



**Fabrication of a New Electrochemical Sensor Based on Carbon Paste Electrode Modified by Silica gel/ MWCNTs for the Voltammetric Determination of Salicylic Acid in Tomato**



**E. M. Rabie, H. F. Assaf\*, A.A. Shamroukh, and M. Khodari**

*Chemistry Department, Faculty of Science, South Valley University, Qena, Postal code 83511, Egypt.*

**H**EREIN, Multi Walled Carbon Nano-tubes a fabrication and application of a novel sensor of carbon paste electrode modified by silica gel/MWCNTs for the determination of salicylic acid (SA) by different voltammetric techniques such as Linear Sweep, Cyclic and Square Wave Voltammetry. The electrochemical behavior of SA has been investigated and the optimum experimental conditions such as the effect of supporting electrolyte, pH and scan rate on the anodic peak of SA was determined. Square Wave Voltammetry (SWV) was employed to determine SA, where the important parameters such as frequency were achieved. Moreover, the results showed that modified electrode exhibited excellent electrocatalytic activity towards the oxidation of SA. The results showed irreversible process with one oxidation peak of SA at the surface of modified electrode and the overpotential of SA decreased significantly compared with that at the bare carbon paste electrode (CPE). This electrochemical sensor shows an excellent performance for detecting SA with a detection limit and limit of quantification were  $0.9 \times 10^{-9}$  M and  $2.99 \times 10^{-9}$  M respectively. In addition, the peak currents increased linearly in the concentration range of 3.0–70 nM. The results showed also, the fabricated sensor was successfully applied to the detection of SA in tomato with good recovery ranging from 96.60 to 103%, Moreover, the proposed electrode revealed good reproducibility and stability, with standard deviation (S.D.) 2.3% for eight successive measurements of SA.

**Keywords:** Salicylic acid, Silica gel, carbon nanotubes, Carbon Paste electrode, Cyclic voltammetry, Square wave voltammetry.

**Introduction**

Plant growth regulators or plant hormones are organic compounds that in very small amounts regulate numerous aspects of plant growth, development, and response to stress[1]. Salicylic acid (o-hydroxybenzoic acid) is considered as an important plant hormone. Where it is widely distributed in various plants and acted as an endogenous signaling molecule. In addition, it plays a substantial role in the regulation of many physiological processes such as flowering, heat production, seed germination, stomatal closure, membrane permeability, and ion absorption. Also, it protects against biotic and abiotic stresses, including drought, chilling, heavy metal, tolerance heat and osmotic stress[2]. Consequently, many

analytical methods had been developed to quantify the concentration of SA in plants. Such as high-performance liquid chromatography[3], gas chromatography-mass spectrometry[4], flow injection atomic absorption spectrometry[5], UV spectrophotometry[6] and voltammetric methods[7–11]. However, most of these methods are lengthy, expensive, require complicated procedure expert knowledge and often need the pretreatment step that makes them unsuitable for routine analysis[12]. On the other hand, voltammetric method is emerging as a powerful approach due to the good electrochemical activity of SA as well as high sensitivity and simplicity of the method[13,14]. In this work, a new electrochemical sensor based on carbon paste electrode modified Silica gel/MWCNTs

\*Corresponding author e-mail: [elprof\\_3ssaf@yahoo.com](mailto:elprof_3ssaf@yahoo.com)

Received 18/9/2019; Accepted 24/11/2019

DOI: 10.21608/ejchem.2019.17087.2048

©2019 National Information and Documentation Center (NIDOC)

has been investigated to the determination of SA in plant samples. In recent years, carbon paste electrodes (CPE) have a wide application in electrochemistry. This due to their advantages over membrane electrodes such as speed, ease of preparation, and stable response, renewability, porous surface, low cost, no need for the internal solution and low ohmic resistance[15–18]. Now a days, modified Carbon Paste electrodes (CPE) are found to enhance sensitivity of the electrodes to obtain new sensor with suitable and predefined properties[19]. Chemically modified electrodes such as Silica gel are an inexpensive material, which possesses some excellent properties such as strong adsorption ability, high surface area, high thermal stability, and easy surface modification. Using silica gel as a modifier in CPE has many functional groups to enrich the surface properties[20–22], Where(MWCNTs) presented great performances in terms of response time, increased sensitivity, resistance to surface fouling, decreased over potential, mass transport, catalysis, high effective surface area and detection limit[22]. Moreover (MWCNTs) have been used as modifier for carbon paste electrodes mainly due to their unique physicochemical properties such as ordered structure with high aspect ratio, ultra-lightweight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area[23–25].

## Experimental

### Reagents and solutions

Standard SA was purchased from USA Sigma-Aldrich, its stock solution was prepared in absolute ethanol. The experiment working solutions were prepared by diluting the stock solution with a selected supporting electrolyte. Different supporting electrolytes, namely KCl (0.1 M), acetate buffer (0.1 M, pH 4.7), Britton-Robinson buffer (0.1 M, pH 2–9), and phosphate buffer (0.1 M, pH 2.0 and 7.4) solutions were used.

All stock solutions were preserved at 4 °C when not in use and protected from daylight during use in the laboratory. All other chemical reagents were of analytical grade and used without further purification. Aqueous solutions were prepared with second distilled water further purified via a Milli-Q unit (Millipore).

### Apparatus and cell

A potentiostat model 263 (EG& G PARC)

Princeton applied corporation (made in the USA), 305 magnetic stirrer (PARC). Electroanalytical software model 270 / 250 version 4.0 (PARC) which control the potentiostat via IEEE 488 GPIB using IBM compatible 386 with a VGA monitor. The characteristic of modern stripping analyzer potentiostat is controlled which minimizes errors from the cell resistance (distorted voltammogram with decreased peak current and shifted and broadened peaks). This is accomplished with a three-electrode system, the working electrode is carbon paste electrode modified by silica gel/MWCNTs electrode, the Ag/AgCl used as reference electrode while a Pt wire was used as the counter electrode.

### Preparation of carbon paste electrode modified by Silica gel/MWCNTs

The modified electrode is prepared by mixing 60% of pure graphite (99.9%) with (10% of MWCNTs+5%Silica gel) in the presence of 25% from paraffin wax as a binder. The mixture is heated and then packing in a Teflon tube with a 2mm diameter. Finally, a copper wire is immersed in the paste to contact with the cell. To activate the electrode surface, cyclic voltammograms were applied in phosphate buffer solution (pH = 5) between 0 and 1.0 V till a steady voltammogram was obtained. By recording the current-voltage curve at different scan rates the active area of the electrode was obtained by cyclic voltammetry (CV) method using 1.0 mM  $K_3Fe(CN)_6$  in 0.1 M KCl. For a reversible process, the following Randles-Sevcik formula was used [26].

$$I_p = (2.69 \times 10^5) n^{3/2} A D_R^{0.5} \nu^{0.5} C_0 \quad (\text{eq-1})$$

Where  $I_p$  refers to the anodic peak current,  $n$  is the number of electrons transferred,  $A$  is the surface area of the electrode,  $D_R$  is the diffusion coefficient,  $\nu$  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,  $n = 1$ ,  $D_R = (7.6 \times 10^{-6} \text{ cm}^2/\text{s})$ , then the electroactive area was calculated from the slope of the plot of  $I_p$  versus  $\nu^{0.5}$ , relation. The effective surface area was 0.0173  $\text{cm}^2$  for bar CPE and increased to 0.062  $\text{cm}^2$  when modified with silica gel/MWCNTs.

### Extraction of salicylic acid from plant samples (tomato leave samples)

Tomato leaves with normal sizes were collected to extract salicylic acid for square wave voltammetric determination according to previous protocols [27]. Briefly, tomato leaves were ground in liquid nitrogen

and resuspended with propanol/water/HCl (2:1:0.002 in volume ratio) in a vial followed by oscillation. Dichloromethane was added for the first extraction and centrifugation. Then, the supernatant was collected and the residue was mixed with dichloromethane for second extraction and centrifugation. Both supernatants were mixed and then dried. Methanol dissolve added to solve the sample by sonication. The methanol solution consisting of samples was passed through the activated C18 column and eluted with methanol. The elution solution with the volume of 2 mL was collected in 4mL bottle and dried with a vacuum at 35 °C. Their residue was solved with 0.5mL methanol and then transferred to a 2mL empty bottle followed by drying with a vacuum. Finally, the dissolved was solved in 400 mL mixture of methanol /formic acid solution with a ratio of 1:1.

## **Results and Discussions**

### *Cyclic Voltammetry (CV)*

The electrochemical behavior of SA was studied by using cyclic voltammetry technique. The votammograms of SA at the (a) bare CPE and (b) CPE modified by silica gel/MWCNTs in the presence of 150 μM SA (phosphate buffer, pH= 2) was shown in Fig. 1. It was founded only one oxidation peak in anodic direction at about 1.16V and no reduction peak was observed on reverse scan that is means the reaction is totally irreversible. The anodic current peak increases about 0.21 μA by the modification with silica gel/MWCNTs which indicates that a higher amount of species was oxidized, while the peak potential shifts to more negative values show the higher facility in oxidizing these species, which enhanced the electrocatalytic activity of the modified electrode towards the oxidation of SA.

On the other hand, a typical cyclic voltammogram of SA in sodium phosphate buffer is depicted in Fig. 2. The first anodic scan shows only a peak *I<sub>a</sub>*, whose peak potential appears around 1.16V depending on the pH, scan rate (*v*) and SA concentration. On the reverse scan, no complementary reduction peak is observed for *I<sub>a</sub>* in all the range of scan rates studied. This behavior is typical for a fast irreversible chemical reaction couple to the charge transfer [28,29]. At potential around 0.68V, a new couple (peaks *I<sub>lc</sub>* and *I<sub>la</sub>*) are defined, which are assumed to correspond to the reduction-oxidation of a product of the

coupled chemical reaction. The nature of this product was not determined, but it might be several different soluble compounds[30] which can be expected to undergo the reversible redox reaction in this potential zone[31]. These results are in agreement with the previous report for SA [10,32,33].

### *Electrochemical effects of the Supporting Electrolyte, its pH and scan rate on SA oxidation peak*

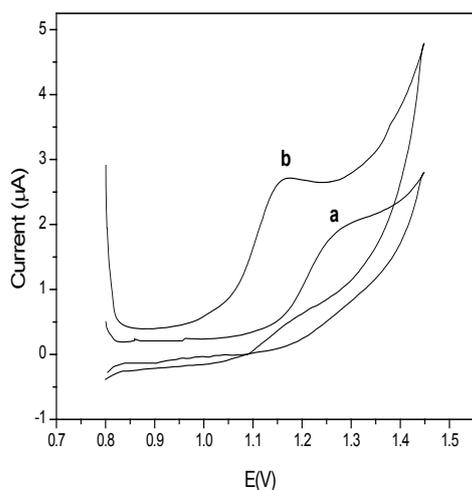
it's a very important stage to achieve the optimum conditions to determine SA by studying the effect of supporting electrolyte, its pH value, and scan rates. SA is studying the effect of supporting electrolyte, its pH value, and scan rates. the properties of the solution as well as the electrode solution interface, modifying the adsorption at the electrode surface, and the thermodynamics and kinetics of the charge transfer process[34]. Therefore, the effect of different supporting electrolytes such as (perchloric acid solution, Britton–Robinson buffer, acetate, and phosphate) was examined on the oxidation peak of SA at the same of conditions.

The shape and the height of the oxidation peak of SA were taken into consideration in choosing the suitable supporting electrolyte. The results showed that the suitable oxidation peak of SA was found in sodium phosphate buffer.

The variation of pH values of supporting electrolytes is an important factor that affects the electrooxidation process of SA compound in aqueous solutions. The effect of pH was studied to determine the optimum pH value and helps to insights into the mechanism of the oxidation of SA on CPE modified by silica gel/MWCNTs. The pH of phosphate buffer was examined over rang from (pH=2.0 to pH=9.0) on the oxidation peak of SA using linear sweep voltammetry at scan rate 50mVs<sup>-1</sup>. Fig. (3A) showed that the best peak shape and the highest current was obtained at pH value equal 2. Also the oxidation currents of SA decreased gradually with increasing the pH value in agreement with previous studies[11]; the. Fig. (3b) illustrated the relation between *E<sub>p</sub>* and pH values which give a linear relation as expressed in the following equation:

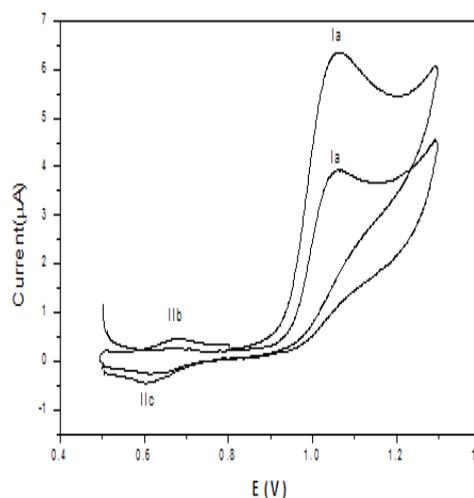
$$E_p (V) = 0.62 - 0.04532 \text{ pH } r^2 = 0.995 \text{ (eq-2)}$$

with a slope of 0.453(V/pH), this value suggests

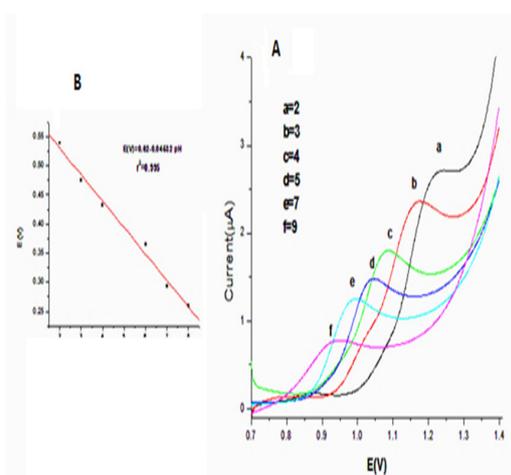


**Fig. 1.** Cyclic voltammograms of  $1 \times 10^{-5}$  M of SA in phosphate buffer pH=2, at scan rate =  $50 \text{ mVs}^{-1}$  on the surface of

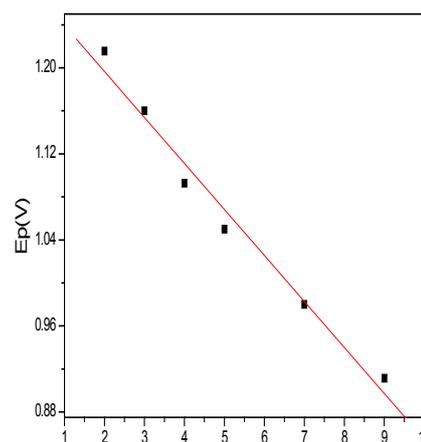
- (a) bare CPE.  
(b) CPE modified by Silica gel/MWCNTs.



**Fig. 2.** Repetitive cyclic voltammogram of  $3 \times 10^{-5}$  M of SA in phosphate buffer pH=2, at scan rate =  $50 \text{ mVs}^{-1}$  using CPE modified by Silica gel/MWCNTs .



**Fig. (3A).** Effect of pH on the oxidation peak current of  $1 \times 10^{-5}$  M of SA at  $50 \text{ mVs}^{-1}$  scan rate using CPE modified by silica gel/MWCNTs.



**Fig.(3B).** The relation between oxidation peak potential versus pH of  $1 \times 10^{-5}$  of SA at  $50 \text{ mVs}^{-1}$  scan rate using CPE modified by Silica gel/MWCNTs.

an equal number of electrons and protons in the SA oxidation[35]. These displacements are in accordance with the ones reported in the literature for SA oxidation[36].

The electro oxidation peak ( $1 \times 10^{-5}$  M) of SA in phosphate buffer at pH=2.0 using CPE modified by Silica gel/MWCNTs was studied at different scan rates varying from 5 to  $300 \text{ mVs}^{-1}$ . By increasing scan rate the oxidation peak current

increased [37,38] and shifted slightly to the positive side as shown in Fig (4A). But at scan rate more than  $250 \text{ mVs}^{-1}$  the peak shape was distorted especially at high concentration of SA. The plots of oxidation peak currents against the square root of the scan rates exhibited a linear relationship that demonstrated in Fig. (4B):

$$I_p = -27.85 + 19.41 v^{(0.5)} (\text{mV/S}) (r^2 = 0.998) \text{ (eq-3)}$$

meaning that the electrocatalytic oxidation of SA

is diffusion control [35]. A plot of the logarithm of peak current versus the logarithm of the scan rate shown in Fig. (4C) gave a straight line with a slope of 0.56:

$$\log(I_p) = 0.171 + 0.56 \log(v) \quad (r^2 = 0.995) \quad (\text{eq-4}).$$

this slope ( $\alpha = 0.56$ ) is very close to the theoretical value of 0.5, which is expected for a diffusion-controlled process [39]. Also Plotting the relation between  $E_{pa}$  vs.  $\log$  scan rate ( $v$ ) produces a

straight line with the linear regression as illustrated in Fig.(4D), according to the following equation

$$E = 0.91 + 0.08 \log(v) \quad (r^2 = 0.995) \quad (\text{eq-5}).$$

The total number of participate electrons was calculated from Laviron equation:

$$\Delta E / (\Delta \log(v)) = 59 / n\alpha$$

(Where  $\alpha$  is the electron transfer coefficient) and found to be 1.3 that is mean only one electron is

(eq-1).

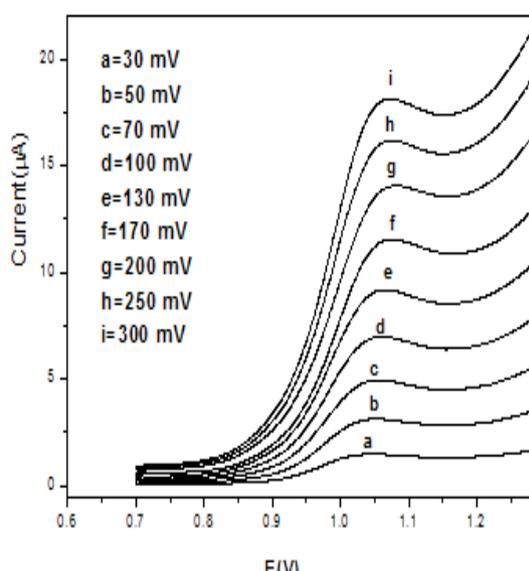
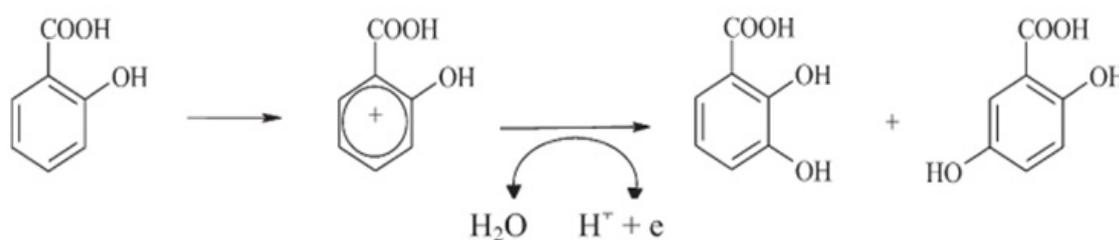


Fig. (4A). Effect of different scan rate on the oxidation peak of  $1 \times 10^{-5}$  M of SA in 0.1M phosphate buffer pH=2.0 using CPE modified by silica gel/MWCNTs.

involved in the oxidation process of SA at the fabricated sensor. So the expected mechanism for the oxidation of SA can be expressed by the following equation [11].

#### Electroanalytical determination of SA

For the electroanalytical determination of SA, SWV was mainly chosen due to its high speed and high sensitive relative to other pulse voltammetric techniques [31]. One of the most important

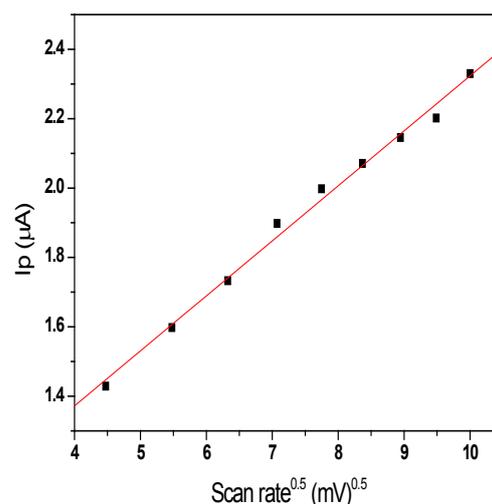


Fig. (4B). The relation between the peak current and the square root of scan rate of  $1 \times 10^{-5}$  M of SA in 0.1M phosphate buffer pH=2.0 using CPE modified by silica gel/MWCNTs

parameters of SWV is the frequency. Since it determines the sensitivity of this method. The effect of SWV frequency in the peak current was investigated in the range of 10 to 250  $s^{-1}$  as shown in Fig.5 (A). It is founded that peak currents increased with the frequency due to the increase in the effective scan rate but the peak shape and baseline were distorted at frequencies higher than 100 Hz. The good linearity between peak current

( $I_p$ ) vs and frequency ( $f$ ) until  $100 \text{ s}^{-1}$  as illustrated in Fig.5 (B), with the linear regression equation:

$$I_p(\mu\text{A}) = 4.074 + 0.102 \times f(\text{S}^{-1}) \quad (r^2=0.997) \text{ (eq-6)}$$

That confirms the irreversible nature of the SA oxidation process, which is in accordance with the SWV theory[40]. So the frequency of  $90(\text{s}^{-1})$  was chosen for the analytical determination of SA. Fig.5(C), shows the linear displacement of the peak potential ( $E_p$ ) with the increase of the frequency according to the equation:

$$E_p(\text{V}) = 1.075 + 0.097 \times \log(f) \text{ S}^{-1} \quad (r^2 = 0.997) \text{ (eq-7)}$$

the  $n\alpha$  value was calculated according to the equation:

$$\Delta E / (\Delta \log(f)) = (0.059) / n\alpha \text{ (eq-8)}$$

The slope was found to be 0.608 which is very close to that calculated previously using LSV. That is confirmed our results that obtained. The pulse high and the pulse amplitude were also varied and the best values for both parameters were fixed at 10 mV and 50 mV, respectively.

$$i_p(\mu\text{A}) = 2.381 + 161.2709C(\mu\text{M}) \quad (r^2=0.998, n=10) \text{ (eq-9)}$$

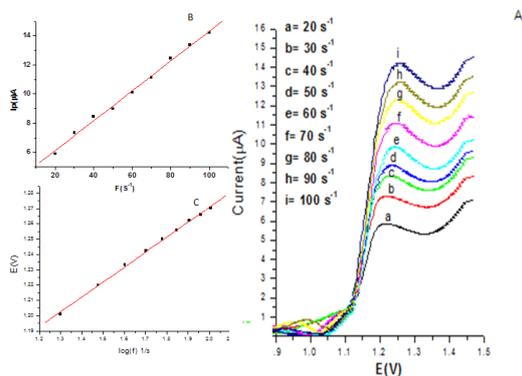


Fig.(5A). SWV of  $5 \times 10^{-6} \text{ M}$  of SA in phosphate buffer ( $\text{pH}=2.0$ ) for various frequencies using CPE modified by Silica gel/MWCNTs.

#### Effect of concentration and calibration curve

The influence of SA compound concentration on the oxidation peak current was studied over the range ( $3 \times 10^{-9}$ –  $7 \times 10^{-8} \text{ M}$ ) under the optimum condition in phosphate buffer ( $\text{pH}=2$ ) at  $50 \text{ mV/s}$ . It was found that the oxidation peak current of SA at a potential of  $+1.16 \text{ V}$  increased proportionally with the SA concentration increases as shown in Fig. (6A).

On plotting concentration of SA versus peak current of different concentrations of SA. A good Linear relation was obtained as illustrated in Fig.(6B) using the regression line as shown in equation (10):

$$i_p(\mu\text{A}) = 2.381 + 161.2709C(\mu\text{M}) \quad (r^2=0.998, n=10) \text{ (eq-10)}$$

Practically, the limit of quantification (LOQ) was found to be  $2.99 \times 10^{-8} \text{ M}$  of SA under the optimum conditions of phosphate buffer,  $\text{pH}=2$ , and scan rate  $50 \text{ mV/s}$ , where limit of detection (LOD) was calculated based on the following equation[41]:

$$\text{LOD} = 3 \text{ S/m. (eq-11)}$$

Where (S) is the standard deviation of the peak

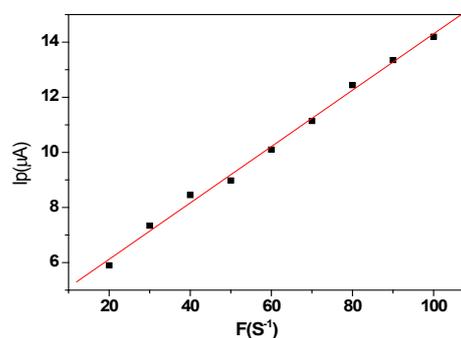


Fig.(5B). The relation between the peak current  $I_p$  ( $\mu\text{A}$ ) versus frequency ( $f \text{ s}^{-1}$ ) of  $5 \times 10^{-6} \text{ M}$  of SA in phosphate buffer ( $\text{pH}=2.0$ ) using CPE modified by Silica gel/MWCNTs.

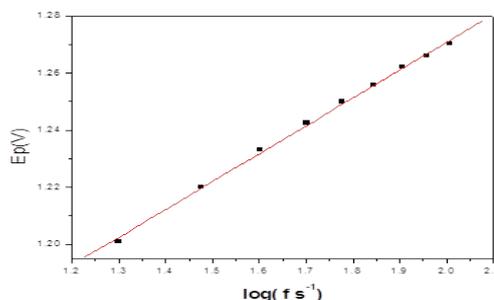


Fig.(5C). The relation between peak potential  $E_p$  (V) and log of frequency ( $f \text{ s}^{-1}$ ) of  $5 \times 10^{-6} \text{ M}$  SA in phosphate buffer ( $\text{pH}=2.0$ ) using CPE modified by Silica gel/MWCNTs.

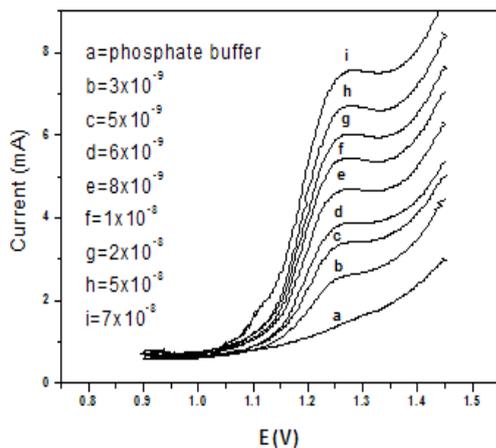


Fig. (6A). SWV for different concentrations of SA in phosphate buffer pH=2.0 at 90(s-1) frequency using CPE modified by silica gel/MWCNTs.

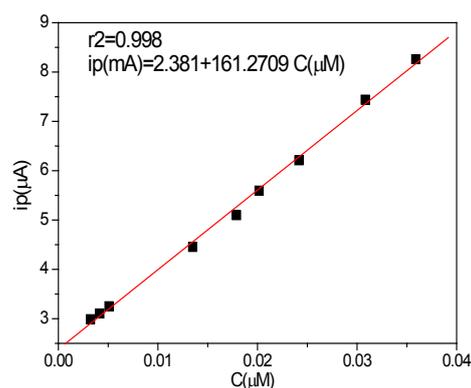


Fig. (6B). Calibration Curve of different concentration of SA in phosphate buffer pH=2.0 at 90(s-1) frequency using CPE modified by silica gel/MWCNTs.

current (three runs) of the lowest concentration of the linearity range and (m) is the slope of the related calibration equation. So LOD was calculated to be  $0.9 \times 10^{-9}$  M.

#### Reproducibility, stability, and interference study

The reproducibility of CPE modified by Silica gel/MWCNTs was examined by eight successive measurements of  $1 \times 10^{-6}$  M of SA under the optimum conditions. No obvious change in peak current was observed. This confirms that (CPE modified Silica gel/MWCNTs) is highly stable. And the relative standard deviation (RSD) was calculated to be 2.3%, which indicates an acceptable reproducibility for the modified electrode. In order to evaluate the selectivity of the modified electrode the possible interferences were investigated at the surface of CPE modified Silica gel/MWCNTs. The effect of various possible interferences such as some metal ions (which are bound up with growth of plants, carbohydrates, organic acids, amino acids and phytohormone compounds (which are usually present in the plants) were examined on the determination of  $1 \times 10^{-6}$  M of SA, and the corresponding voltammograms were recorded. The tolerance limit was defined as the maximum concentration of an interfering substance that causes a relative error more or less than  $\pm 5\%$  for determination of  $1 \times 10^{-6}$  M of SA. At about 200-folds of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , gibberellic acid, and abscisic acid were added to a concentration of  $1 \times 10^{-6}$  M of SA at the surface of CPE modified Silica gel/MWCNTs that is shown in Table (2). In

addition, 150-fold of other organic species such as the effect of benzoic acid, citric acid, oxalic acid, sucrose, and glucose were studied on the peak current of  $1 \times 10^{-6}$  M of SA. We found that no obvious effect on the peak height of  $1 \times 10^{-6}$  M of SA at CPE modified Silica gel/MWCNTs surface and that is illustrated in Table (2). On the contrary, the addition of 70-folds of L-alanine and L-cysteine to  $1 \times 10^{-6}$  M of SA were studied. The results demonstrated that all examined compounds have no effect on peak current of  $1 \times 10^{-6}$  M of SA at the surface of CPE modified Silica gel/MWCNTs under optimum conditions and the all data collected in Table (2). This means that the proposed method was found to be quite satisfactory for the selective determination of SA.

#### Analytical application

This proposed method was used to determine SA in tomato leave samples applying the optimum conditions selected before. The Recovery of SA was calculated by comparing the concentration obtained from the spiked mixtures with those of the pure SA using the following equation:

$$\text{Recovery \%} = \frac{(Q_{\text{DET}} - Q_{\text{P}}) \times 100}{Q_{\text{ADD}}} \quad (\text{eq-12})$$

Where  $Q_{\text{DET}}$  represents mM of Salicylic acid determined in the extracted sample,  $Q_{\text{P}}$  represents mM of Salicylic acid previously present in the extracted sample and  $Q_{\text{ADD}}$  is mM of SA added to the extracted sample. In Table 3, the results of the analysis of spiked samples of orange and lemon fruits are shown. It was found that SA amount can be quantitatively recovered by the proposed

TABLE 1. Comparison between our study and other studies using the same techniques.

Reference	LOD (M)	Working Electrode	Voltammetric Technique
[11]	$0.68 \times 10^{-7}$	Modified CPE with nickel nickel titanate nano ceramic	DPV
[9]	$0.10 \times 10^{-6}$	Gold electrode modified with copper nanoparticles	DPV
[8]	$0.80 \times 10^{-6}$	Modified glassy carbon electrode with a well-aligned multiwalled carbon nanotubes	DPV
[10]	$10.5 \times 10^{-4}$	ITO substrates modified with layer-by-layer films of carbon nanotubes and iron oxide nanoparticles	DPV
<b>Present study</b>	$0.9 \times 10^{-9}$	CPE modified by Silica gel\MWCNTs	SWV

TABLE 2. Effect of interferences on the oxidation peak current of  $1 \times 10^{-6}$ M Salicylic Acid.

Foreign species	Concentration (M) Upper Limit	Signal change (%)
Na <sup>+</sup>	$2 \times 10^{-4}$	+1.15
K <sup>+</sup>	$2 \times 10^{-4}$	+ 3.05
Zn <sup>2+</sup>	$2 \times 10^{-4}$	-3.60
Cu <sup>2+</sup>	$2 \times 10^{-4}$	-4.70
Mg <sup>2+</sup>	$2 \times 10^{-4}$	-3.20
Ca <sup>2+</sup>	$2 \times 10^{-4}$	-2.70
Fe <sup>3+</sup>	$2 \times 10^{-4}$	-3.50
Gibberellic acid	$2 \times 10^{-4}$	- 2.55
Abscisic acid	$1.5 \times 10^{-4}$	- 3.95
Citric acid	$1.0 \times 10^{-4}$	- 4.65
Benzoic acid	$1.0 \times 10^{-4}$	- 3.33
Oxalic acid	$1.0 \times 10^{-4}$	-4.30
Sucrose	$1.5 \times 10^{-6}$	-3.40
Glucose	$1.5 \times 10^{-6}$	-3.25
L. Alanine	$7 \times 10^{-5}$	-4.02
L. Cysteine	$7 \times 10^{-5}$	-3.60

TABLE 3. Results of analytical application and recovery of SA in Tomato.

Recovery (%)	Level determined [SA] ( $\mu$ M)	SA added ( $\mu$ M)
96.60	4.38	5.00
103.00	10.30	10.00
97.00	19.40	20.00

method, is thus a guarantee of the accuracy of the voltammetric determination of SA in tomato leaves.

### Conclusion

In this study, a new sensor CPE modified by silica gel/MWCNTs was prepared. with special characters such as, large specific surface area and good biocompatibility, as well as favorable electrochemical comparing to unmodified electrode. The electrochemical oxidation of SA over the surface of CPE modified by silica gel/MWCNTs was investigated. It was demonstrated that the new sensor exhibits a higher electrocatalytic activity, selectivity, reproducibility and sensitivity towards SA oxidation. From the CVs and the other analytical measurements, it was clear that from the CVs and the other analytical measurements, it was clear that the reaction of SA irreversible and the anodic current achieved under diffusion-controlled of SA irreversible and the anodic current achieved under diffusion-controlled. Also, the anodic peak current was strongly depends on pH values, scan rates and concentrations of the analyte. And good linearity range was obtained after achieved the optimum conditions to detect SA. The limit of detection was estimated to be  $0.9 \times 10^{-9}$ .

### Conflicts of interest

Nothing

### References

- Davies P. J. The Plant Hormones: Their Nature, Occurrence, and Functions. *Plant Hormones* 1–15 (2010).
- Wang Z., et al. Electrocatalytic activity of salicylic acid on the platinum nanoparticles modified electrode by electrochemical deposition. *Colloids Surfaces B Biointerfaces* **76**, 370–374 (2010).
- LONG X., CHEN F., DENG M. Determination of Salicylic Acid in Human Serum and Urine Samples by High-Performance Liquid Chromatography with Post-column  $\text{Ru}(\text{bipy})_3^{2+}$   $\text{Ce}(\text{SO}_4)_2$  Chemiluminescence Detection. *Anal. Sci.* **29**, 227–231 (2013).
- Lacina P., Mravcov L., Vávrová M. Application of comprehensive two-dimensional gas chromatography with mass spectrometric detection for the analysis of selected drug residues in wastewater and surface water. *J. Environ. Sci.* **25**, 204–212 (2013).
- Rivas G. A., Calatayud J. M. FIA-AAS determination of salicylic acid by a solid-phase reactor of copper carbonate incorporated in polyester resin beads. *Talanta* **42**, 1285–1289 (1995).
- Scott I. M., Yamamoto H. Mass spectrometric quantification of salicylic acid in plant tissues. *Phytochemistry* **37**, 335–336 (1994).
- Gualandi I., Scavetta E., Zappoli S., Tonelli D. Electrocatalytic oxidation of salicylic acid by a cobalt hydrotalcite-like compound modified Pt electrode. *Biosens. Bioelectron.* **26**, 3200–3206 (2011).
- Ribeiro C.de L., Santos J. G. M., de Souza J. R., Pereira-da-Silva M. A., Paterno, L.G. Electrochemical oxidation of salicylic acid at ITO substrates modified with layer-by-layer films of carbon nanotubes and iron oxide nanoparticles. *J. Electroanal. Chem.* **805**, 53–59 (2017).
- Wang Z., et al. Electrocatalytic oxidation of phytohormone salicylic acid at copper nanoparticles-modified gold electrode and its detection in oilseed rape infected with fungal pathogen *Sclerotinia sclerotiorum*. *Talanta* **80**, 1277–1281 (2010).
- Torriero A. A. J., Luco J. M., Sereno L., Raba J. Voltammetric determination of salicylic acid in pharmaceuticals formulations of acetylsalicylic acid. *Talanta* **62**, 247–254 (2004).
- Ghoreishi S. M., Kashani F. Z., Khoobi A., Enhessari M. Fabrication of a nickel titanate nanoceramic modified electrode for electrochemical studies and detection of salicylic acid. *J. Mol. Liq.* **211**, 970–980 (2015).
- Kalambate P. K., Srivastava A. K. Simultaneous voltammetric determination of paracetamol, cetirizine and phenylephrine using a multiwalled carbon nanotube-platinum nanoparticles nanocomposite modified carbon paste electrode. *Sensors Actuators, B Chem.* **233**, 237–248 (2016).
- Khalil M., Abdul Aleem A. Novel Potentiometric Sensors Based on Carbon and  $\text{TiO}_2$  Nano tubes/ $\beta$ -cyclodextrin for Meclofenoxate Hydrochloride Micro Determination in Spiked Surface Water and Urine Samples. *Egypt. J. Chem.* **62**(4), 727-738 (2019)
- Salem W. M. Sensitive Determination of Paracetamol Using Ferrocene Nanoparticles by Chitosan-Functionalized - Modified Carbon Past *Egypt. J. Chem.* **62**, Special Issue (Part 1) (2019)

- Electrode. *Egypt. J. Chem.* **62**, 679–690 (2019).
15. Javanbakht M., et al. A Biomimetic Potentiometric Sensor Using Molecularly Imprinted Polymer for the Cetirizine Assay in Tablets and Biological Fluids. *Electroanalysis* **20**, 2023–2030 (2008).
  16. Javanbakht M., et al. Carbon Paste Electrode Modified with Functionalized Nanoporous Silica Gel as a New Sensor for Determination of Silver Ion. *Electroanalysis* **19**, 1307–1314 (2007).
  17. Ganjali M. R., Khoshsafar H., Shirzadmehr A., Javanbakht M., Faridbod F. Improvement of Carbon Paste Ion Selective Electrode Response by Using Room Temperature Ionic Liquids (RTILs) and Multi-Walled Carbon Nanotubes (MWCNTs). *Int. J. Electrochem. Sci* **4**, 435–443 (2009).
  18. Moghaddam A B ,et al Fabrication and electrochemical behavior of single-walled carbon nanotube/graphite-based electrode. *Mater. Sci. Eng. C* **29**, 187–192 (2009).
  19. Khodari M., Mersal G. A. M., Rabie E. M., Assaf H. F. Electrochemical sensor based on carbon paste electrode modified by TiO<sub>2</sub> nanoparticles for the voltammetric determination of resorcinol. *Int. J. Electrochem. Sci.* **13**, 3460–3474 (2018).
  20. Walcarius A., Despas C., Bessiere J. Selective monitoring of Cu(II) species using a silica modified carbon paste electrode. *Analytica Chimica Acta* **385**, 79–89(1999).
  21. Gamemara D., Seoane G. A., Saenz-Méndez P., de María P. D. Redox Biocatalysis: Fundamentals and Applications. (2012).
  22. Walcarius A., Bessiere J. Silica-Modified Carbon Paste Electrode for Copper Determination in Ammoniacal Medium. *Electroanalysis* **9**, 707–713 (1997).
  23. Rezaei B., Damiri S. Multiwalled Carbon Nanotubes Modified Electrode as a Sensor for Adsorptive Stripping Voltammetric Determination of Hydrochlorothiazide. *IEEE Sens. J.* **8**, 1523–1529 (2008).
  24. Siswana M., Ozoemena K. I., Nyokong T. Electrocatalytic Detection of Amitrole on the Multi-Walled Carbon Nanotube – Iron (II) tetra-aminophthalocyanine Platform. *Sensors* **8**, 5096–5105 (2008).
  25. Li G., et al. A pyrrole quinoline quinone glucose dehydrogenase biosensor based on screen-printed carbon paste electrodes modified by carbon nanotubes. *Meas. Sci. Technol.* **19**, 065203 (2008).
  26. Shikandar D. B., Nagaraj P. S. Voltammetric oxidation and determination of loop diuretic furosemide at a multi-walled carbon nanotubes paste electrode. *Electrochim. Acta* **60**, 95–101 (2012).
  27. Li Y., et al. Simultaneous Analysis of Multiple Endogenous Plant Hormones in Leaf Tissue of Oilseed Rape by Solid-phase Extraction Coupled with High-performance Liquid Chromatography-Electrospray Ionisation Tandem Mass Spectrometry. *Phytochem. Anal.* **22**, 442–449 (2011).
  28. Nicholson R. S., Shain I. Theory of Stationary Electrode Polarography for a Chemical Reaction Coupled between Two Charge Transfers. *Anal. Chem.* **37**, 178–190 (1965).
  29. Mastragostino M., Nadjo L., Saveant J. M. Disproportionation and ECE mechanisms—I. Theoretical analysis. Relationships for linear sweep voltammetry. *Electrochim. Acta* **13**, 721–749 (1968).
  30. Ole H, Berend. S. Organic Electrochemistry. (2016).
  31. Papouchado L., Sandford R. W., Petrie G., Adams R. N. Anodic oxidation pathways of phenolic compounds Part 2. Stepwise electron transfers and coupled hydroxylations. *J. Electroanal. Chem. Interfacial Electrochem.* **65**, 275–284 (1975).
  32. Zhang W.-D., et al. Electrochemical oxidation of salicylic acid at well-aligned multiwalled carbon nanotube electrode and its detection. *J. Solid State Electrochem.* **14**, 1713–1718 (2010).
  33. Evans D., Hart J. P., Rees G. Voltammetric behaviour of salicylic acid at a glassy carbon electrode and its determination in serum using liquid chromatography with amperometric detection. *Analyst* **116**, 803 (1991).
  34. Khodari M., Rabie E. M., Shamroukh A. A. Carbon Paste Electrode Modified by Multiwalled Carbon Nanotube " for Electrochemical Determination " of Vitamin C. *Int. J. Biochem. Biophys.* **6**, 58–69 (2018).
  35. Toledo R. A., Vaz C. M. P. Use of a graphite-polyurethane composite electrode for electroanalytical determination of indole-3-acetic acid in soil samples. *Microchem. J.* **86**, 161–165 (2007).

36. Nezamzadeh A., Amini M. K., Faghihian H. Square-Wave Voltammetric Determination of Ascorbic Acid Based on its Electrocatalytic Oxidation at Zeolite-Modified Carbon-Paste Electrodes. *Int. J. Electrochem. Sci* **2**, 583–594 (2007).
37. Ansari. S.A.M.K., Sangshetti.J.N., Kokare.N.D., Wakte.P.S., Shinde.D.B. Indian Journal of Chemical Technology, *Adsorpt. J. Int. Adsorpt. Soc.* **17**, 5–6 (2010).
38. Kulova T. L., Skundin A. M. High-voltage materials for positive electrodes of lithium ion batteries (review). *Russ. J. Electrochem.* **52**, 501–524 (2016).
39. Gosser D. K. Cyclic voltammetry: Simulation and analysis of reaction mechanisms. Vol. 43(1994).
40. Lovrić M., Komorsky-Lovric Š. Square-wave voltammetry of an adsorbed reactant. *J. Electroanal. Chem. Interfacial Electrochem.* **248**, 239–253 (1988).
41. Edwardson P.A., Bhaskar G., Fairbrother J.E. Method validation in pharmaceutical analysis. *J. Pharm. Biomed. Anal.* **8**, 929–933 (1990).