Physical and Electrical Study of Different Carbone Nanomaterials as Modifying Material for SPCE

Issam A. Latif*, Sundus H. Merza

Department of Chemistry, College of Education for Pure Science /Ibn-Al-Haitham, University of Baghdad, Iraq

Abstract- In this work was prepared three different types of modified screen printed carbon electrode (SPCEs) with drops casted method, the used carbone nanomaterials were the MWCNT, functionalized –MWCNT (f-MWCNT) and After several experiments were made to find an appropriate ratio to make good GOT/f-MWCNT nanocomposite, and found the suspension mixture (1:1) from GOT/f-MWCNT (f-MWCNT-GOT). The electrical and physical properties were performed with cyclic voltammeter technique, and studied the maximum current response, the effective surface area, effect of the pH value and the determination of active surface area for MWCNT-SPCE , f-MWCNT-SPCE and f-MWCNT-GOT/SPCE as   (0.04 cm^2), (0.119 cm^2) and (0.115 cm^2) respectively, the surface coverage concentration (Γ) of the material on each area was calculated and was 9.447×10^{-10}, 9.449×10^{-10} and 9.3×10^{-10} mol cm^{-2} ,for MWCNT ,f-MWCNT and f-MWCNT-GOT respectively, The values of Γ for all three types of electrodes were almost the same and no noticeable difference. These electrodes were used to study the electrochemical behavior of organic compound which consisting an amide functional group, these group founded in huge spectrum of pesticide and medicine compounds etc. the penicillin antibiotic drug family has a β-lactam group (Azetidine-2-one) group. Therefore it was expected to show hydrolysis with opening of the four membered ring azetidine-2-one, in a H+/1ē process. In this work used ampicillin antibiotic AMP. The cyclic voltammetry investigation was shown the signals of anodic peak current were higher than the cathodic current signals $I_{pa}/I_{pc} \neq 1$, which indicated an irreversible electrode reaction, with differential pulse voltammetry was studded the limit of detection (LOD), the modification of SPCE with the f-MWCNT-GOT show the best result than the other two carbone nanomaterial MWCNT and f-MWCNT.

1. Introduction

Carbone nanomaterial like carbon nanotubes (CNTs) and reduced graphene oxide (RGO) were occupied an interested area in the electrochemical researches [1-4] due to their small size and very large surface area, chemical stability and good mechanical properties in addition to its very well electrical properties [5,6]. Carbone nanomaterial can provide information about the chemical composition of its environment as sensors [7] whenever they were used as surface modifiers for electrodes [8, 9]. Moreover, the functionalization of the carbone nanomaterials can affect the surface morphology and change the surface area of the carbone nanomaterials. The edge and/or the basal plane of the carbone nanomaterials can be used as sites to covalent Functionalize .The existence of functional groups on these sites can provide chemical reactivity and utilize to change their surface functionality. In addition, simple reduction of graphene oxide (GO) removes partially oxygen groups and rehybridize the sp^3 carbon atoms to sp^2 leaving it aromatic. The advantage from using residual oxygen groups for chemical functionalize wasn't create additional defects on the graphene surface compared with the reaction with double bonds. The strategies of covalent functionalization of GO and reduced graphene oxide (RGO) were included acylation, amidation, nucleophilic and electrophilic Substitution and an esterification [10, 11]. The nanocomposites of carbon nanotubes with other carbone nanomaterials (GO and / or RGO) have the possibility to enhance the performance of electrochemical sensors, due to the combine of excellent physical and chemical properties of carbone nanotubes with the other nanomaterials [12]. The surface modification of carbone nanomaterials by functionalization with other molecules were made them ideal for use in electrochemical reactions. Electrochemical sensor measured the electron transfer between the analyte and electrode directly, whereby the electrical resistance changes depending on the analyte concentration and related material based on their exceptional properties [13, 14]. The presence of defects and oxygen functional groups on the surface of carbone nanomaterials made them a goal template to obtained nanocomposites through covalent and noncovalent bonding. Carbone nanomaterials and related functionalized nanomaterial nanocomposite are widely used for electrochemical sensing application through decreasing over potential of electrochemical reaction [15, 16]. The aim of this work was to examine the physical and electrical properties of a new functionalized carbone nanomaterial composite (functional graphene oxide composite) as electrode modifier on the working electrode of SPCE to sensing the *β*-lactam group of an antibiotic medicine like ampicillin (AMP).

2. Experimental

2.1. Chemicals and Reagents

All chemicals were analytical grade and purchased from sigma Aldrich and samara drugs industry and used as received without further purification.

2.2. Apparatus

The electrochemical measurements were recorded with Cyclic voltammetric and Differential pulse voltammogram measurements were performed on a potentiostat model 200 μ stat (drop Sens S.L. Oviedo, Spain) with screen printed carbon electrode (SPCE) existing counter electrode CE, reference electrode RE and a carbon working electrode WE with 4 mm diameter printed on a ceramic.

2.3. Preparation and functionalization

2.3.1 Preparation and functionalization of GO and MWCNT.

The GO was prepared and functionalized with thiocarbohydrazide TCH to form (GOT), the functional groups were connected through covalent bonds between 5-substituted 4-amino, 3-mercapto 1, 2, 4 Triazole (ASTT) and the – COOH groups of the GO as illustrated in our previous work [17]. Also the as-received multi walls carbone nanotubes (MWCNT) were refluxed with concentrated hydrochloric acid for 30 min. filtered with polycarbonate filter (What man pore size 0.2μm), washed with double distil water and drayed to remove the impurities, one gram from the treated MWCNT was placed in round bottom flask and dispersed using ultrasonic bathwater in a mixture of concentrated sulfuric acid / nitric acid (v/v =3:1). Then the sample was sonicated for 10 min and refluxed for 5 h. The resulting dispersion was diluted in water, filtrated through the polycarbonate filter (What man pore size 0.2μm) and washed until the pH was neutral, then dried in vacuum oven at 55 °C for 12 h to degas adsorbed CO_2 and hydrogen [18].

2.4. Modification and Pretreatment of the working electrode with GOT/f-MWCNT composite.

After several experiments were made to find an appropriate ratio to make good GOT/f-MWCNT nanocomposite, and found the suspension mixture (1:1) from GOT/f-MWCNT. About 0.1 mg/10ml from each GOT and f-MWCNT was mixed with 3μL Nafion and sonicated for 1h. Two micro liters from the prepared mixture (GOT/f-MWCNT) was deposit on the WE of screen printed carbone electrode (SPCE) and leaved to dry at 25^oC and washed with double distilled water and leaved to dry again. The WE pretreatment made like in our previous work [17].

3. Results and discussion.

3.1. FTIR characterization

A comparison between MWCNT and acidic functionalized f-MWCNT were showed a significant differences between the two spectra in fig.(1), the peak at 1739 cm^{-1} corresponded to stretching vibration of carboxylic group indicated clearly that carboxylic group present in the surface of MWCNT due to the success of the carbon atoms oxidation [19,20]. The peaks of f-MWCNTs at 3741 cm^{-1} is assigned to free OH groups, and the peak at 3448 cm^{-1} can be attributed to the O-H vibration of carboxyl groups (O=C−OH) and C−OH. Appearance peak at 1360 cm^{-1} may be related with O–H bending deformation in COOH groups also increased strength of the signal at 1219 cm−1 may be related with C–O stretching vibration in the carboxylic groups. The peaks at 1641 cm^{-1} and 1512 cm^{-1} associated with the stretching vibration of the MWCNT backbone [21]. The f-MWCNT-GOT nanocomposite was shown a broad peak at 3440 confirms formation hydrogen bonding between carboxylic groups of f-MWCNT and the nitrogen atom of the functional groups of GOT. The absorption of carbonyl group, OH bending, C–O stretching vibration in the carboxylic groups and aromatic C=C bonds are still presence but at slightly lower wave number, due to formation of the nanocomposites f-MWCNT-GOT.
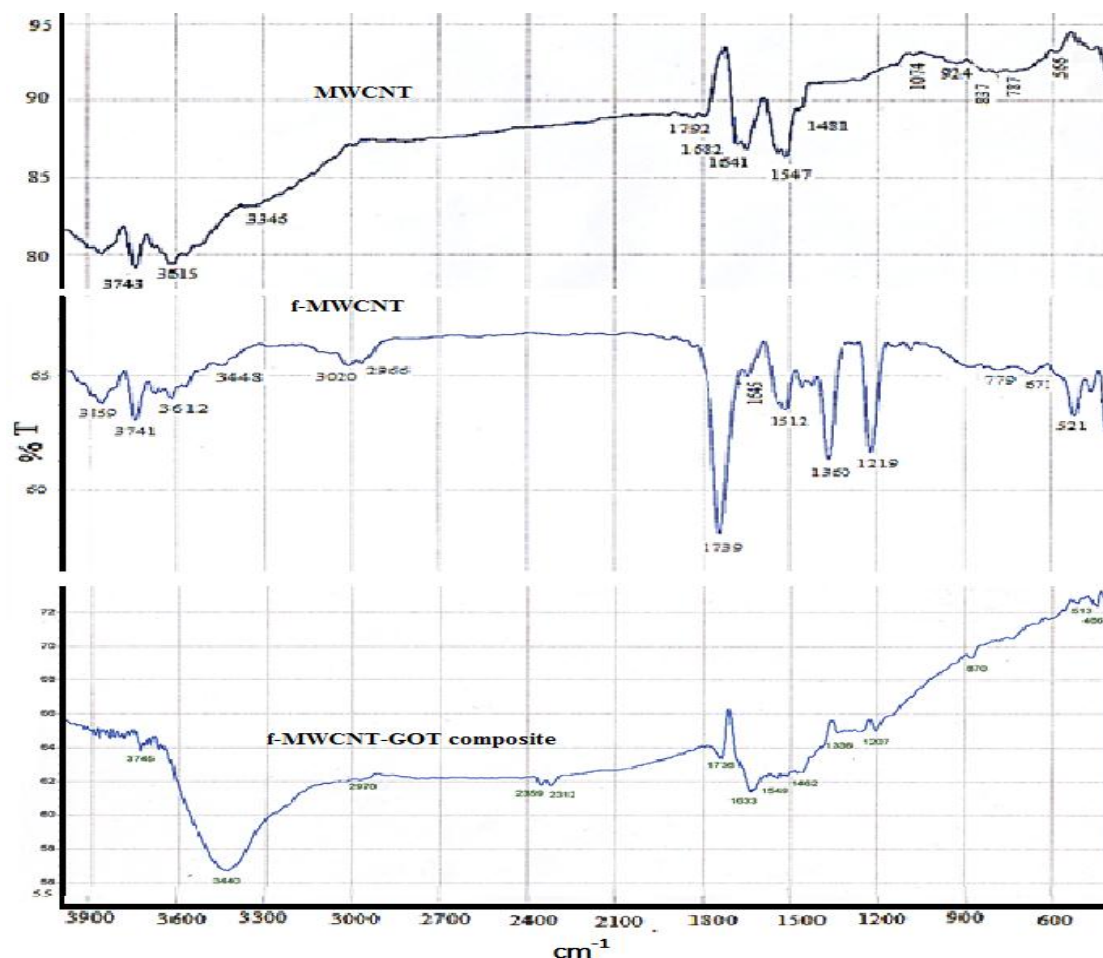
Figure1. FT-IR spectrum of pristine MWCNT, acidic f-MWCNT and f-MWCNT-GOT nanocomposite

3.2. Surface characterization of modified SPCE.

The SEM images were show good distribution of f-MWCNT and f-MWCNT-GOT nanocomposite on the WO of the SPCE surface respectively fig.(2, A and B). The fig.(2-1) shown very clear good distribution of the MWCNT, fig.(2-B) was clearly show that the composite well distributed even though some MWCNT still visible. There are several proposals clarify the mechanism of dispersed the MWCNT with nanosheets Chen S, et al [22] proposed the sheets can wrap around the CNTs while Shin M *et al.* [23] proposed the CNTs are attached to the edges and surfaces of the graphene sheets. The two proposals were confirms that the MWCNTs and the nanosheets were connected with each other; these mechanism were supported with the FTIR results.
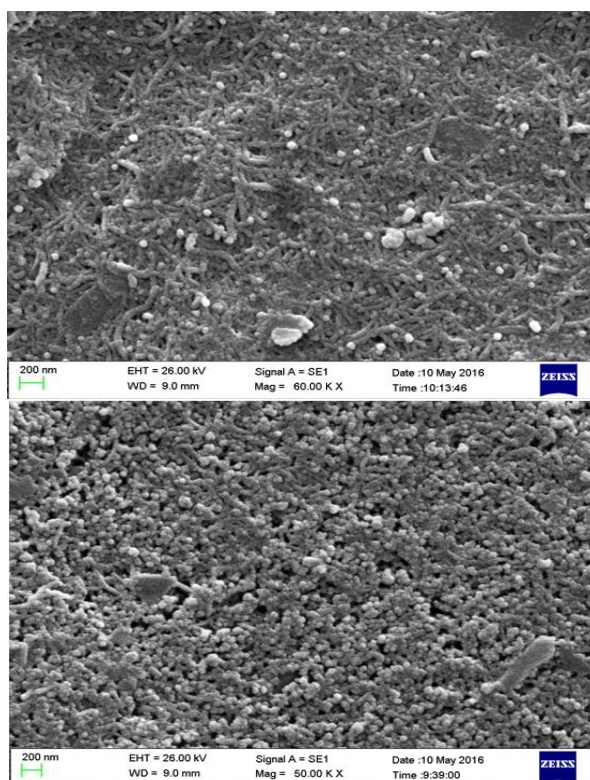
Figure (2) A) SEM image of surface of f-MWCNT, (B) SEM image of the surface of f-MWCNT-GOT nanocomposite

3.3. Electrochemical properties of (f-MWCNT) and its nanocomposites.

All the cyclic voltammetric measurements were performed at various scan rates ranging from 0.01 to $0.1V.s^{-1}$ and drops casted method was used to study the voltammetric response of modified SPCE. The modification of the SPCE with volumes of MWCNT, f-MWCNT and its nanocomposites with GOT (f- MWCNT-GOT) using ferri/ferro redox couple system was used to study the maximum current response, Fig (3) showed the modifier f-MWCNT and f-MWCNT-GOT nanocomposites exhibit higher current response in presence of ferric/ferro couple and can be use more volumes (18µL) and (14µL) respectively compared with pristin MWCNT (2µL). The big differences in the responses may due to the heterogeneous electron transfer rate in f-MWCNT which included an oxygen's functional moieties at the tips of MWCNT according to reference [24], Also the attached functional groups ASTT at the edge of GO sheets in nanocomposite accelerate electron transfer between ferro/ferric and electrode surface.
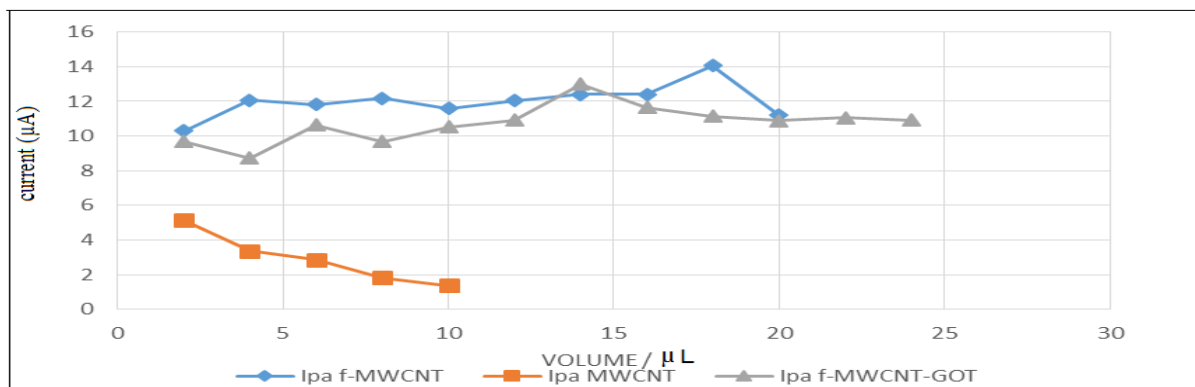
Figure (3) The behavior of the used volume in (µL) of MWCNT, f-MWCNT and f-MWCNT-GOT on the WE of the SPCE with cyclic voltammeter in 0.8 mM Potassium ferricyanide in 0.1M KCl ⁱ

The differences in the voltammetric responses of the different modified SPCEs were depended on many factors; the effective surface area is one of more important factors. Randles Sevick equation (equ.1) [25] was used to estimate effective surface area of the modified SPCE with MWCNT, f-MWCNT and f-MWCNT-GOT using 0.5mM potassium ferrocyanide as probe.

$$I_p = 0.4463\ n\ F\ A\ C\ (nF/RT)^{1/2}\ v^{1/2}\ D^{1/2} \quad \ldots\ldots..(1)$$

where n = 1 is the number of electrons involved in the redox reaction, F is Faraday's constant, C is the bulk concentration of the analyte, R is the molar gas constant, T is the temperature, and D is the diffusion constant of potassium ferricyanide in 0.1 M KCl (0.76×10^{-6} cm^2 s−1) [26], and v was the scan rate (V s−1).

From the cyclic voltammeter results was plotted I_p versus square root of scanning rates fig. 4- (A, B and C). The active surface area of modified SPCE with MWCNT-SPCE, f-MWCNT-SPCE and f-MWCNT-GOT-SPCE respectively, and from the slope of I_p versus v½ was estimated the active surface areas as 0.04, 0.119 and 0.12 respectively. These results show very clearly that the f-MWCNT-SPCE and f-MWCNT-GOT-SPCE possessed the higher active areas than MWCNT-SPCE.
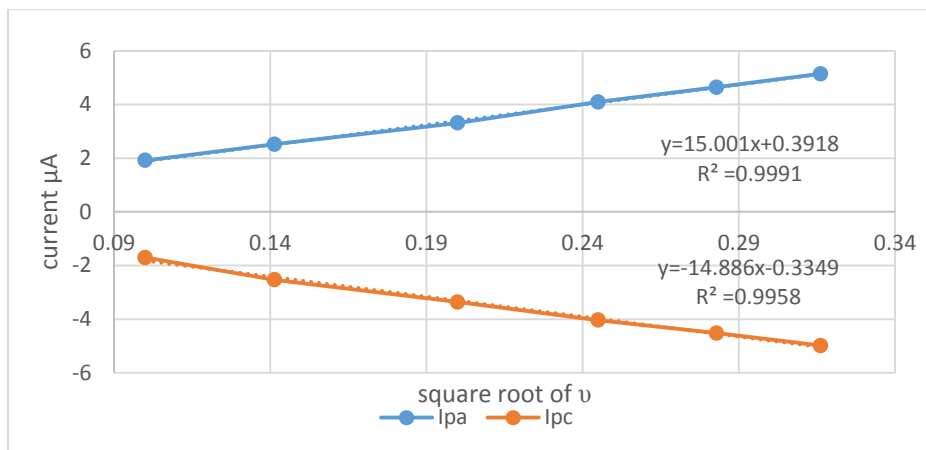
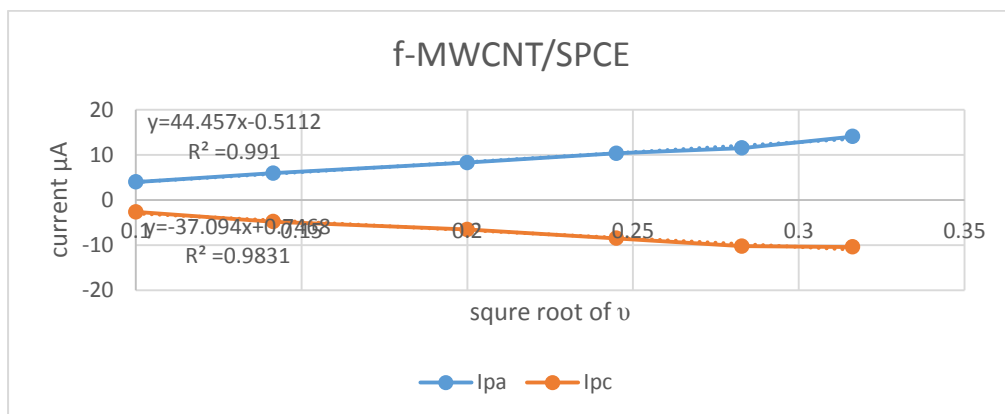Figure (4-A) linear relationship between I pa *vs.* square root of scan rate for MWCNT-SPCE

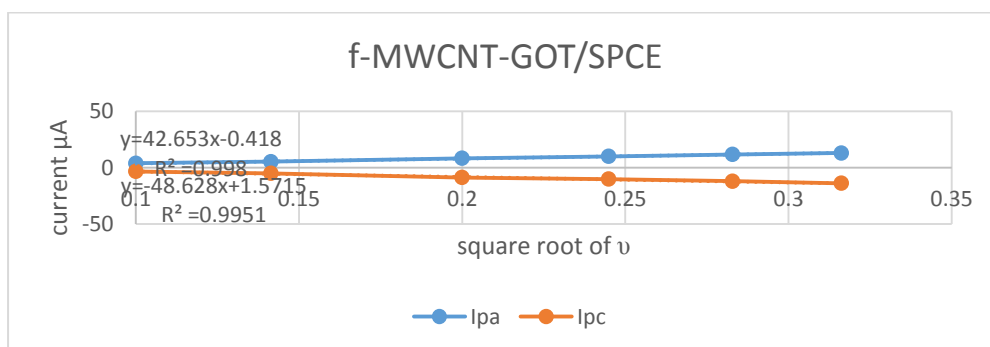Figure (4-B) linear relationship between Ipa *vs.* square root of scan rate for f-MWCNT-SPCE.

Figure (4-C) linear relationship between I_{pa} *vs.* square root of scan rate for f-MWCNT-GOT.

3.4. Determination of electrochemical active surface area.

To estimate the covered area of the WEs with examined material, Sharp method   was used using equation below [27]

$$I_{pa} = n^2 F^2 \, \Gamma \, Av \, /4RT \qquad \text{……. (2)}$$

According to this method was sketched the slope of the anodic peak currents *versus* various scan rates as shown Fig. (5) an approximate surface coverage Γ (mol cm^{-2}) of the modified electrodes were estimated, the concentration of the material on each area was calculated and found as 9.447×10^{-9}, 2.36×10^{-10} and 2.32×10^{-10} mol cm^{-2}, for MWCNT ,f-MWCNT and f-MWCNT-GOT respectively, The values of surface coverage concentration Γ for SPCE modified with MWCNT lower than other electrodes may be due to absence of functionalities .
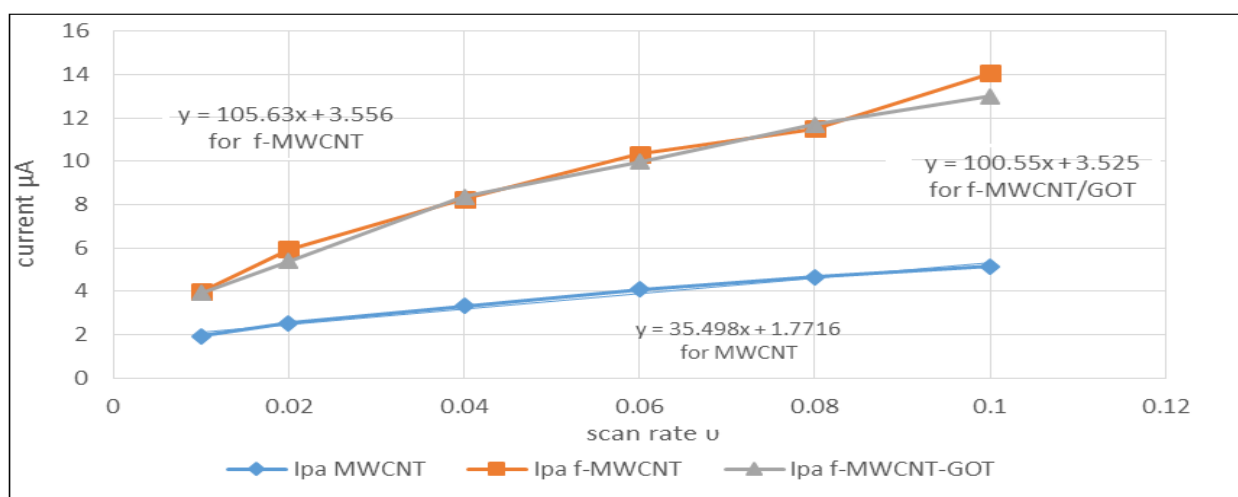

Figure (5) Variation of the peak current (I_{pa}) and (I_{pc}) with the sweep rate for modified SPCE MWCNT, f-MWCNT and f-MWCNT-GOT in 0.8mM potassium ferrocyanide.

3.5. The effect of pH.

The electrochemical behaviors of ampicillin antibiotic were dependent on the pH value of solution [28, 29]. To evaluate the optimum pH for ampicillin detection on the surface of the modified electrode, its electrochemical behavior was investigated in the buffered solutions with various pHs in the range of 2-8. A buffered solution of pH 2 was chosen as an optimum value in order to obtain the best sensitivity in all voltammetric measurements fig.(6).
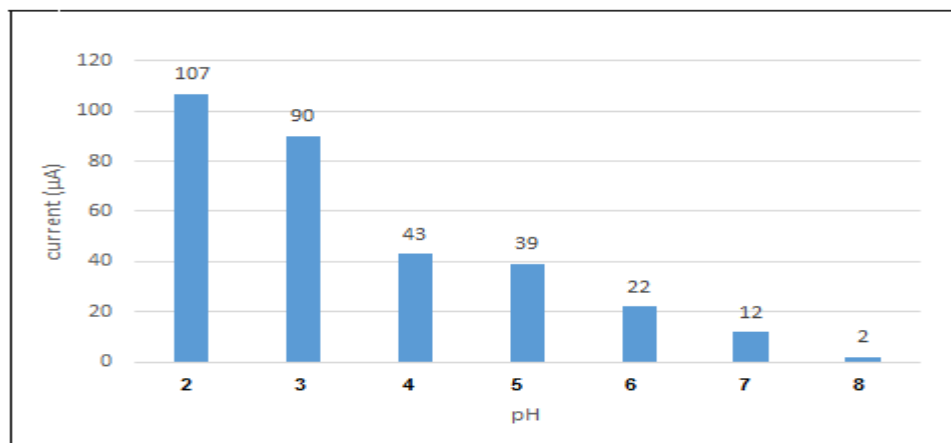
Figure 6. Electrochemical behavior of AMP at different pH value in PBS at sweep rate 0.1V s^{-1}.

3.6. The behavior of the modified electrodes with AMP.

The cyclic voltammograms of the bare SPCE was shown very weak anodic peak current (0.6µA) in PBS at (pH=2) and in the presence AMP in the same pH was (0.67 µA). The modified electrodes MWCNT, f-MWCNT and f-MWCNT-GOT were appeared better values for the anodic peak currents at (pH=2) and same scan rate 0.1V/s. fig. (7), The MWCNT-SPCE showed the lowest oxidation peak for AMP with oxidation current (6.273µA at potential 0.12 V), the current peak of AMP clearly increased with f-MWCNT-SPCE to 46.072 µA at potential 0.13V for anodic and -19.26 µA at potential -0.19V for cathodic, indicating that the functional carboxylic groups significantly enhanced the electron transfer between AMP and surface of f-MWCNT on the WE of SPCE. The modified SPCE with f-MWCNT-GOT nanocomposite was produced the highest peak currents (105.279 µA at potential 0.19V) for anodic and (-23.976 µA at potential -0.36V) for cathodic, this big increasing in the current peak of the modified SPCE with f-MWCNT-GOT due to the nanocomposite material and the effect of the Triazole functional groups too, which assisted the electron transferring between the AMP molecules and the surface of WE. The above results were showed the modified WE of the SPCE with MWCNT possessed the lowest peak current value than the other two modified WEs.
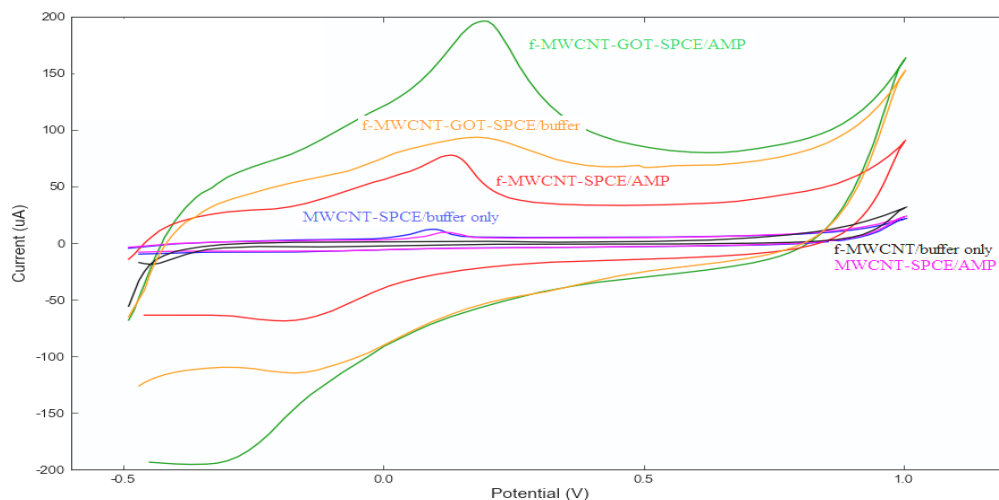
Figure 7. Cyclic voltammograms for bare and modified electrode MECNT, f-MWCNT and f-MWCNT-GOT in presence and absence of 0.1mM AMP.

3.7. Effect of scan rate.

Cyclic voltammograms of the AMP were recorded at different scan rates (from 0.03 to 0.18 V s^{-1}) Fig. (8). the peaks current were increased with increasing of the scan rate values from 0.03 to 0.16Vs^{-1}and decreased at the 0.18 Vs^{-1}. The dependence of anodic peaks current (I$_{pa}$) and cathodic peaks current (I$_{pc}$) on the scan rate (v) observed a linear relationship Y=447.16x+34.354 and y=101.95x-9.2829 with a correlation coefficient R^2=0.8456 and R^2=0.5964 for anodic and cathodic peaks respectively Fig (9).
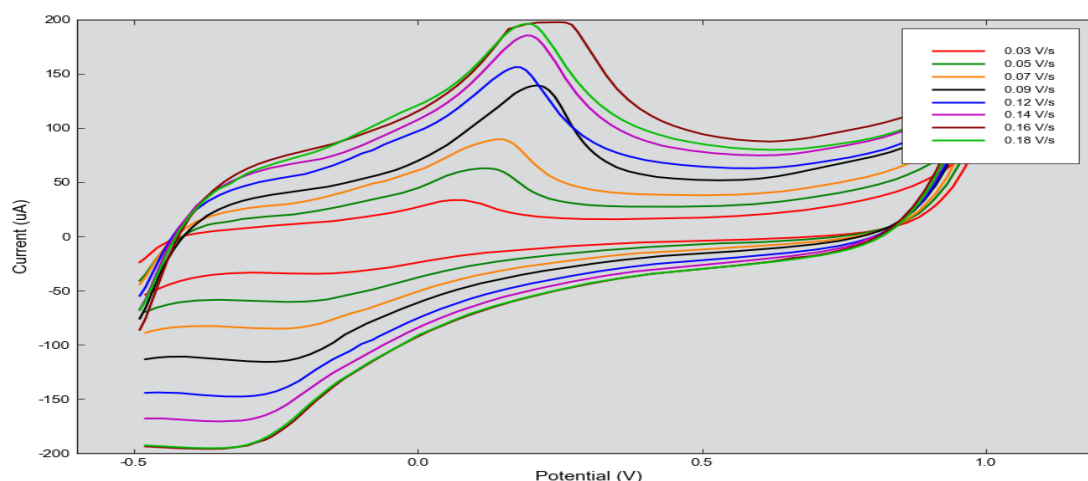

Figure (8) Cyclic voltammograms for modified electrode f-MWCNT-GOT in presence of 0.1mM AMP at different scan rates.
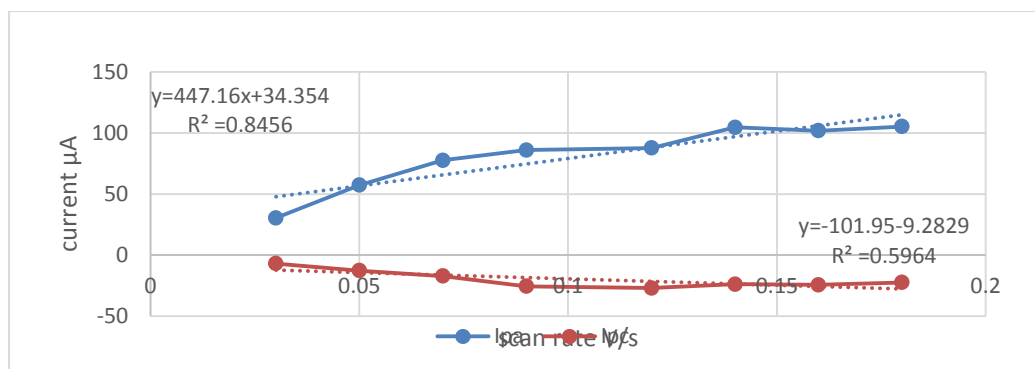
Figure (9) Variation of the peak current (I_{pa}) and (I_{pc}) with the sweep rate for 0.1mM AMP at f-MWCNT-GOT nanocomposite modified SPCE.

The irreversibility was indicated in the signals of anodic peak current were higher than the cathodic current signals $I_{pa}/I_{pc} \neq 1$, this result with cyclic voltammetry were found numerous redox processes quasi-reversible or non-reversible. In these cases were the thermodynamic potential $E^0_{1/2}$ often deduced by simulation. The deviations from unity were attributable to a subsequent chemical reaction which triggered by the electron transfer. These electrochemical processes can be complex, involving isomerization, dissociation, association, etc.[30].

The potential difference ΔE between the anodic and cathodic potential increased with varying scan rates between 0.03 and 0.18 Vs^{-1}. The reverse wave was noticed and the potential difference found at $\Delta E_p > 0.4V$ which indicated that the AMP appeared irreversible charge transfer process and agreed with [31,32]. The Ep of the oxidation peak was also dependent on scan rate. The peak potential shifted to more positive values on increasing the scan rate, which confirms the irreversibility of the oxidation process fig 10A.

According to the equations (3) for an irreversible electron transfer ET [33].

$$\partial Ep/\partial \log \upsilon = 1.15 RT/F\alpha \qquad \text{....... (3)}$$

The values of the electron transfer coefficient α, which have been estimated from the peak potential slope, and found to be 0.15 this diminished due to breaking bonds (high activation energy).

As for the irreversible electrode process of the oxidation reaction of AMP, the Laviron's equation (equ.4) [33] was used to estimate n and ks values as follows:

$$E_p = E^{0'} + (2.303RT/\alpha nF) \log(RTk_s/\alpha nF) + (2.303RT/\alpha nF) \log \upsilon] \qquad \text{.... (4)}$$

Where α is the electron transfer coefficient, ks is the standard rate constant of the surface reaction, v is the scan rate, n is the electron transfer numbers and E^0 is the formal potential. Ks and n values can be concluded from the intercept and slope of the linear plot of E_p with respect to log v fig. (10A). The E^0 value at f-MWCNT-GOT nanocomposite of the modified SPCE can be deduced from the intercept of Ep *vs. v* fig.(10B) plot on the ordinate by extrapolating the line to *v*=0 . Knowing E^0, and from the graphical representations of E_p *vs.* Log *v* for AMP fig. (10A), the value of n=2 obtained

from the slope and indicated that two electron was involved in the oxidation of AMP on the f-MWCNT-GOT nanocomposite of the modified SPCE. Also the values of $k_s=432.68$ s^{-1} was obtained from the intercept this high enhancement in value of k_s compared with other modified electrode clearly demonstrate that the introduction of a nanocomposite f-MWCNT-GOT in the surface of electrode opens an efficient ET between AMP and the modified WE.
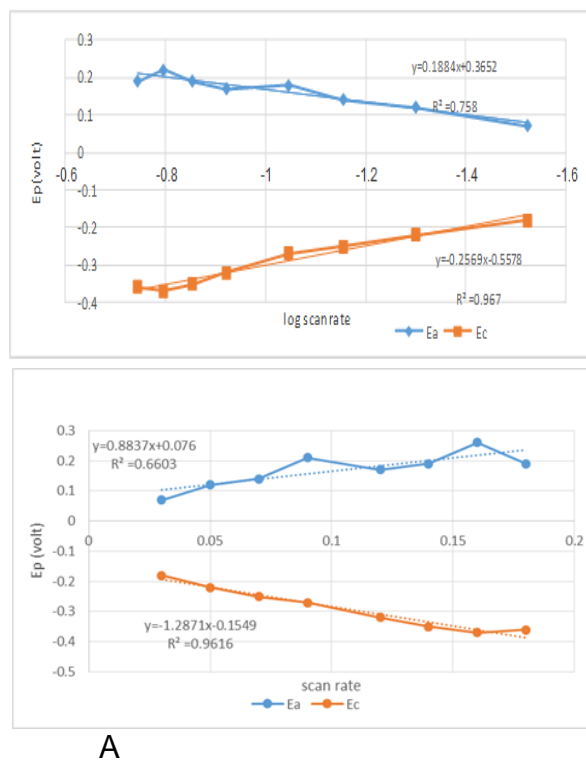

A   B

Figure 10 (A)The variations of peak potential *vs. v* and (B) The variations of peak potential *vs.* Log*v* at f-MWCNT-GOT/SPCE.

Linear relationships were observed between log Ip and log υ over the scan range 0.03-0.18 V s^{-1} with slope of 0.6442 and 0.6781 of anodic and cathodic peak respectively as shown in Fig. (11). The slope of the straight lines were shown intermediate value between 1 the theoretical value of the adsorption controlled electrode process and the theoretical value of 0.5 which was expressed for the diffusion controlled electrode process, this indicated that the electrode process was controlled simultaneously both by diffusion and adsorption for redox process[33-35].
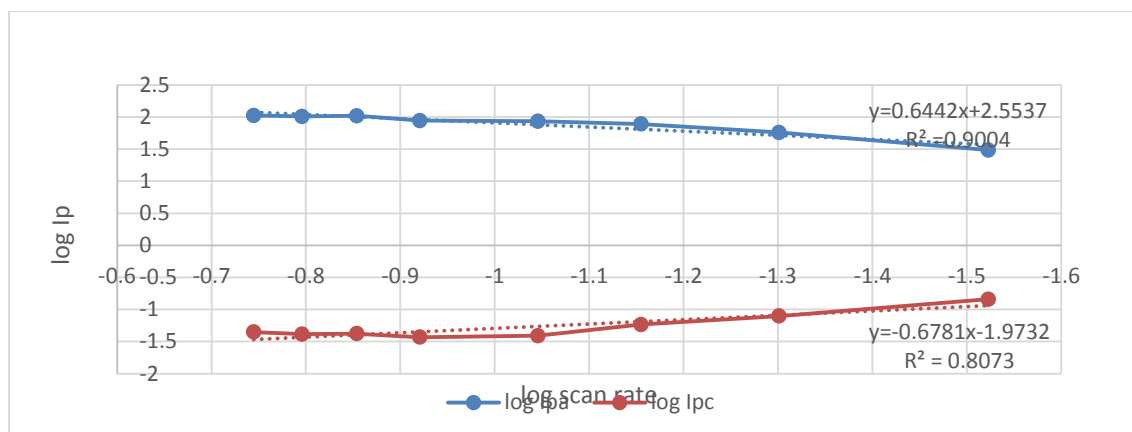
Figure 11. Plot of log current vs. log scan rate υ (V/s).

3.8 DPV measurements

The DPV of the f-MWCNT-GOT modified SPCE in the presence of various concentration of AMP are shown in Fig. (12). The oxidation of AMP was accompanied by an increase in the anodic current which could significantly improve the detection limits of electrochemical measurement. Figure (12) show linear relationships of the oxidation peak at different concentration of AMP (1 × 10^{-6} - 5 × 10^{-5} mol.). The linear regression equation was I (µA) = 1.4648 (µM) + 26.264, with the correlation coefficients of 0.8139.The limit of detection was calculated according to eqau.5 [36].

$$LOD = 3S_{y/x} / b \qquad ……….. \qquad (5)$$

Where $S_{y/x}$ was the standard deviation of peak current for blank PBS solution which obtained from 15 replicated measurements and b is the slope of the related calibration (0.8585 µA µM) curve Fig. (13). under optimum experimental conditions the calibration curve was obtained. The peaks current were increased linearly with the increase of AMP concentration in range of 1.52×10^{-7} to 1.46 ×10^{-5} M. The detection limit was estimated at 1.46×10^{-7}M using the same equation.
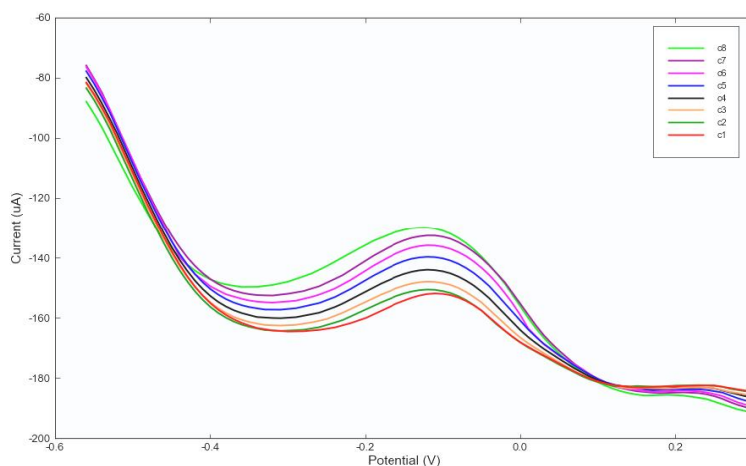
Figure (12) Differential pulse voltammogram for modified SPCE with f-MWCNT-GOT nanocomposite in presence of different concentrations of AMP.
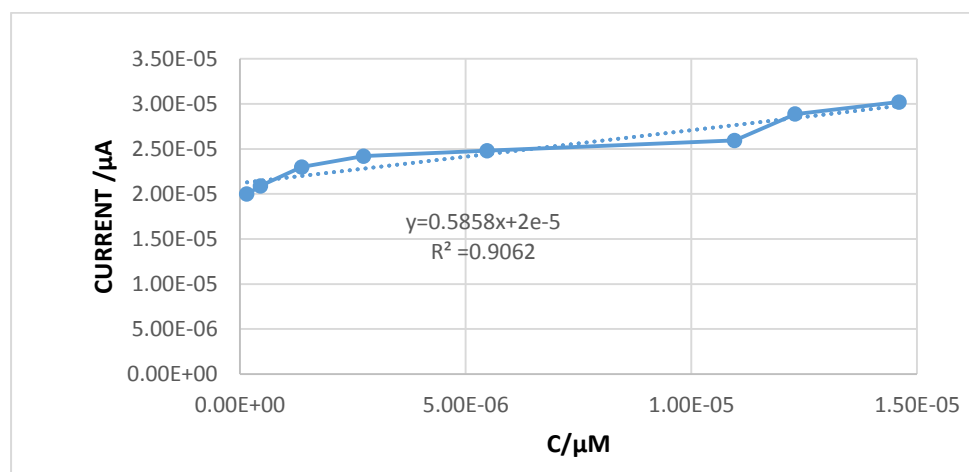

Figure (13) the relationship between current and the concentration of AMP.

4. Conclusion

The three carbone nanomaterials MWCNT, f-MWCNT and f-MWCNT-GOT were shown different electrical and physical properties in the cyclic voltammetry technique. The effects of the functionalization were attached the carboxylic groups with the MWCNT and the Triazole with graphene oxide, and show that the electrons transfer were supported with carboxylic functional groups and the Triazole groups on f-MWCNT and GOT respectively, whereas the concentrations values were of the examined materials on the surface area of WE of the SPCEs of f-MWCNT and f-MWCNT-GOT higher than MWCNT , this supported with DPV results and the value of the LOD was shown good results with the f-MWCNT-GOT/SPCE.

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