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Arginine Electropolymerized Carbon Nanotube Paste Electrode as Sensitive and Selective Sensor for Electrochemical Determination of Vanillin

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Abstract

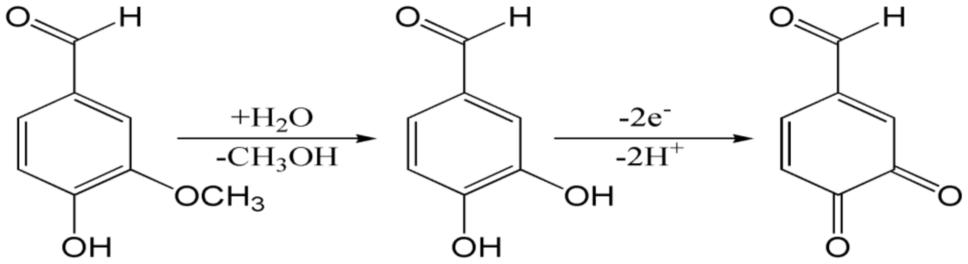
Poly(Arginine) modified carbon nanotube paste electrode (PAMCNTPE) was prepared and it was approachable and discriminatory electrocatalytic sensor for Vanillin (VAN) determination using Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV). The surface morphology of the formulated sensor is investigated by Field Emission Scanning Electron Microscope (FESEM). The tailor made electrode has exposed an exceptional electrocatalytic effect to VAN detection when compared to bare carbon nanotube paste electrode (BCNTPE). Under the optimized circumstances, the quantification of VAN at the developed electrode has revealed the linear range 2×10^{-6} M to 1×10^{-5} M and 1.5×10^{-5} M to 4.5×10^{-5} M and a limit of detection 3.3×10^{-8} M. Instantaneous resolving of VAN and Caffeine (CAF) shows a well separated peaks at 0.508 V and 1.281 V. Applicability of the developed electrode is studied using food sample, shows the recovery in the range of 95.92%to 99.73%, this indicates that the modified electrode is having better analytical performance and can be used for the determination of VAN in commercial food samples.

1. Introduction

Vanilla, one of the world's best flavor extract obtained primarily from Vanillia Planifolia. Among 110 species hardly 3 species of Vanillin (VAN) finds commercial importance. Vanillia planifola, Vanilla tahitensis and Vanilla pompon [1]. The fragrance and essence of vanilla extract is mostly due to the occurrence of Vanillin, which is present in the concentration of 1.0 to 2.0% w/w in cured Vanilla pods [3]. VAN (4- hydroxy - 3- methoxybenzaldehyde) is one of the foremost components of natural Vanilla. Every year more than 12,000 tons of Vanillin produced, however lesser than 1% of it is from natural Vanilla. The remaining is synthesized from either chemical or biochemical processes [1-2]. VAN is used extensively in beverages, foods, perfumery, and confectionary and even in pharmaceutical drugs like aldomet, L-dopa etc. [3-4]. It also finds applications in soft drinks as a preservative, in corrosion reactions as an inhibitor and in methacrylate polymerization reaction as a catalyst [5]. However, extreme intake of VAN can result in vomiting, headache, nausea, and also potential damage to liver and kidney [6].

Varieties of methods have been reported for the determination of VAN such as spectrophotometry [6-7], High-performance Liquid Chromatography (HPLC) [8-10], Capillary electrophoresis [11-12], LC-MS and GCMS [13-14], Chemiluminescence [15-16], etc. However these methods can be referred for the identification of VAN in a variety of samples, but these are expensive and generally time consuming or complicated. Nowadays, using extremely low consumption of sample, novel approaches for the detection of VAN have been reported [17-22]. Electrochemical sensors come across promising advantages for the VAN determination owing the rapid response, elevated sensitivity and straight forwardness [23-27]. Polymer formation layers by electrochemical oxidation of pyrrole [28] and aniline [29] were reported for the determination of VAN. The polymer developed on the electrode surface shows controllable thickness, good stability and high conductivity [30-33]. Due to this, polymer modified electrodes developed by electropolymerization has becomes popular in biosensors research [34-38].

The present effort reveals the electrochemical behavior of VAN at PAMCNTPE in the phosphate buffer solution (PBS, pH = 7.5), a sensitive and rapid technique to resolve VAN. The developed modified electrode was utilized for the VAN determination in beverage. The electron transfer mechanism of VAN is shown in scheme 1.



Scheme 1. Vanillin electron exchange mechanism

2. Experimental

2.1 Apparatus

Electrochemical measurements were carried out on a CHI 6038 E (USA), coupled to a personal workstation for managing and saving the data. A conventional three electrode system is used during the entire work. A bare or a poly(Arginine) modified CNTPE (3.0 mm diameter) is used as working electrode, a platinum wire electrode as Auxillary electrode and a saturated calomel Electrode (SCE) as reference electrode.

2.2 Reagents

VAN, Arginine and Caffeine were purchased from Molychem chemicals, Cochin, India and used without refinement. VAN was made soluble in distilled water to form a standard solution of concentration 1×10^{-4} mol/dm^3. Arginine and Caffeine solutions were prepared in distilled water (1×10^{-3} mol/dm^3). All other reagents used are of high-quality analytical grade, used as received. Phosphate Buffer Solutions (PBS) is prepared by mixing Na_2HPO_4, NaH_2PO_4 and pH values are accurately determined at room temperature.

2.3 Preparation of carbon nano tube paste electrode

Carbon nanotube paste is made ready by grinding carbon nanotube paste and silicone oil in the proportion 60:40 (w/w) in a mortar and pestle for about half an hour. The paste should be homogenized and a portion of it packed compactly into the cavity (3 mm diameter) at the end of Teflon tube. To provide the electrical contact a copper wire is introduced into the tube. The external surface of the electrode renewed for every measurement, smooth and shiny surface has to be maintained by polishing with tissue paper.

3. Results and discussion

3.1 Characterization

The surface morphology of the developed electrodes is examined and studied by FESEM. The images of BCNTPE and PAMCNTPE developed are represented in figure 1. It is evident from the image (Figure 1a) that the BCNTPE reveals the random distribution of carbon nanotubes. Figure 1b represents the surface morphology of PAMCNTPE, which shows cluster like arrangements of polymer layer. This shows that the polymer film deposited on the surface tends to increase the surface area. It confirms the BCNTPE is covered with polymer layer.

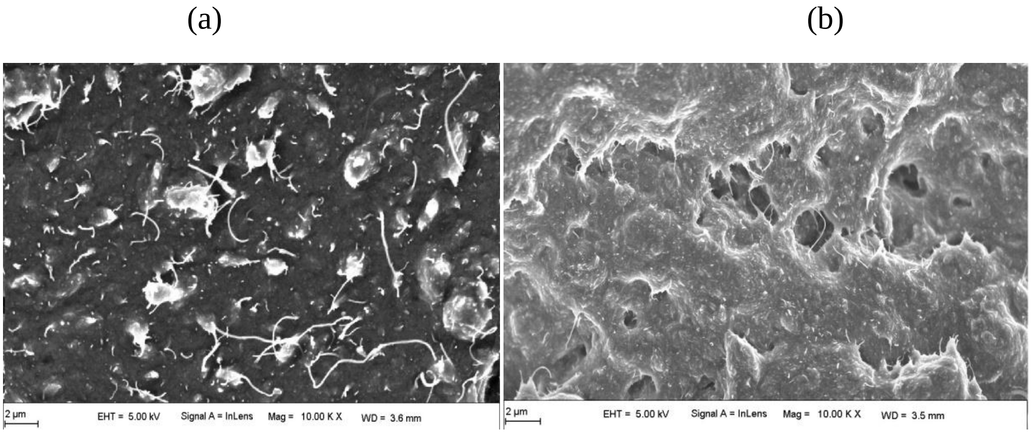


Figure1. FESEM images of BCNTPE (a) and PAMCNTPE (b)

3.2 Preparation of poly (arginine) modified carbon nanotube *paste electrode*

1 mM solution of arginine, 0.1 PBS of pH 5.7 is introduced in an electrochemical cell. It is then scanned from the potential range -0.2 to 1.5 V at the scan rate of 0.1 V/s for ten times to develop PAMCNTPE. The electrode is rinsed with distilled water to separate untreated arginine. The cyclic voltammogram obtained for the electropolymerisation of arginine is represented in figure 2.

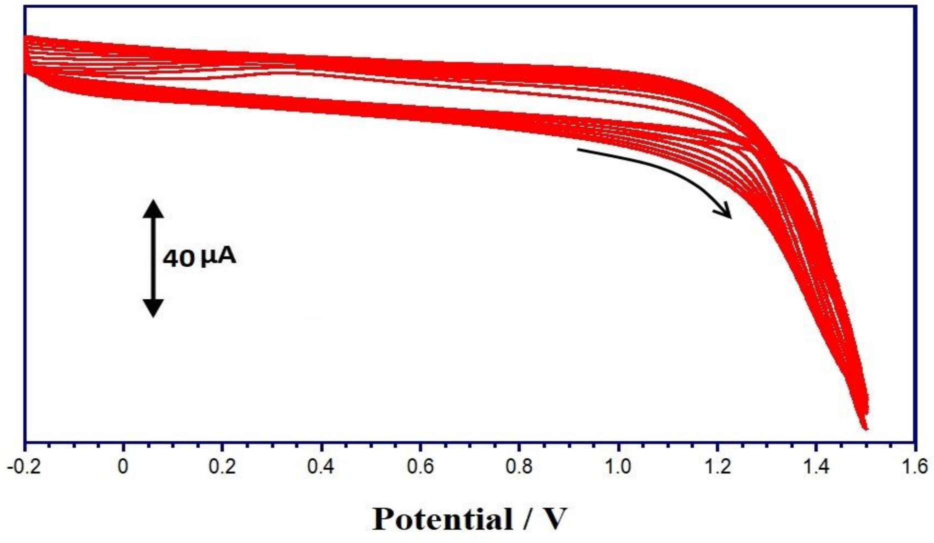


Figure 2. The Cyclic Voltammogram of poly (arginine) coat on the surface of CNTPE with 1mM arginine in 0.1 M PBS, 5.7 pH at 10 cycles at the sweep rate of 0.1V/s.

3.3 Electrochemical behavior of VAN

The electrochemical behavior of VAN investigated by the techniques such as DPV, CV and LSV. The voltammogramms of VAN at BCNTPE and PAMCNTPE in 0.1 M PBS of pH 7.5 was revealed in Figure 3. As DPV has superior sensitivity to a greater extent and enhanced resolution than cyclic voltammetry.

The oxidation peak current obtained for VAN at PAMCNTPE (curve a) is much higher than that obtained for BCNTPE (curve b) (Fig.3a). Figure 3b represents the CVs of VAN indicating that the oxidation of VAN at PAMCNTPE (curve a) developed at 0.544 V, with an enhanced anodic peak current when compared with BCNTPE (curve b). A shift with very small oxidation potential of VAN can be explained on the basis of electrostatic interaction between VAN and modified electrode. The LSV of the bare (curve b) as well as modified electrode (curve a) in 0.1 M PBS, 7.5 pH at the sweep rate of 0.1 V/s is shown in figure 3c. The response obtained for VAN at bare electrode was very low compared to modified electrode, indicates that the high surface area and conductivity of the modified electrode. Which indicates that the electrochemical effect improves towards VAN oxidation.

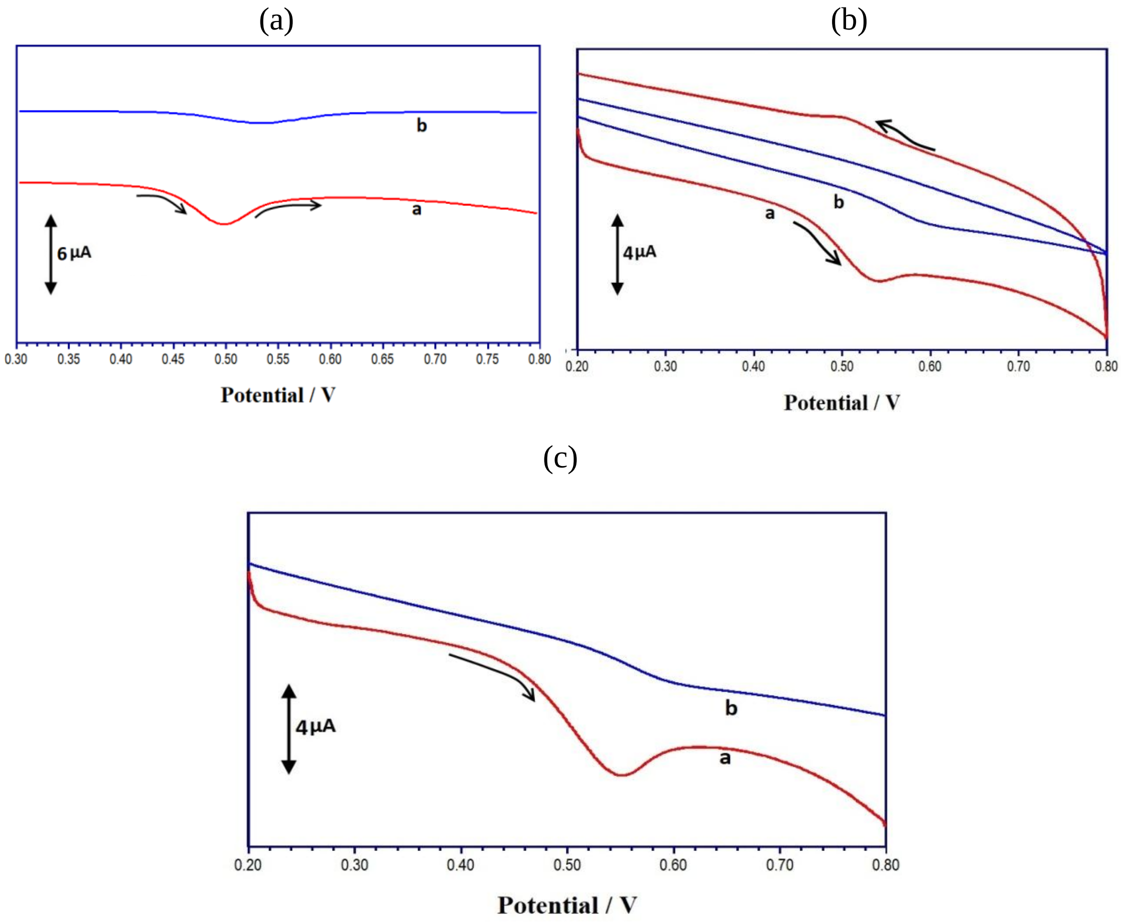


Figure 3. (a) Differential pulse Voltammogram of VAN at bare (b) and PAMCNTPE (a) in 0.1 M PBS, 7.5 pH at the sweep rate of 0.05 V/s. (b) Cyclic Voltammogram of VAN at bare (b) and PAMCNTPE (a) in 0.1 M PBS, 7.5 pH at the sweep rate of 0.1 V/s. (c) Linear sweep Voltammogram of VAN at bare (b) and PAMCNTPE (a) in 0.1 M PBS, 7.5 pH at the sweep rate of 0.1 V/s.

3.4 Effect of pH of VAN

The effect of pH on the electrochemical oxidation response of VAN at PAMCNTPE is examined by LSV. Figure 4 represents the effect of pH of the solution on the electrochemical response of VAN at PAMCNTPE. The dependency of peak potential on the pH of the solution is shown in Figure 4a. Higher peak current found that pH = 7.5 (figure 4c). Therefore this pH is chosen for subsequent analytical experiments. Figure 4b represents that the peak potential of VAN has shifted to more negative direction with increase in pH values from 6.5 to 8.5. The linear dependency of the peak potential with pH indicates that protons involved in electro-oxidation of VAN. The relation between peak potential and pH is explained by regression equation, E_{pa} (V) = – 0.0506 pH +1.40 with R = 0.98. The slope is found to be 0.0506 V/pH, which is near to the theoretical value of 0.059 V/pH, shows that transfer of electrons and protons are equal.

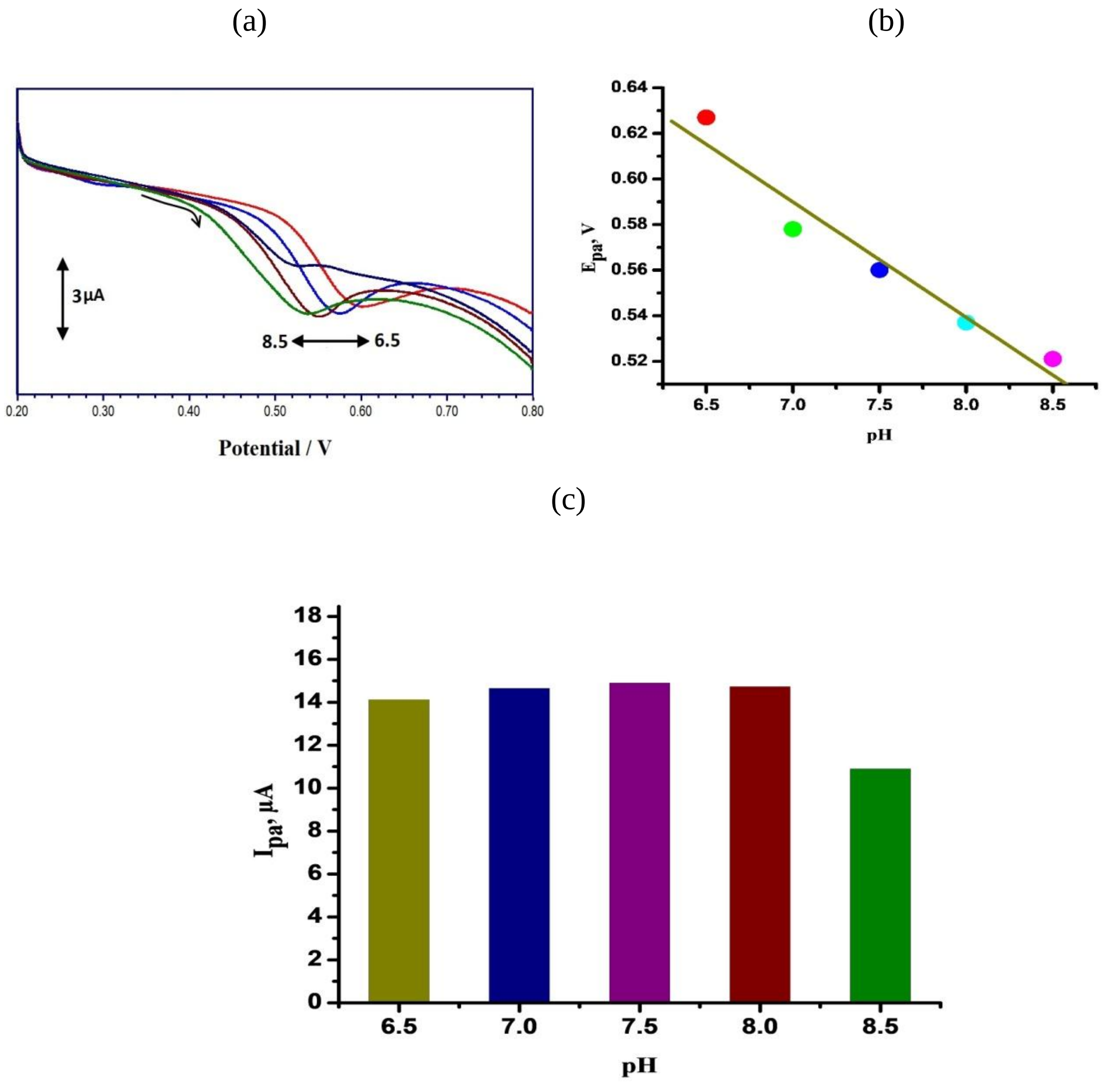


Figure 4. (a) Linear pulse voltammogram of VAN (1×10^{-4} M) at PAMCNTPE in 0.1 M PBS at different pH values, 6.5, 7.0, 7.5, 8.0, 8.5 (b) E_{pa} vs. pH.(c) I_{pa} vs. pH

3.5 Impact of scan rate

The most essential information involving electrochemical performance can be successfully acquired by the connection of scan rate and peak current. Effect of scan rate on the oxidation of VAN was analyzed. The voltammograms of 0.1 mM VAN with different scan rates with 0.1 M PBS are mentioned in figure 5a. With the increase in the scan rate, I_{pa} has enlarged and I_{pa} has shifted to the positive direction to some extent. The values of I_{pa} (Figure 5b) are linearly increased with the scan rate in the range 0.1 V/s – 0.225 V/s with the linear regression equation of $I_{pa}(\mu A)= 6.45+ 93.96\, v$ (V/s) with R value of 0.99. The outcome of this have shown that the process of oxidation of VAN in PBS (pH = 7.5) on the PAMCNTPE is an adsorption controlled process [39].

3.6 Calibration curve and limit of detection

DPV technique is used to construct the calibration plot between the oxidation peak current and the concentration of VAN. The results are plotted in Figure 6. Under the optimized circumstances the oxidation peak currents were linearly proportional to the concentration of VAN in the range 2×10^{-6} M to 1×10^{-5} M and 1.5×10^{-5} M to 4.5×10^{-5} M, with the linear regression equation $I_{pa}(\mu A) = 2.04\times10^{-5} + 0.397\, C_{VAN}$ (M), (R= 0.99). Detection limit (LOD) and quantification limit (LOQ) were calculated from 3σ/m and 10σ/m. Here, σ – is determined as the standard deviation of 5 DPV measurements in blank solution and m – is the slope of the calibration curve. LOD and LOQ are found to be 3.3 ×10^{-8}mol L^{-1} and 1.144 ×10^{-7}mol L^{-1} respectively. These values are closure to the values numerous modified electrodes (table 1) [40-43]. The developed method provides advantages like easy preparation, sensitivity, elevated reliability, and reasonably priced.

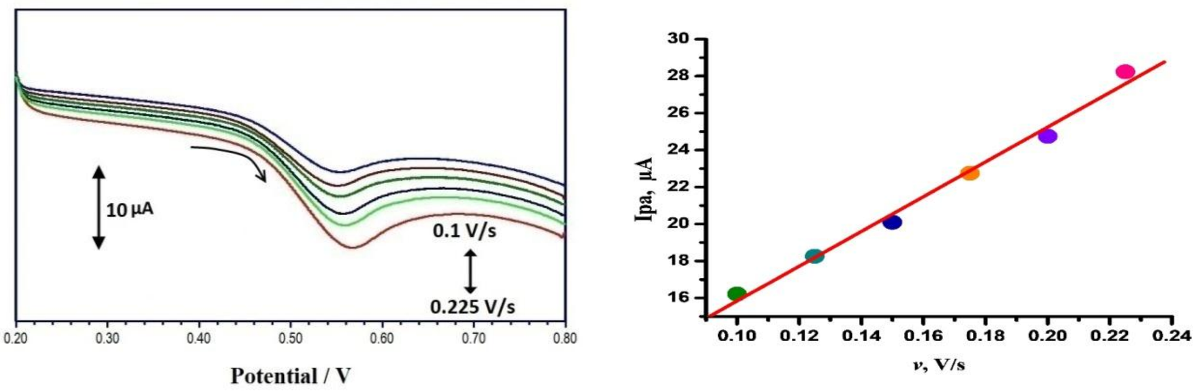

(a) (b)

Figure 5. (a) Linear pulse Voltammogram of VAN (1×10^{-4} M) at PAMCNTPE in 0.1 M PBS of pH 7.5 at different scan rate (0.1, 0.125, 0.150, 0.175, 0.2, 0.225), (b) Anodic peak current (I_{pa}) vs. scan rate (*v*).

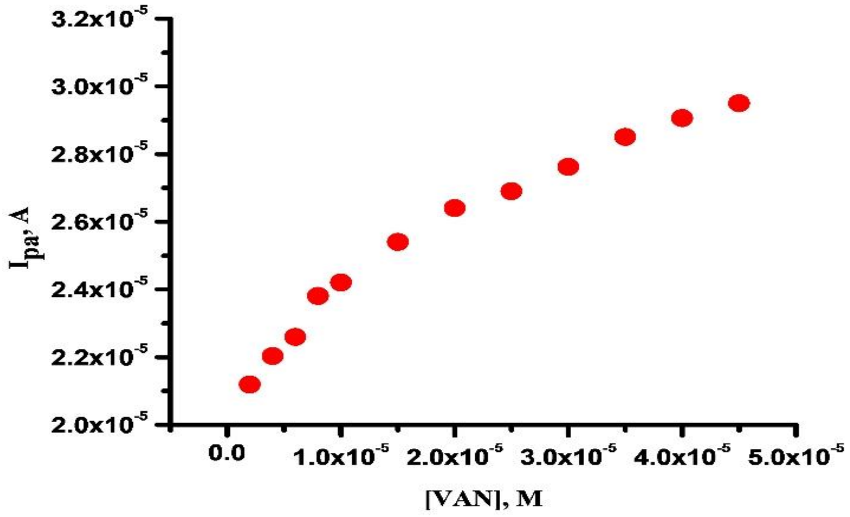


Figure 6. Calibration plot for the determination of VAN at PAMCNTPE in 0.1 M PBS of 7.5 pH & scan rate of 0.05 V/s.

Table1. Linear range and limit of detection produced by means of PAMCNTPE for the determination of VAN with other methods.

Electrodes	**Technique**	**Detection limit** (µM)	**Reference**
CF	SWV	4.2	40
GCE/ Poly(Acid Chrome Blue K)	DPV	0.032	41
GCE/ AuPd-GR	DPV	0.02	42
ABPE/GR-PVP	Deriv- LSV	0.01	43
PA/CNTPE	DPV	0.03	Present work

CF, carbon fiber; CPE, carbon paste; GCE, glassy carbon; ABPE, acetylene black paste electrode; GR, graphene; PVP, polyvinylpyrrolidone; SWV, square-wave voltammetry

3.7 Simultaneous determination of VAN and CAF at PAMCNTPE by DPV

DPV technique is performed for the simultaneous determination of VAN and CAF at BCNTPE PAMCNTPE as depicted in Figure 7. BCNTPE detects VAN and CAF at 0.530 V and 1.45 V with small current response. The PAMCNTPE provides two distinct peaks at 0.508 V and 1.281 V for VAN and CAF with higher current response. This reveals that developed PAMCNTPE can be used for the instantaneous determination of VAN from CAF.

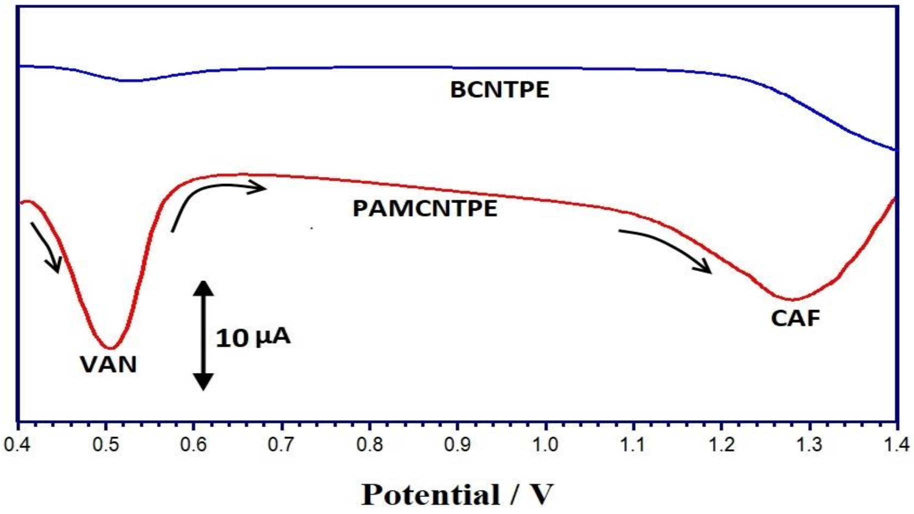


Figure 7. DPVs of the solution containing VAN (1×10^{-4} M) and CAF (1×10^{-4} M) in 0.1 M PBS (pH 7.5) at the PAMCNTPE and BCNTPE

3.8 Stability, Reproducibility, and repeatability

The reproducibility of the electrode is investigated by comparing the responses of the electrode by using the 4-different electrodes keeping in the same solution. The RSD for the resulting signals of VAN is found to be 2.76%.The stability of the PAMCNTPE measured by testing the current responses of VAN solution successfully by running 40 cycles at room temperature. 93**%** of its initial response was retained signifying that the stability is adequate. The repeatability of the modified electrode was also evaluated by using the same electrode under the different solutions by doing the 4 measurements, yielded RSD of 2.45%. Results indicate that the developed electrode having good repeatability.

3.9 Real sample analysis

In order to study the practical application of proposed electrode, PAMCNTPE was used to determine VAN in food stuffs. Experimentation is carried out by standard addition method. It is observed that the recovery of VAN is in the range of 95.92% to 99.73%. This shows the analytical applicability of the developed sensor food sample.

Conclusions

Because of simplicity and reproducibility, electrochemical polymerization has become a rapid preferred technique for preparing electrically conducting polymers. Successfully Poly (arginine) was fabricated for the simultaneous determination of VAN and CAF by voltammetry. The linear range was found to be from 2×10^{-6} M to 1×10^{-5} M and 1.5×10^{-5} M to 4.5×10^{-5} M and a limit of detection is 3.3×10^{-8} M. Oxidation peak potentials of both are well separated and the peaks obtained at 0.508 V and 1.281 V for VAN and CAF leading to a rapid and discriminating study of VAN with existence of CAF. The developed electrode shows a good recovery in food sample (95.92%to 99.73%).

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