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# Sensitive electrochemical detection of L-tryptophan using a glassy carbon electrode modified with pectin extracted from *Arthrocnemum indicum* leaves

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## Abstract

Pectin from *Arthrocnemum indicum* leaves (PAI) extracted from plants, harvested in the Tunisian Sahel, was used for the first time as a sensitive matrix for the design of an electrochemical sensor of L-tryptophan via differential pulse voltammetry (DPV). A glassy carbon electrode (GCE) was modified by a PAI layer through simple adsorption, leading to a DPV signal of L-tryptophan that was increased by a factor of 15. The PAI-modified electrode exhibited a good analytical performance towards the detection of L-tryptophan with a wide linear range between  $9.10^{-5}$  mM to  $2.10^{-2}$  mM, a detection limit of 0.09  $\mu$ M, and a sensitivity of 90.15  $\mu$ A. mM<sup>-1</sup>. Compared to other reported electrochemical sensors, PAI/GCE presents a lower detection limit, even without the use of nanomaterials. In addition, the PAI/GCE showed good reproducibility and good selectivity towards the determination of L-tryptophan versus other amino acids, uric acid, and ascorbic acid, making it suitable for the determination of L-tryptophan in biological fluids.

**Keywords:** pectin, *Arthrocnemum indicum* leaves, differential pulse voltammetry, modified GCE, L-Tryptophan.

## 1. Introduction

Some oxidizable amino acids such as L-Tryptophan (L-Trp) play important roles in many biochemical processes [1] and recently, the interest in amino acid detection has increased, due to their potential application in diagnosis of numerous diseases [2-5]. L-Trp, an essential amino acid, is vital to the human body's metabolism. It is a precursor for niacin, melatonin and serotonin involved in regulating mood. The detection of L-Trp levels is very important because its deficiency can lead to metabolic and neurological disorders [6]. When L-Trp is improperly metabolized, toxic metabolites are produced in the brain which probably causes schizophrenia, drowsiness, nausea, hallucinations, headache, loss of appetite, and Parkinson's disease. As humans and animals are not able to synthesize L-Trp themselves, it must be obtained from food and pharmaceutical formulas [7]. Thus, determining this amino acid in biological samples, as well as in food samples is of high importance. Tryptophan whose formula is presented in Fig. 1, has the standard chemical name (2S)-2-amino-3-(1H-indol-3-yl) propanoic acid and the molecular formula  $C_{11}H_{12}N_2O_2$ ; it has a molecular weight of 204.22 g/mol.

**Figure 1.** Formula of L-tryptophan

Various classical analytical methods have been applied to the detection of L-Trp, such as high-performance liquid chromatography (HPLC) [8], capillary electrophoresis [9], mass spectrometry and fluorescence [10]. These methods are quite accurate, but they are dependent on multi-step sample clean-up procedures, high-cost equipment, and sophisticated skills, then are relatively expensive and time-consuming.

In recent years, electrochemical sensors gained considerable interest for the detection of these electroactive compounds and showed promising potential for the detection of tryptophan, they also provide several advantages: simplicity, low-cost, rapid response and high sensitivity. There are some reports on the determination of L-Trp by electrochemical methods [11]. However, in most cases, the oxidation of L-Trp at the aforementioned modified electrodes always requires a high overpotential. Hence, it is imminently required to use a sensitive

modified electrode which could decrease the overpotential and increase the current of L-Trp oxidation with a low detection limit and wide linear range [12,13]. Khoshnevisan et al demonstrated the use of reduced graphene oxide/gold nanoparticles for L-Trp detection, the modified sensor demonstrated LOD of 0.48 $\mu$ M in the concentration range of 0.1 to 2.5  $\mu$ M [14]. Zhou et al presented the use of Ta<sub>2</sub>O<sub>5</sub>/rGO nanocomposite modified electrodes for the detection of L-Trp with a LOD of 0.84  $\mu$ M [9]. Qian et al demonstrated the use of multi-walled carbon nanotube/polydopamine composite loaded with copper (II) for L-Trp detection with LOD of 0.2  $\mu$ M in the concentration range of 1.0 to 100 $\mu$ M [15].

Over past years, natural polymers have appeared as a promising substitute for synthetic ones and they can be used as polymer host presenting many advantages such as biodegradability, reactive functional groups, low cost, non-toxicity and abundant availability in nature. Different polysaccharides, as well as their derivatives, can be widely used to modify electrode and cellulose, alginate, chitosan, chitin are some examples [16]. Yang et al demonstrated the use of perylene-functionalized graphene sheets modified with chitosan for voltammetric discrimination of L-Trp, the modified sensor demonstrated LOD of 1.2  $\mu$ M in the linear range of 1000 to 10000 $\mu$ M [17]. Roushani et al demonstrated the use of carbon nanodots/chitosan nanocomposite for the detection of L-Trp, the modified electrode demonstrated LOD of 0.09  $\mu$ M in the linear range of 0 to 90  $\mu$ M [18].

In this work, a polysaccharide from *Arthrocnemum indicum* leaves (PAI) harvested from natural sources in the region of Monastir (Tunisian Sahel) was used for the first time to modify a glassy carbon electrode for L-L-Trp determination. *Arthrocnemum indicum* is a perennial, shrubby halophyte plant of the family of *Amaranthaceae*, mainly abundant in salt marshes along the coastlines of North Africa. In these regions, this plant has been well-known as a traditional medicinal plant for hundreds of years. Polysaccharide was extracted through aqueous extraction [19] and characterized before its use for modification of the GCE.

## 2. Experimental

### 2.1 Chemicals and reagents

K<sub>4</sub>[Fe(CN)<sub>6</sub>].3H<sub>2</sub>O, K<sub>3</sub>[Fe(CN)<sub>6</sub>], KCl, L-tryptophan, uric acid, ascorbic acid were purchased from FlukaChemika.

The buffer solution used for all experiments was phosphate buffer saline (PBS) containing 137 mM NaCl, 2.7 mM KCl, 0.01 M  $\text{KH}_2\text{PO}_4$  and 0.01 M  $\text{K}_2\text{HPO}_4$ , pH 7. All solutions were prepared in ultrapure water (resistance 18.2 M $\Omega$ /cm) produced by a Millipore Milli-Q system. The PAI material was extracted from the *Arthrocnemum indicum* plant harvested in the region of Monastir (Tunisian Sahel), in the form of dry leaves [19].

## 2.2 Apparatus

The infrared (IR) spectra of the extracted polysaccharide (PAI) was performed using an FTIR spectrophotometer (BX FTIR system spectrometer, Perkin Elmer Company, Waltham, MA, USA) at the absorbance mode from 4000 to 400  $\text{cm}^{-1}$ . The sample was incorporated into potassium bromide (KBr) powder and thereafter pressed into a 1mm pellet.

The electrochemical measurements were performed using an Autolab (PGSTAT 302N, Eco Chemie) in a dark Faraday cage. An electrochemical cell containing a three-electrode was used : a modified glassy carbon electrode (GCE;  $\Phi = 3$  mm) as the working electrode, a Ag/AgCl/KCl as the reference electrode and a platinum wire ( $\Phi = 1$  mm) as the counter electrode. Differential pulse voltammetry (DPV) was used to investigate the electrochemical behavior of L-Tryptophan at scan rate of 50  $\text{mV}\cdot\text{s}^{-1}$  with an accumulation time of 20 s.

## 2.3 Production of PAI

The extraction conditions of the polysaccharide (PAI), from the Tunisian *A. indicum* leaves, were optimized as reported earlier [19]. Dried and grounded *A. indicum* leaves were degreased with petroleum ether for 48 h to remove lipids and then discolored with ethanol via a Soxhlet treatment for 48 h. After that, discolored sample was treated three times with deionized water (pH value adjusted at 2 by addition of diluted HCl solution) in a thermostated cell surmounted by a refrigerant. Then, the aqueous extract was centrifuged for 15 min at 3500 rpm, precipitated with 4 volumes of ethanol (96%) and then kept 12h at around 4°C. The resulting precipitate was obtained via a vacuum filtration; it was then dissolved in deionized water and dialyzed using a dialysis membrane tubing with a molecular weight cut off of 14 kDa. Lastly, the dialysate was lyophilized to recover the PAI fraction.

## 2.4 Functionalization of the GCE

The GCE was polished with an alumina solution (0.5  $\mu\text{m}$ ), rinsed and ultrasonicated in water for 3 min. Then, the GCE was scanned between -0.2 and 1.3 V in 0.5 M  $\text{H}_2\text{SO}_4$  at 50  $\text{mV s}^{-1}$  for 10 cycles until a stable CV curve was obtained. Subsequently, 5  $\mu\text{L}$  of PAI solution was deposited on the electrode. The modified surface was dried at ambient temperature overnight. A good adhesion of the PAI film on the GC surface was obtained.

### 3. Results and Discussion

#### 3.1 FTIR characterization of PAI

Fourier transform-infrared spectroscopy (FTIR) spectrum of PAI is illustrated in Fig. 2 and shows distinct absorption bands of polysaccharide. A large absorption band at around 3348  $\text{cm}^{-1}$  is typical of the hydroxyl groups (O-H), involved in inter molecular and intra molecular interaction of the polysaccharides chains [20]. Likewise, the band at 2921  $\text{cm}^{-1}$  is referred to (C-H) absorption stretching vibrations. Furthermore, the band at 1731  $\text{cm}^{-1}$  is allotted to the (C=O) stretching vibration of the O-acetyl groups and the little band at around of 1603  $\text{cm}^{-1}$  is assigned to the band of carboxylate ion stretching ( $\text{COO}^-$ ). The additional band at 1424  $\text{cm}^{-1}$  shows the existence of uronic acid [21]. Also, the presence of the absorption band at 1230  $\text{cm}^{-1}$  may be attributable to the stretching vibration of non-symmetrical (C-O-C). The intense characteristic band at around 1011  $\text{cm}^{-1}$  in the infrared spectrum exhibits the stretching vibration of (C-O-C) of glycosidic structure [21]. Finally, the two characteristics of bands of absorption at 848  $\text{cm}^{-1}$  and 814  $\text{cm}^{-1}$  indicate the  $\beta$  and  $\alpha$ -glycosidic  $\text{C}_1\text{-H}$  deformation, respectively [21]. These bands are in agreement with the composition of the extracted PAI found through GC-MS [19]: high amount of uronic acid and presence of neutral sugars (rhamnose, galactose, arabinose). The extracted PAI are arabinan-rich pectic polysaccharides.

**Figure 2.** The Fourier transform-infrared spectroscopy (FTIR) spectrum of PAI

#### 3.2 Electrochemical characterization of PAI/GCE

Cyclic voltammetry was used for monitoring the change of the electrode behavior after all the modification steps. Fig. 3 shows the electroactivity change of the bare GCE and the GCE modified by the PAI matrix versus the  $[\text{Fe}(\text{CN})_6]^{3/4-}$  redox probe. The CV of the bare GCE shows a quasi-reversible redox signal, with a peak potential difference ( $\Delta E_p$ ) of 100 mV and a ratio of about 1:1 between anodic and cathodic peak currents, demonstrating that the glassy carbon electrode(GCE) presents a reversible redox reaction with  $[\text{Fe}(\text{CN})_6]^{3/4-}$  couple [22].

After the deposition of the PAI matrix the current decreases which demonstrates that the functionalization process occurred.

**Figure 3.** Cyclic voltammograms of PAI-modified and unmodified GCE in 0.1 M KCl solution containing 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  at scan rate of 50 mV s<sup>-1</sup>.

### 3.3 Electrochemical behavior of L-tryptophan

DPV was used to investigate the electrochemical behavior of 0.1 mM L-Tryp in phosphate buffer solution (pH 7.0) on a GCE and a PAI/GCE. (Fig. 4). It was found that L-Tryp presents only one oxidation peak in the cyclic voltammogram from 0.2 to 1.0 V at bare GC and at PAI/GCE, suggesting that the oxidation of tryptophan is an irreversible process, which is in accordance with the literature [9]. The oxidation peak potential is 0.64 V for L-Trp at PAI/GCE and 0.76V for bare electrode and the intensity is increased by a factor of 15. The results indicate that PAI/GCE increases the peak currents and reduce the overpotential, which proves that, due to the interaction of L-Trp with the PAI film, the Trp oxidation becomes easier.

**Figure 4.** Electrochemical response of 0.1 mM of L-Tryptophan on a GCE and a PAI/GCE at scan rate of 50 mV.s<sup>-1</sup> (0.01 M phosphate buffer solution (pH 7.0)).

### 3.4 Optimization of the experimental parameters

In order to optimize the sensitivity of the PAI modified GCE towards L-Tryptophan, the effect of some parameters such as electrolyte pH and deposited quantity of PAI were investigated and optimized.

#### 3.4.1 Effect of pH

The pH is an important factor in electrochemical detection since protons are involved in the redox reaction [23]. The peak potential corresponding to the L-Tryp oxidation shifted negatively in the range of 4.5 to 8.5 revealing that protons takes part in the oxidation of L-Tryp. As shown in Fig. 5a, a linear relationship between peak potential ( $E_p$ ) and pH was observed for L-Tryp following the equation,

$$E_p = -50.05 \text{ pH} + 0.94, R^2 = 0.983 \text{ (Eq. 1)}$$

The obtained value of the slope is -50.05 mV/pH, in agreement with the theoretical value (59 mV/pH); based on that, it can be assumed that an equal number of electrons and protons participated in the process at the electrode.

The intensity of current peak also changed with pH (Fig 5b) when increasing the pH value from 4.5 to 8.5. The oxidation current peak of L-Tryp reaches a maximum at pH 7.0. Therefore, pH value of 7.0, close to the physiological level, was chosen for the further analytical experiments.

**Figure 5.** Effect of pH on peak potential (a) and peak current (b) of 0.1mM L-Trp at PAI-GCE (0.01 M phosphate buffer solution (pH 7.0)).

### 3.4.2 Effect of scan rate

In order to study the nature of electrode process occurring at the electrode surface, the effect of scan rate on the oxidation peak current of 0.1 mM L-Tryp was studied by cyclic voltammetry at different scan rates (25 to 500 mV s<sup>-1</sup>) (Fig. 6a). The oxidation peak current for L-Trp increases linearly with increasing scan rate, indicating that the electrochemical reaction of L-Trp at the PAI modified GCE is a surface-controlled electrochemical process. The linear regression equation is expressed as:

$$I_{p_a} (\mu A) = 2.86 + 0.024 v \text{ (mV} \cdot \text{s}^{-1}) \text{ (R} = 0.995\text{). (Eq. 2)}$$

Moreover, the oxidation peak potentials shift positively with increasing scan rate. So, 50 mV·s<sup>-1</sup> is chosen as a moderate scan rate in the following experiments.

The plot of peak current vs. square root of scan rate ( $v^{1/2}$ ) is linear over the whole studied range of scan rate (Fig. 6b), which indicates that it is a typical diffusion-controlled process, and the equation can be expressed as:

$$i_p (\mu A) = 0.635v^{1/2} - 0.4, R^2 = 0.984. \text{ (Eq. 3)}$$

Also, a plot of logarithm of peak current, log (ip), versus the logarithm of scan rate was studied. This relationship was found to be linear (Fig. 6c),

$$\log i_p (\mu A) = 0.495 \log v - 0.21, R^2 = 0.975 \text{ (Eq. 4)}$$

with a slope of 0.49 which is near to the theoretical value of 0.5 for a diffusion-controlled process.

The number of electrons involved in the oxidation of L-L-Trp was calculated using the equation:

$$i_p = nFQv/4RT \text{ (Eq. 5),}$$



where  $i_p$  represents the anodic peak current,  $Q$  is the amount of charge integrated from the area of voltammetric peak,  $T$  is the temperature in Kelvin (298 K),  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1}$ ),  $F$  is the Faraday constant ( $96500 \text{ C/mol}$ ) and  $n$  is the number of electrons transferred. From the slope of  $i_p$  versus  $v$ ,  $n$  was calculated to be 1.79 ( $\approx 2$ ). Hence it can be concluded that the oxidation of L-Tryp involves two electrons and two protons. It can be assumed that L-Trp is oxidized into 2-amino-3-(5-oxo-3,5-dihydro-2H-indol-3-yl) propionic acid, which was indicated by the appearance of one irreversible oxidation peak on the cyclic voltammogram. Having in mind the literature data and the results obtained in this study, the mechanism of L-Tryptophan oxidation on the PAI/GCE is designed in Fig. 7.

The linear relationship of the anodic peak potential and logarithm of the scan rate presented in Fig. 6d. The relationship between the oxidation peak potentials and scan rates can be described as follows:

$$E_{pa} = 0.035 \log v + 0.54, R^2 = 0.975 \text{ (Eq. 6)}$$

According to Laviron's theory [24], the linear plot of  $E_{pa}$  versus  $\log v$  presents a slope ( $2.3RT/\alpha nF$ ) equal to 0.035, the value of  $\alpha n$  is calculated to be 0.73. As for a totally irreversible electrode reaction process,  $\alpha$  is equal to 0.37.

**Figure 6.** Scan rate study: (a) overlay of cyclic voltammogram for oxidation of L-Tryp at different scan rates, (b) plot of peak current vs. square root of scan rate, (c) plot of logarithm of peak current vs. logarithm of scan rate, (d) plot of peak potential vs. logarithm of scan rate.

**Figure 7.** Mechanism of L-Tryptophan oxidation.

### 3.4.3 Influence of the volume of PAI suspension

The influence of the dosage (4-7  $\mu\text{L}$ ) of PAI suspension on the electrode was investigated in 0.1 mM L-Tryptophan solution at  $v = 50 \text{ mV.s}^{-1}$  (Fig.8). The results show that the current peak increases with the volume of PAI suspension until 5  $\mu\text{L}$  and then decreased which may be ascribed to the optimum PAI film thickness. So 5  $\mu\text{L}$  was chosen as the optimum dosage.

**Figure 8.** Effect of the volume of PAI suspension on the L-Trp peak current. Experimental conditions: 0.01 M phosphate buffer solution (pH 7.0), 0.1mM L-Trp, scan rate 50 mV/s.

## 3.5 Analytical performance of the L-tryptophan sensor

The electrochemical performance of L-Tryptophan was investigated by DPV on bare GCE and PAI modified GCE in PBS (pH7.0) at 50 mV.s<sup>-1</sup>. Fig. 9 (a) displays the DPV signal for different concentrations of L-Trp at the bare GCE. It was found that the anodic peak current increased linearly with the increasing concentrations of L-Trp in the range from 5x10<sup>-4</sup> to 10<sup>-2</sup> mM, the sensitivity was obtained to be 9.80 μA. mM<sup>-1</sup>. The peak maximum potential shifted towards anodic values when the concentration of L-Trp increases. This overpotential is due to an increase in the charge transfer resistance; this phenomenon was observed when a film of peptin was in contact with a solution of propylphosphonic acid (100ppm), the charge transfer resistance was increased of 13% [25].

Fig.9 (b) shows the DPV for different concentrations of L-Trp at the PAI modified GCE; it was found that the anodic peak current at 0.64V increased linearly with the increasing concentrations of L-Trp in the range from 9x10<sup>-5</sup> mM to 2x10<sup>-2</sup> mM, the sensitivity is 90.15 μA. mM<sup>-1</sup> and a detection limit of 9x10<sup>-5</sup> mM was obtained. Fig.10 shows the linear relationship between the current and the concentration of L-Trp on bare GCE (a) and on PAI/GCE (b). The sensitivity of detection is improved by a factor 9.2 due to the presence of the PAI film. L-Trp is concentrated in the PAI film through its adsorption on the PAI sites. This adsorption is optimum at a pH value of 7 (Fig. 5). The iep value of L-Tryp is 5.88 [26], which shows that the global charge of the L-Tryp molecule at pH 7 is slightly negative. In the study of interactions of a protein HvPR5c with a polysaccharide (1,3)-β-D-glucan, it has been shown through molecular models that hydrogen bonds were formed between both entities through several involved aminoacids [27].

**Figure 9.** DPV detection of L-Tryptophan in the concentration range from 5.10<sup>-4</sup> to 10<sup>-2</sup> mM on (a)bare GCE, (b) on PAI/GCE in 0.01 M phosphate buffer solution (pH 7.0), scan rate 50 mV/s.

**Figure 10.** Calibration curve of L-Tryptophan at bare GCE (a) and at PAI/GCE (b). Experimental conditions: 0.01 M phosphate buffer solution (pH 7.0), scan rate 50 mV/s.

**Table 1.** Comparison of PAI/GCE sensor with other reported electrochemical sensors for the determination of L-Tryptophan.

Table1 presents the comparison between the proposed sensor and other reported electrochemical sensors for L-Trp. By comparing the values of limit of detection shown in

Table 1, it can be noticed that the PAI/GCE presents the lower detection limit, even without the use of nanomaterials (rGO or MWNCNTs).

A pectin/GCE presents an excellent reproducibility for the detection of L-Trp (RSD = 1.5%). The stability of the modified electrode was investigated by measuring the oxidation current of 0.1 mM of L-Tryptophan in pH 7.0 PBS after storage in a refrigerator at 4°C for one month, no apparent decrease of current was observed after the first week and the response is maintained at 90.2% of its initial value after 3 weeks.

The inter-sensor reproducibility of the modified electrode for the determination of L-Trp was also examined by repetitive measurements (4 modified electrodes). The relative standard deviation (RSD) was 2.13% (n=4).

### 3.51. Interference study

The possible interference for the detection of L-Trp at PAI-GCE in PBS (pH 7.0) was investigated. **Experimental results show that the presence of the other amino acids (leucine, isoleucine, proline, lysine, aspartic acid, valine and, glutamine) with a total concentration of 0.2 mM shows an influence of less than 2% on the current response for 0.1 mM L-Trp.**

Fig 11 displays the detection of L-Trp signal in the presence two kinds of important biological substances uric acid (UA) and ascorbic acid (AA). These substances are detected respectively at 0.12 V and at 0.27 V, without disturbing L-Trp signal.

**Figure 11.** Simultaneous detection of 0.2 mM ascorbic acid 0.1 mM uric acid and 0.2 mM tryptophan on PAI/GCE in 0.01 M phosphate buffer solution (pH 7.0), scan rate 50 mV/s.

### 3.5.2. Analysis of urine samples

In order to evaluate the practical application of the PAI-GCE electrode, the analytical performances were evaluated by measurement of L-Trp in human urine sample. The DPV conditions were established under optimized parameters. The real sample was collected from healthy patients, then, human urine sample was 100-fold diluted in 0.1 M PBS (pH 7.0). After that, the standard addition method was applied; different concentrations of L-Trp were added to the previously prepared human urine. Fig 12 shows the differential pulse voltammetry of L-Trp in the concentration range from  $1.25 \times 10^{-3}$  mM  $1.5 \times 10^{-2}$  mM on PAI/GCE, scan rate 50

mV.s<sup>-1</sup>. The obtained concentration of L-Trp was  $8.10 (\pm 0.17) \times 10^{-3}$  mM ( $165.4 \pm 3.0$  mg/L). As literature reported, the normal concentrations of tryptophan in human urine are between 137 and 240 mg/L [33]. The detected value is in the normal concentration range. This human urine sample was controlled by HPLC/MS/MS giving a concentration of  $161 \pm 2$  mg/L.

**Figure 12.** Differential Pulse Voltammograms for detection of Tryptophan in human urine sample. Experimental conditions: 0.01 M phosphate buffer solution (pH 7.0), scan rate 50 mV/s.

### 3.6 Conclusion

In this study an electrochemical sensor based on a new sensing PAI matrix for the determination of L-Tryptophan was developed. The PAI/GCE modified electrode exhibits high sensitivity, selectivity and low detection limit. Furthermore, the designed working electrode has been efficiently used for the L-tryptophan in the human urine and provided satisfactory results. The design and preparation of the electrode materials were simple and effective and the results demonstrate that the PAI/GCE sensor with excellent analytical performances towards amino acids could serve in future for efficient application in biological fluids.

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## Figure captions:

**Figure 1:** Formula of L-tryptophan

**Figure 2:** The Fourier transform-infrared spectroscopy (FTIR) spectrum of PAI

**Figure 3:** Cyclic voltammograms of PAI-modified and unmodified GCE in 0.1 M KCl solution containing 5 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  at scan rate of 50 mV s<sup>-1</sup>.

**Figure 4:** Electrochemical response of 0.1 mM of L-Tryptophan on a GCE and a PAI/GCE at scan rate of 50 mV.s<sup>-1</sup> (0.01 M phosphate buffer solution (pH 7.0)).

**Figure 5:** Effect of pH on peak potential (a) and peak current (b) of 0.1mM L-Trp at PAI-GCE (0.01 M phosphate buffer solution (pH 7.0)).

**Figure 6:** Scan rate study: (a) overlay of cyclic voltammogram for oxidation of L-Tryp at different scan rates, (b) plot of peak current vs. square root of scan rate, (c) plot of logarithm of peak current vs. logarithm of scan rate, (d) plot of peak potential vs. logarithm of scan rate.

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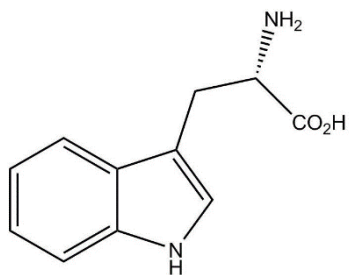
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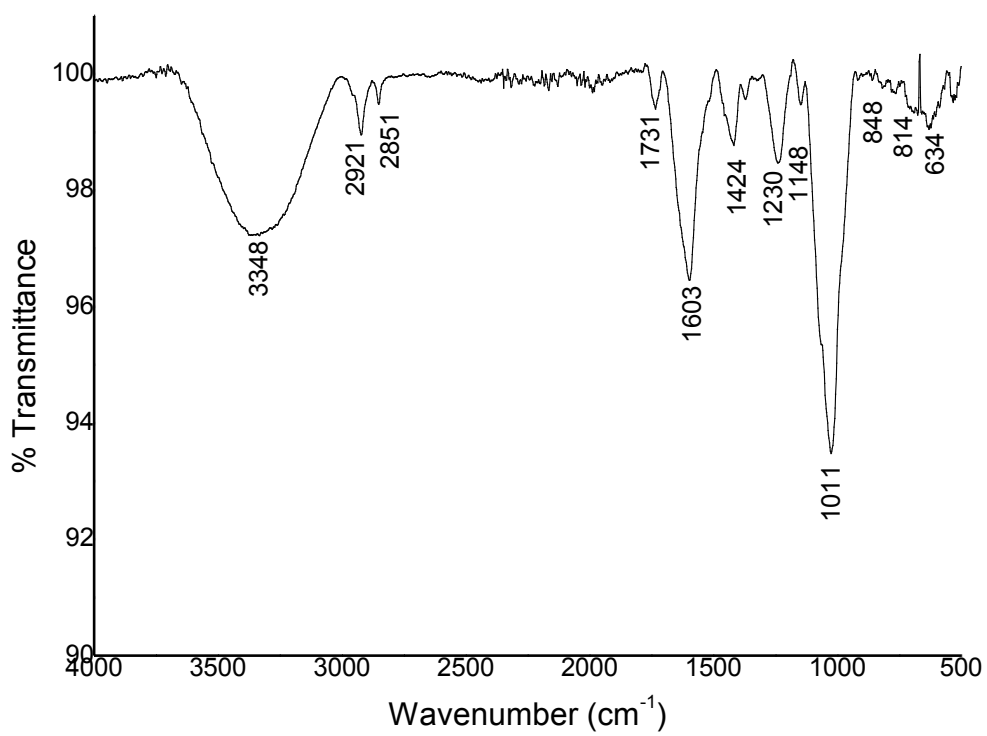
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## Table caption:

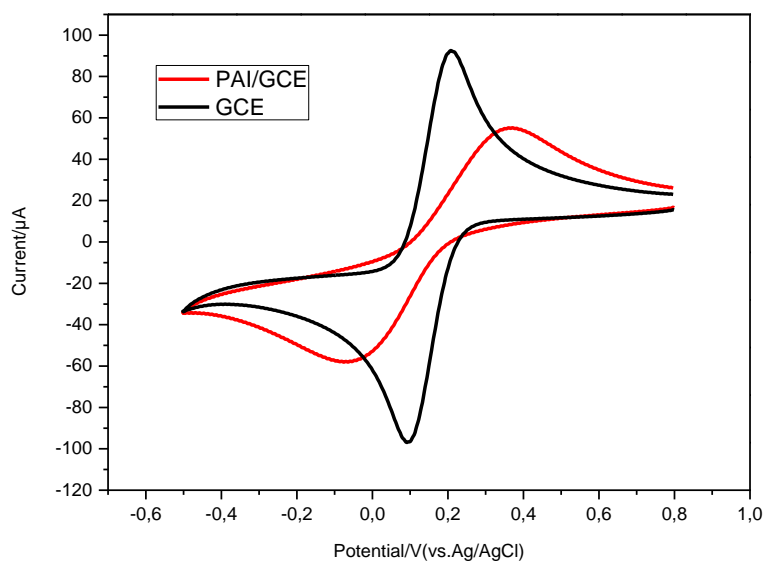
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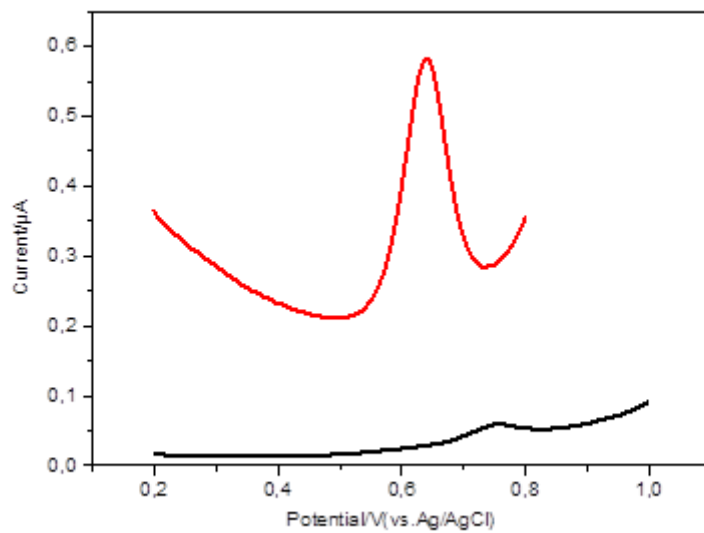
**Figure 1**



**Figure2**



**Figure 3**



**Figure 4**



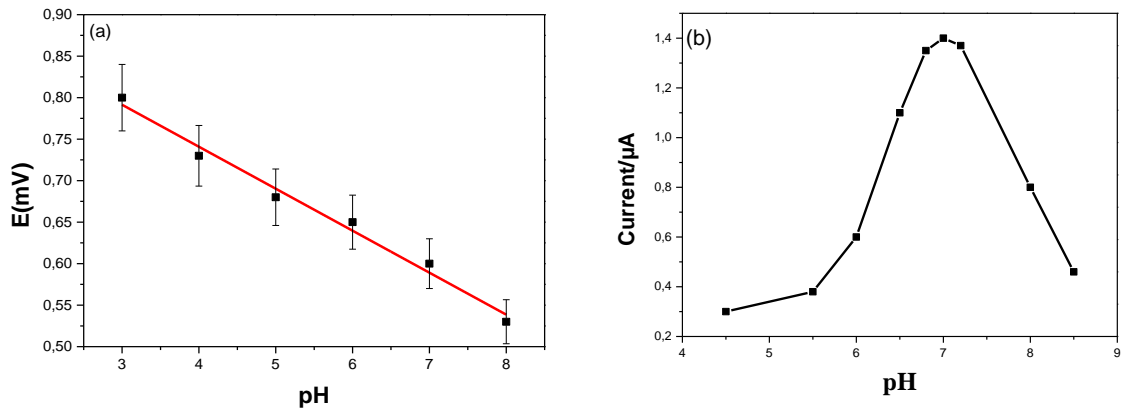
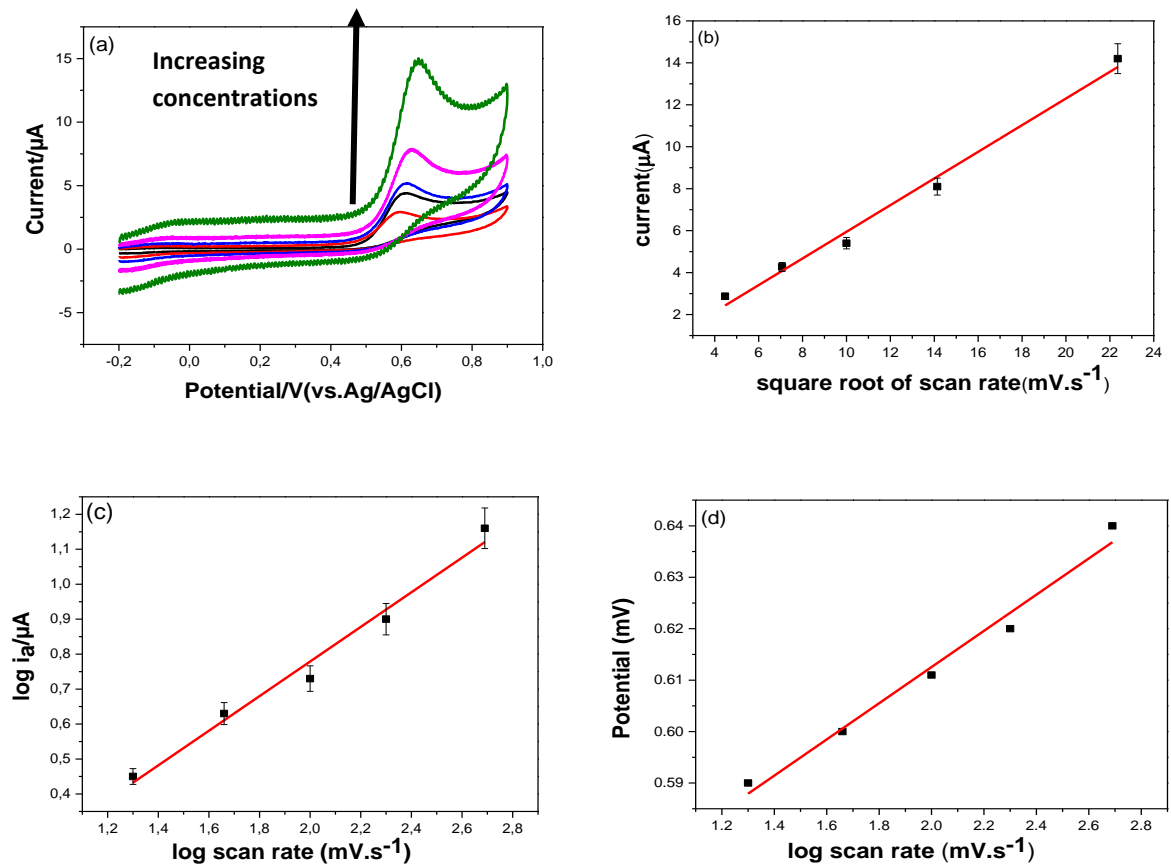
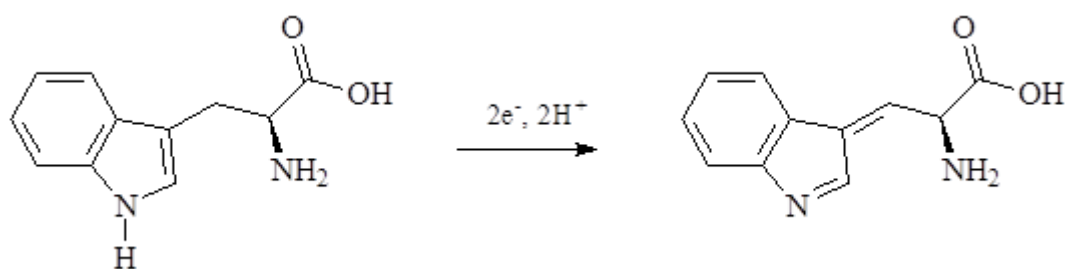


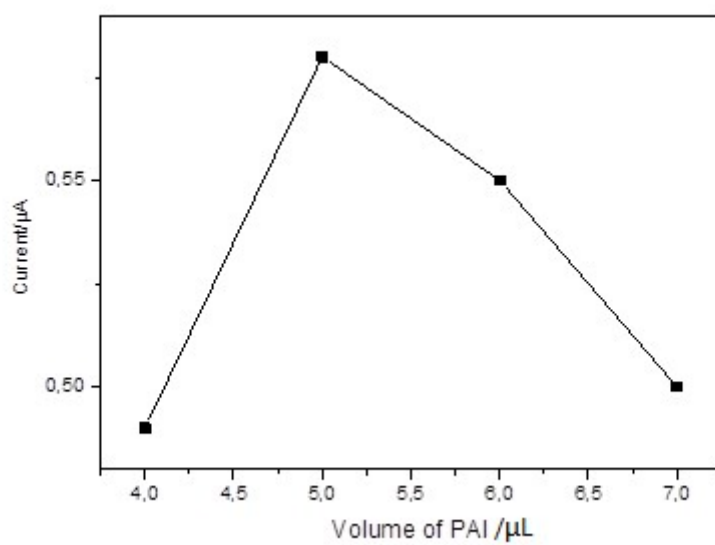
Figure 5



**Figure 6**



**Figure7**



**Figure 8**

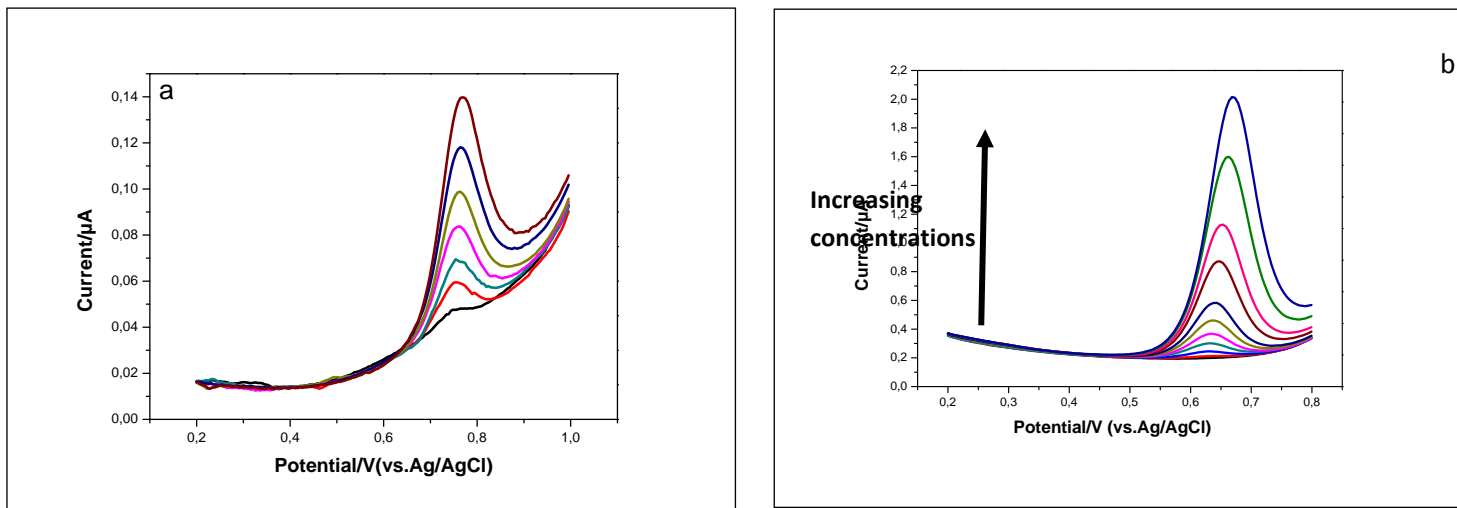


Figure 9

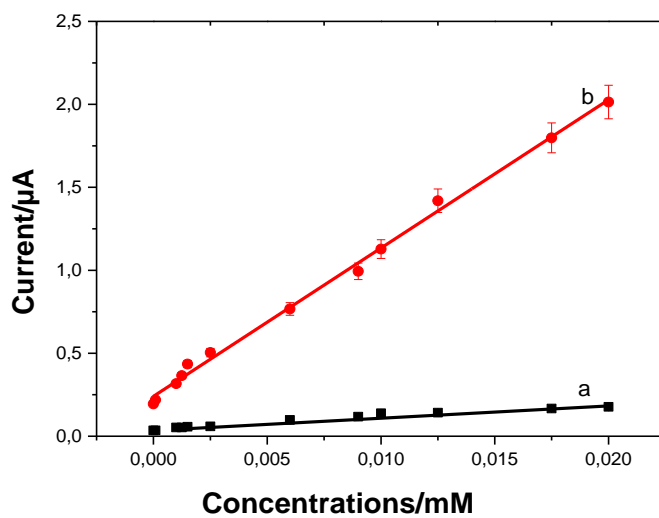


Figure 10

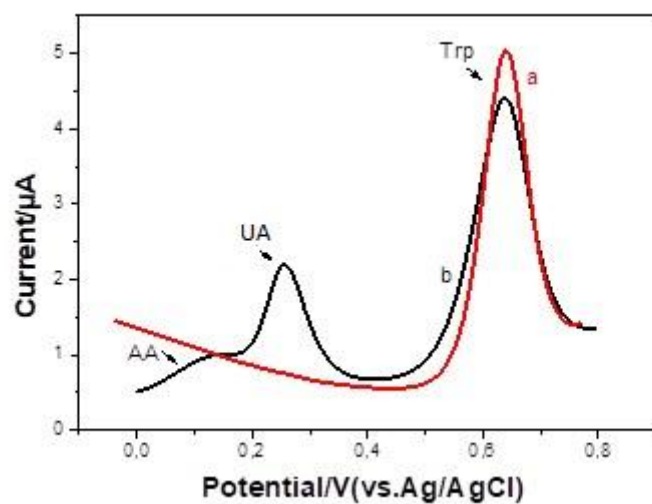


Figure 11

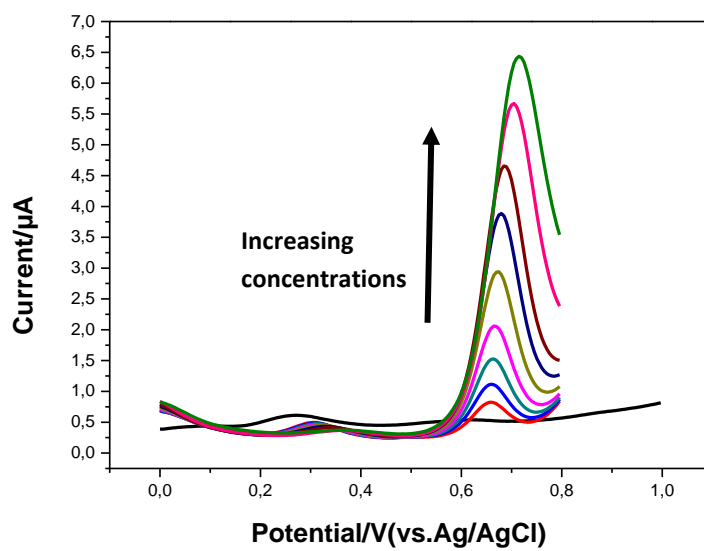


Figure 12

**Table 1**

Working Electrode	Modification	Method	Potential	Detection limit $\mu\text{M}$	Linear Range ( $\mu\text{M}$ )	reference
GCE	Ta <sub>2</sub> O <sub>5</sub> -rGO	CV	0.7 V vs. SCE	0.84	1.0-8.0;8.0-80	[9]
GCE	TBABr/ $\beta$ -CD/MWCNTs	DPV	0.8 V vs.Ag/AgCl	0.07	1.5-30.5	[28]
GCE	CeO <sub>2</sub> /RGO	DPV	0.65 V vs. SCE	0.08	0.2-25	[29]
GCE	rGO-PTCA-chitosan	DPV	0.8 V vs. SCE	1.2	1000-10000	[17]
CPE	3-neomenthylindene	DPV	0.79 V vs.Ag/AgCl	1.71	2.5-300	[30]
CPE	rGO/AuNPs	DPV	0.75 V vs.Ag/AgCl	0.39	0.5-500	[31]
CPE	MWCNT	DPV	0.9 V vs.Ag/AgCl	0.06	0.6-100	[32]
GCE	pectin	DPV	0.65 V vs.Ag/AgCl	0.09	0.09-20	This work

GCE: Glassy carbon electrode; CPE: Carbon paste electrode; SPCE: Screen printed carbon electrode; DPV: Differential pulse voltammetry; CV: Cyclic voltammetry.

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