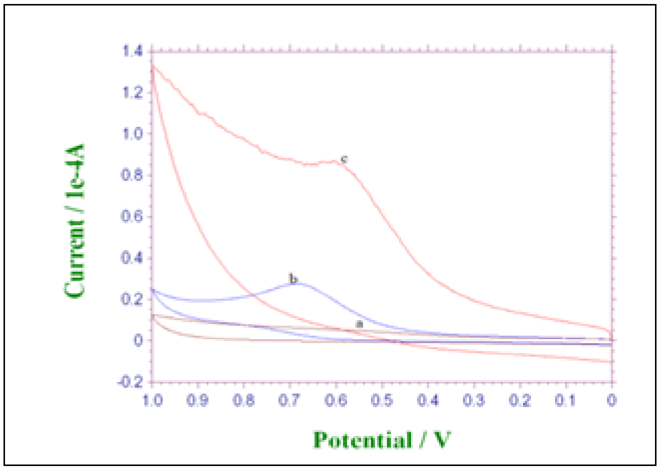


**FIG. 5: COMPARATIVE CYCLIC VOL-TAMMOGRAMS FOR ACB WITH (CURVE A) BLANK, (CURVE B) BARE GCE AND (CURVE C) F-MWCNTS/NAFION/GCE**

**Kinetics of Oxidation of ACB:** Determination of parameter [αn'] and heterogeneous rate constant (ks) According to Laviron's theory [29, 39] the Ep is defined as by the following equation-6 [22, 24].

$$E_p = E^{\circ} + RT/\alpha n\ F\ [0.78 + 1n\ (D^{1/2}/^{0}/K_s)\ -0.51n\ RT/\alpha n] + (RT/\alpha n\ F)\ 1n\upsilon$$

Where α is the transfer coefficient, ν is the scan rate, n is the number of electrons transferred, ks is the standard heterogeneous rate constant of the reaction, and E0 is the formal redox potential, and R, T, and F have their usual meanings. **Fig. 6A.** Shows the plot between Ep and scan rate. Thus, αn' was easily calculated to be 0.0878 from the slope, and ks was easily calculated to be 0.7594 from the intercept of Ep versus log ν as plotted in **Fig. 6B**. A straight line of Ep versus logν plot is expressed by the following linear regression equation-7.

$$Ep = 0.021\ \log\nu + 1.113,\ r^2 = 0.983$$

The value of αn' and ks were calculated by comparing the slope of equation-7 with theoretical values and were found to be 0.916 and 0.52, respectively.

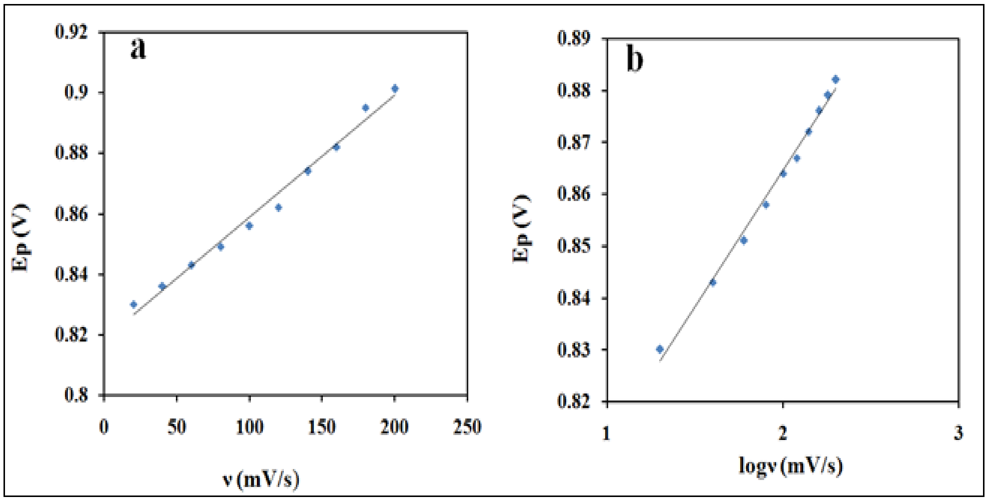


**FIG. 6: PLOT OF PEAK POTENTIAL VERSUS SCAN RATE FROM RECORDED VOLTAMMOGRAMS OF FIG. 5: FOR ACB IN 1.82×10$^{-4}$ M CONCENTRATION IN BR BUFFER OF PH 11 (A), AND PLOT OF PEAK POTENTIAL VERSUS LOGARITHM OF SCAN RATE (B)**

**Determination of Total Number of Electrons:** The total number of electrons involved during the overall oxidation process was calculated by analyzing the charge consumed by the optimized concentration of ACB. This was accomplished by taking 5 mL of 50 mg mL$^{-1}$ ACB in a cell and electrolysis was performed at a potential of 0.625 V against Ag/AgCl for 10 h. During the long-term electrolysis, solutions were stirred and purged with nitrogen. Due to this electrolysis, current efficiency and completion of electrolysis were assumed to be nearly 100% and 99.98%, respectively. The total number of electrons involved in the overall oxidation process was calculated using the formula Q = nFN; where Q is charge in coulombs, N is number of moles of ACB, and F is Faraday's constant. The value of n was found to be 4 for ACB at f-MWCNTs/GCE [28, 39, 40].

**Determination of Diffusion Coefficient (Do Cm2/s):** Electro-oxidation of 1.82×10$^{-4}$ M ACB at the GCE and NAF/CNTs/GCE was investigated by employing chronocoulometry (CC) for the determination of the kinetics and mechanisms of electrode reactions. Employing double-potential step CC, after point-by-point background subtraction, the plot of charge (Q) versus the square root of time ($t^{1/2}$) showed a linear relationship. According to the integrated Cottrell equation, the diffusion coefficient and $Q_{ads}$ of ACB could then be estimated from the slope and intercept, respectively, of the plot of total Q versus $t^{1/2}$, given by the Anson equation [28, 41, 42]. As can be seen from the table, the value of the slope and the $Q_{ads}$ for the f-MWCNTs/GCE were more than that for other electrodes, confirming that NAF along with CNT makes the compilation of ACB into the electrode surface more effective. The surface coverage (Γ́^O) for all four electrodes was calculated using the following relationship equation-8.

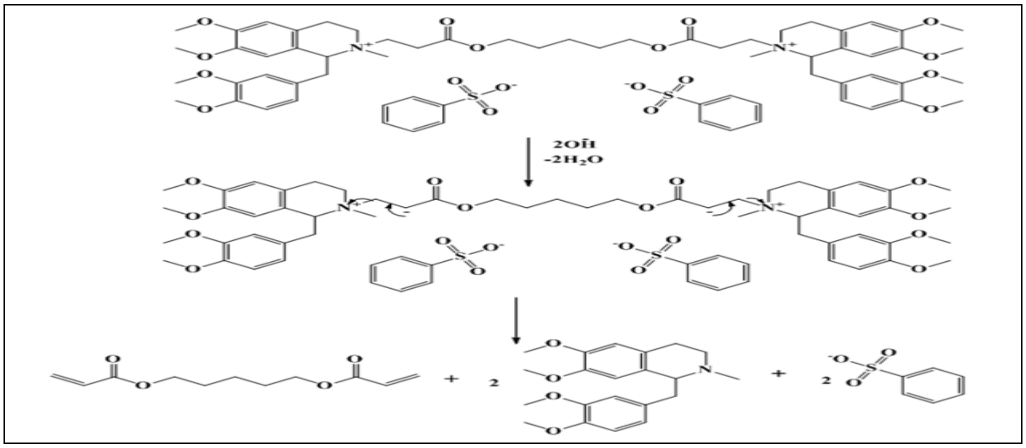
$$Qads = (I^{o})\ n\ FAI^{o}$$

From these values, it was observed that the surface coverage was highest in the case of the NAF/CNTs/GCE. Thus, due to the synergistic effect of NAF and CNTs, the electrode surface coverage by ACB drastically increased, and the kinetics of oxidation became more facile, confirming the results obtained from CV. The Integrated Cottrell equation is equation-9.

$$Qd = 2nFAD1/2oCot1/\ 2/\ \pi\ 1/2$$

The apparent diffusion coefficient (Do) of ACB in the presence of bare GCE and f-MWCNTs in $1.82\times10^{-4}$ g/mL was also calculated. The diffusion coefficient of f-MWCNTs/GCE is larger than bare/GCE.

**Proposed Oxidation Mechanism of ACB:** On the basis of CV, CPC, and pH studies, Scheme-2 might be proposed for the oxidation of ACB in which participation of 4e- and 4H+ is shown. Literature also supports such mechanism [43, 44].



**SCHEME 2: OXIDATION REACTION MECHANISM OF THE ATRACURIUM BESILATE**

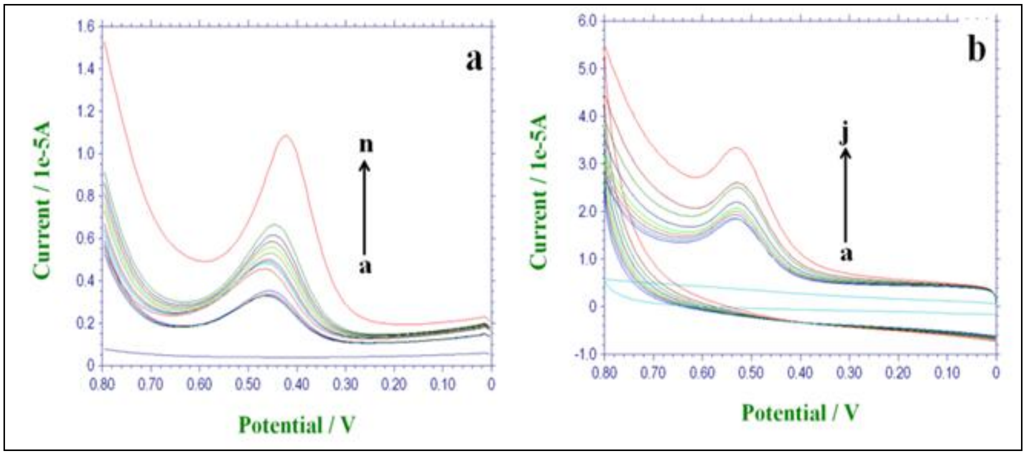


**FIG. 7: (A) THE DP-AADS VOLTAMMOGRAMS OF ACB AT DIFFERENT CONCENTRATIONS (A) BLANK (B) $1.25\times10^{-7}$ M (C) $5.45\times10^{-7}$ M (D) $7.78\times10^{-7}$ M (E) $8.63\times10^{-7}$ M (F) $4.78\times10^{-6}$ M (G) $5.95\times10^{-6}$ M (H) $7.89\times10^{-6}$ M (I) $8.04\times10^{-6}$ M (J) $2.46\times10^{-5}$ M (K) $3.42\times10^{-5}$ M (L) $2.43\times10^{-5}$ M (M) $5.34\times10^{-5}$ M AND (N) $7.75\times10^{-5}$ M IN BULK FORM IN BR BUFFER (pH 11) at f-MWCNTs/NAFION/GCE. (B) THE CYCLIC VOLTAMMOGRAMS OF ACB AT DIFFERENT CONCENTRATIONS (A) BLANK (B) $4.72\times10^{-7}$ M (C) $6.34\times10^{-7}$ M (D) $9.46\times10^{-7}$ M (E) $4.78\times10^{-6}$ M (F) $6.12\times10^{-6}$ M (G) $8.74\times10^{-6}$ M (H) $9.45\times10^{-6}$ M (I) $4.67\times10^{-5}$ M AND (J) $5.78\times10^{-5}$ M in BULK FORM IN BR BUFFER (pH 11) AT f-MWCNTs/NAFION/GCE**

Since, voltammetry methods are cost-effective, more accurate, sensitive, precise, and absent of lengthy extraction processes, they are widely used for analytical purposes. In the present paper, differential pulse voltammetry and DP-AAdSV technique were optimized for the determination of ACB in bulk form and in human urine at GCE.

**Effect of Concentration:** The peak current was found to be linearly dependent on the concentrations of the analytic present in the solution. Under optimized conditions, the linear relationship between peak current and concentrations were examined DP-AAdSV and CV method **Fig. 7A.** and **7B**) was validated for the determination of ACB in the bulk form [44, 46].

The quantitative evaluation of ACB is based on the peak current of the concentration. The peak current increased linearly with increasing concentration of ACB in the range 1.25×10-7-8. 42×10$^{-4}$ M at the f-MWCNTs/GCE sensor [44]. **Fig. 8A** and **8B** are obtained as linear calibration curves for the used techniques and can be expressed by the following equations 10 and 11.

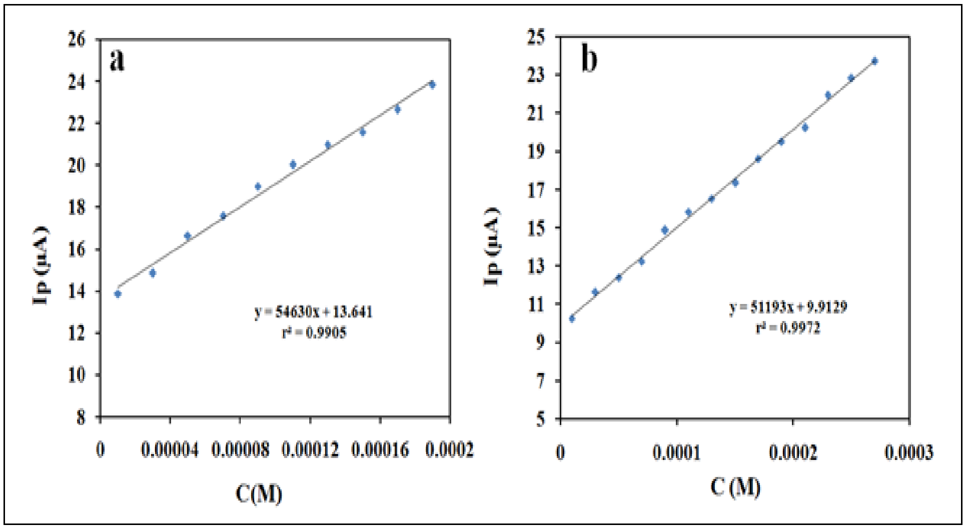


**FIG. 8: (A) DP-AADSV AND (B) CV PLOTS OF PEAK CURRENT (IP) VERSUS CONCENTRATION (C) FROM VOLTAMMOGRAMS AS SHOWN IN FIGURE-6 OF ACB WITH VARYING CONCENTRATIONS IN BR BUFFER OF PH 11**

**Validation of the Proposed Method:** A linearity range over the concentrations in the working range of (1.25×10$^{-7}$ -8.42×10$^{-4}$ M) was examined, and peak response was found to be linear over range 4.72×10$^{-7}$ -8.82×10$^{-4}$ M for CV and 1.25×10$^{-7}$ -7.75×10$^{-4}$ M for DP-AAdSV as tabulated in **Table 1**.

$$\text{DP-AAdSV: Ip } (\mu\text{A}) = (5.463\times10^{4})\ \text{C(M)} + 13.641,\ r^2 = 0.9905$$

$$\text{CV: Ip } (\mu\text{A}) = (5.1193\times10^{4})\ \text{C(M)} + 9.9129,\ r^2 = 0.9972$$

Detection limit is calculated by the formula LOD = 3SD/M, where SD is standard deviation of intercept and M is slope of the regression line.

The calculated LOD values of ACB are 6.21×10$^{-8}$ g/mL for CV and 1.43×10$^{-9}$ g/mL for DP-AAdSV. The quantification limit (LOQ) is examined by the equation LOQ =10 SD/M. These values are 1.85×10$^{-7}$ g/mL for CV and 4.23×10$^{-8}$ g/mL for DP-AAdSV method [45, 46]. The proposed method based on the electrocatalytic behavior of ACB is much sensitive for its determination at f-MWCNTs/GCE. The detection limit of ACB has been compared with bare-GCE and f-MWCNTs/GCE. The f-MWCNT/GCE electrode's detection limit is less compared to the bare-GCE electrode, and the modified electrode is more sensitive than the bare electrode **Table 1**.

**Accuracy and Precision:** The intra-day and inter-day accuracy and precision of the proposed procedure were estimated by analyzing 3.25×10$^{-6}$-7.28×10$^{-4}$ g ACB solutions three times in six successive days.

The relative error of 0.054 to 0.072 and % RSD of 0.46-1.54 indicates the high accuracy and precision of the proposed method [46, 48].

**TABLE 1: COMPARABLE ELECTROCHEMICAL STATICS OF ACB DRUG DETERMINED AT BARE/GCE AND F-MWCNTS/GCE WITH DP-AADSV AND CV TECHNIQUES**

| Statistical values | DP-AAdSV | CV |
|---|---|---|
| **Bare GCE** | | |
| Concentration range | $5.45\times10^{-6}$-$7.28\times10^{-4}$ M | $3.25\times10^{-6}$-$4.56\times10^{-4}$ M |
| Slope | $1.7877\times10^{4}$ | $2.2099\times10^{4}$ |
| Intercept | 0.6092 | 0.8582 |
| $R^2$ | 0.9881 | 0.9929 |
| LOD | $1.4\times10^{-8}$ g/mL | $60.21\times10^{-8}$ g/mL |
| LOQ | $4.23\times10^{-7}$ g/mL | $1.85\times10^{-7}$ g/mL |
| S.D | 0.0054 | 0.072 |
| **Modified GCE** | | |
| Concentration range | $1.25\times10^{-7}$-$7.75\times10^{-4}$ M | $5.45\times10^{-6}$-$7.28\times10^{-4}$ M |
| Slope | $5.1193\times10^{4}$ | $1.7877\times10^{4}$ |
| Intercept | 9.929 | 0.6092 |
| $R^2$ | 0.9972 | 0.9881 |
| LOD | $1.43\times10^{-9}$ g/mL | $6.21\times10^{-8}$ g/mL |
| LOQ | $5.26\times10^{-8}$ g/mL | $1.85\times10^{-7}$ g/mL |
| S. D | 0.000118 | 0.0029 |

**CONCLUSION:** Electrochemical behavior of anesthetic medication ACB was studied at bare and modified glassy carbon electrode, using CV and DP-AAdSV techniques, in the bulk formulation. It was found that the oxidation process of ACB was irreversible, diffusion-controlled, and pH-dependent.

Furthermore, kinetic parameters such as diffusion coefficient (Do), number of electrons (n'), and electron transfer coefficient (ks) were also calculated, which were used to propose an oxidation mechanism. The proposed method is direct, simple, and cost-effective, requires only a small amount of analyte, and does not involve tedious steps such as separation, filtration, extraction, and evaporation, *etc*., required by chromatographic methods. Furthermore, the proposed method has good operational characteristics such as extremely low values of detection limits (LOD), sensitivity and selectivity, wide liner working range, and exhibit good accuracy and precision for the determination of ACB in bulk. So, in the future, it might be more selectively valuable for investigations of ACB in biological samples like blood, serum and urine.

**ACKNOWLEDGMENTS:** This work is financially supported by the Council of Scientific and Industrial Research, New Delhi, India, as grant File Number 09/149(0685)/2016/EMR-I. Authors are also thankful to the Material Research Center, MNIT, Jaipur for FESEM characterizations.

**CONFLICTS OF INTEREST:** There are no conflicts to declare.

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**How to cite this article:**
Singh MJ, Jakhar Vand Sharma DK: An effective and facile voltammetric study of atracurium besilate at functionalized mwcnts modified glassy carbon electrode. Int J Pharm Sci & Res 2021; 12(12): 6432-41. doi: 10.13040/IJPSR.0975-8232.12(12).6432-41.