



A NEW SEPIOLITE CLAY/TiO₂/MULTIWALL CARBON NANOTUBE MODIFIED CARBON PASTE SENSOR FOR THE ADSORPTIVE STRIPPING SQUARE WAVE VOLTAMMETRIC ANALYSIS OF VANILLIN IN LOCAL FOOD SAMPLES

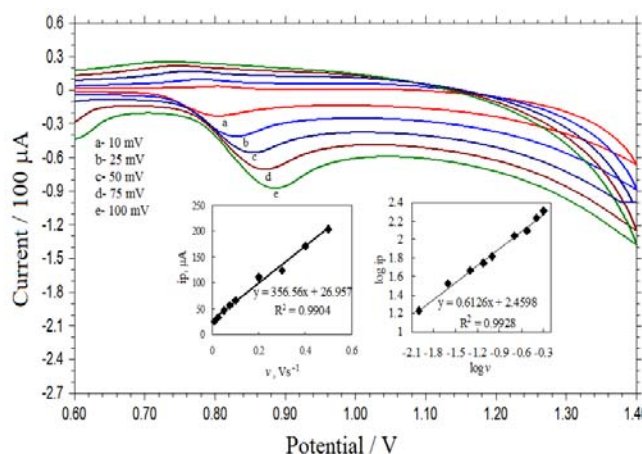
Sevcan ERDEN^{a*} and Zehra YAZAN^b

^a General Directorate of Mineral Research and Exploration, 06800 Ankara, Turkey

^b Faculty of Science, Department of Chemistry, Ankara University, 06100 Ankara, Turkey

Received March 29, 2017

A new composite electrode comprising sepiolite clay/TiO₂/multiwall carbon nanotube and carbon paste (SC/TiO₂/MWCNT/CPE) was developed and used for the voltammetric quantitative analysis of vanillin (VAN) in processed food. Adsorptive stripping square wave voltammetric (AdsSWV) method was employed. The effects of pH, ratios of electrode ingredients, accumulation potential and accumulation time were investigated. The electrode exhibited a good linear working range of $3.0 \times 10^{-7} - 9.0 \times 10^{-5} \text{ molL}^{-1}$ and a detection limit of $2.3 \times 10^{-8} \text{ molL}^{-1}$ for VAN compared to the other modified electrodes. The sensitivity and selectivity in the presence of glucose, ascorbic acid, citric acid, Na⁺, Ca²⁺, Mg²⁺, Al³⁺, K⁺, Fe²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Cl⁻, and NO₃⁻ were found to be satisfactory. The electrode system developed has a lifetime not shorter than 2 months and proved to be practical for the analysis of real samples. The percent repeatability and reproducibility of voltammetric currents are 2.55% and 2.94% respectively at a VAN concentration of $1.0 \times 10^{-5} \text{ molL}^{-1}$.



INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is a phenolic aldehyde. It is produced from three different plant species belonging to the genus *Vanilla*. However, taking into account the annual world consumption of 15000 tons, the vanilla orchids are scarce as natural sources (less than 1% of the total) and the compound is also obtained from guaiacol and lignin.¹ Vanillin is used in foods, beverages, pharmaceuticals, perfumes and also in the production of derivative chemicals.² Apart from its pleasant smell and flavor it is also

known to have antioxidant and antimicrobial properties.³ Vanillin contents of processed food is an important issue because an excess amount of vanillin is known to induce headaches, qualm, retching and adverse effects on the liver and kidney functions.⁴ As a consequence, vanillin analysis in foods is of interest.

Several methods for the quantitative determination of vanillin in various samples are based on ultraviolet (UV) spectrophotometry,⁵ gas chromatography–mass spectrometry (GC–MS),^{6,7} high-performance liquid chromatography (HPLC)^{8,9} and capillary electrophoresis (CE).^{10,11} Notwithstanding

* Corresponding author: sevcanerden@hotmail.com

their suitability and reliability, many of the methods may be considered to be costly and time-consuming as they require sample pretreatment processes. Electrochemical techniques for vanillin assay are established and have proven to be cost effective, fast and highly sensitive. Non-destructive nature and extremely low sample consumption is another facet of the techniques making them preferable.¹²⁻¹⁸

Many researchers focused on the design of the electrochemical sensors using alternative electrode materials to modify the electrode so as to improve the quality of signal. Among many electrode improvement components, polymer films,¹⁹ carbon nanotubes,²⁰ graphene,²¹ nanosized metal oxides²² and clay minerals²³ proved to be promising.

Metal oxide nanoparticles came into use as they provide a conductive sensing interface and also have catalytic properties on the electrochemical process. Various clays, on the other hand, were noticed to impart an adsorptive capacity to composite electrodes. They are also known to provide positive contribution in holding the ingredients of the composite material in place.^{24,25}

We chose sepiolite (natural clay mineral) for our sensor composition because of its high surface area and surface activity. In our previous studies we have tried the sepiolite with alone and other modifiers in carbon paste electrodes and obtained good results.²⁶

Here, we focused on a novel voltammetric sensor combining sepiolite, TiO₂ nanoparticles, multiwall carbon nanotube and carbon paste in various proportions and use it for the electrochemical oxidation of vanillin. The anodic signal obtained by adsorptive stripping square wave voltammetry was used as the basis of a sensitive and reliable electroanalytical method for the determination of the compound. The voltammetric method developed was applied to vanillin assay in real samples. The working range, sensitivity, stability, and selectivity against some possible interference were investigated.

EXPERIMENTAL

1. Reagents and solutions

All of the chemical substances used were of reagent grade, and were used without further purification. All solutions were prepared with ultra pure water obtained from a Human Power I⁺, Ultra Pure Water System. Nitrogen (99.999%) was purged through the system to remove the dissolved oxygen.

Sepiolite clay, graphite powder, samples of TiO₂ nanoparticles and mineral oil were purchased from Sigma

Aldrich. Multi walled carbon nanotube samples were supplied by DropSens.

Potassium ferrocyanide K₄Fe(CN)₆ was obtained from Sigma-Aldrich.

Britton Robinson (BR) buffer solution (0.04 molL⁻¹, pH 2.0 – 12.0) was used as the supporting electrolyte in the electrochemical determination.

Vanillin stock solutions of 1.0×10⁻² and 1.0×10⁻³ molL⁻¹ concentration were prepared by dissolving the appropriate amount of standard vanillin in ethanol (Merck analytical reagent grade).

Stock solutions of ascorbic acid, citric acid, glucose, Ca(NO₃)₃, Mg(NO₃)₂, KCl and NaCl were prepared by dissolving the appropriate amount of the compounds in pure water so as to adjust the final concentrations to 1.0×10⁻³ molL⁻¹. Aluminium(III), iron(III), copper(II), zinc(II), and lead(II) solutions of the same concentrations were prepared from standard solutions purchased from Fluka.

2. Apparatus

Square wave adsorptive stripping voltammetry was performed on a CH Instruments Electrochemical Workstation CHI660C instrument connected to a C4 Cell Stand. A combination of three electrodes consisting of the working electrode, a platinum wire auxiliary electrode (CHI 115) and an Ag/AgCl reference electrode (CHI 111) was employed.

Electrochemical impedance spectroscopy was also run on a CHI660C in BR buffer solution at pH 7.0. The impedance measurements were recorded at open circuit voltage within the frequency range of 0.1–10⁵ Hz.

pH adjustments were performed using a Hanna HI 2211 pH/ORP meter calibrated with buffer solutions (Thermo Scientific).

3. Fabrication of sensors

Bare and modified CP electrodes were prepared for comparative purposes. For the preparation of CPE composites, varying proportions of sepiolite, TiO₂, MWCNT (1.0; 1.5; 2.0; 2.5 and 3.0 mg) proper masses of graphite powder and mineral oil (10 µL) making the final weight to 30 mg were mixed in a mortar and ground for 5 minutes with a pestle. Both bare and modified pastes were filled into the hole of the electrode body and the electric contact was made with a copper wire in the center of the cylindrical body. The outer-looking surface of the electrode was polished with a piece of polishing paper until it had a shiny surface. CP sensor surfaces were rinsed by water before all experiments.

4. Voltammetric measurements

The cyclic and square wave voltammetric experiments were carried out at room temperature in an electrochemical cell containing BR buffer solution and the required volume of vanillin standard solution. CV measurements were recorded by cycling the potential between +0.6 and +1.4 V at a scan rate of 0.10 Vs⁻¹. The AdsSWV measurements were performed by scanning the potential from +0.4 to +0.8 V at a frequency of 20 Hz, pulse amplitude of 0.05 V and with scan increments of 0.008 V. The solution was stirred at 550 rpm at 0.0 V accumulation potential during the 60 s accumulation time. After the pre-concentration period, the stirring was stopped and AdsSW voltammograms were recorded.

5. Preparation of real samples and procedure for the determination of vanillin

Commercial samples of vanilla sugar and pudding powder samples were purchased from a local supermarket in Ankara (Turkey). Known amounts of vanilla sugar (0.26 g) and pudding powder (5.0 g) samples were dissolved in ethanol and each volume was completed to 50 mL in volumetric flasks. The solutions were shaken for 30 minutes in an ultrasonic bath to facilitate the complete dissolution of vanillin. After keeping aside for a day the solutions have served as the stock solution for the preparation of the samples of analysis. Appropriate volumes of aliquots were taken from the clear part of these solutions and transferred into the working cells. The volume of the working solutions was completed to 10 mL by BR buffer (pH 7.0) and the voltammetric measurements were done as such.

Standard addition method was used for the determination of the vanillin content. The calibration graph was constructed by consecutive addition of 10 μL aliquots of the standard vanillin solution ($1 \times 10^{-3} \text{ molL}^{-1}$) into the voltammetric cell containing 10 mL BR buffer (pH 7.0) and 10 μL of commercial sample solution. AdsSW voltammograms were recorded after the addition of each vanillin increment. The modified electrode surface was carefully cleaned by rinsing with a mixture of water and ethanol (1:1) before taking each voltammogram.

RESULTS AND DISCUSSION

Cyclic voltammetry (CV) is known to be a powerful tool in investigating the electroactivity and possible surface activity of various compounds.²⁷ As a contribution to these investigations, we have studied electrochemical behaviours of five different electrodes all made up of bare and modified carbon paste.

Electrochemical characterization of SC/TiO₂/MWCNT/CPE

Bare CPE and the electrodes made of TiO₂/CPE, MWCNT/CPE, SC/CPE and SC/TiO₂/MWCNT/CPE composites were prepared as described in the section Experimental. The mass ratios of the additives were always 3.33% and graphite contents were adjusted so as to make up a total of 100. Using each electrode, CVs of $1.0 \times 10^{-3} \text{ molL}^{-1} \text{ K}_4\text{Fe}(\text{CN})_6$ were taken in $0.10 \text{ molL}^{-1} \text{ KCl}$ solution. The trial experiments were carried out at a scan rate of 100 mVs^{-1} .

The voltammograms obtained with the five different electrodes are shown in Fig. 1A. The SC/TiO₂/MWCNT/CPE composite produced a remarkable increase in the peak current (curve e) compared to the other electrodes. A close examination of the anodic and cathodic peaks of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple shows that the curves obtained with SC/TiO₂/MWCNT/CPE composite indicate a quasi-reversible behaviour of the electrochemical process on this electrode (Fig. 1A). This is indicated by the peak-separation potential (E_p) of 0.065 V which is a bit higher than the value of 0.059 V expected for an ideally reversible process. The fact that the SC/TiO₂/MWCNT/CPE composite gives rise to a voltammogram closer to the ideally reversible case may be attributed to the fact that the ingredients added increase the surface area of the carbon paste so as to attract the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ions to the electrode surface.²⁸

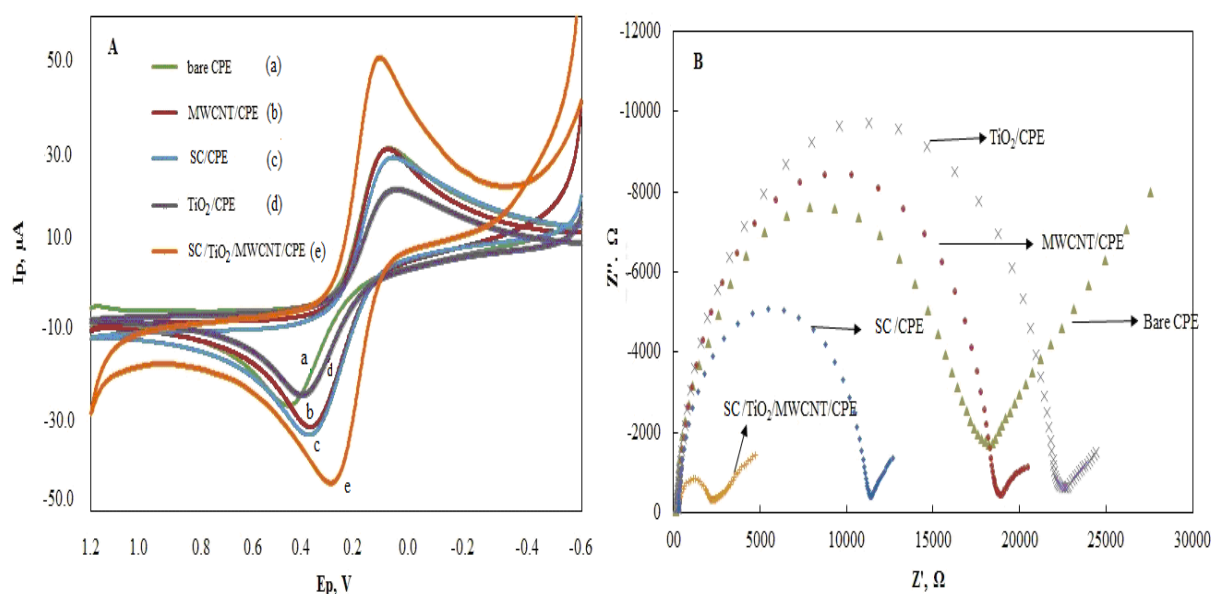


Fig. 1 – A) Cyclic voltammograms and B) Nyquist plots of $1.0 \times 10^{-3} \text{ molL}^{-1} \text{ K}_4\text{Fe}(\text{CN})_6$ at different modified electrodes.

Voltammograms of $1.0 \times 10^{-3} \text{ molL}^{-1} \text{ K}_4\text{Fe}(\text{CN})_6$ solutions run at different scan rates ($10 - 100 \text{ mVs}^{-1}$) were used to find the active surface areas of the five electrodes. The Randles–Sevcik equation²⁹ was used to correlate the peak currents (i_{pa}), square root of scan rate $v^{1/2}$ and the electrode surface area (A). The equation is as follows:

$$i_{\text{pa}} = 2.69 \times 10^6 n^{3/2} A D_R^{1/2} C_0 v^{1/2} \quad (1)$$

here n is the electron transfer number, D_R is the diffusion coefficient, C_0 is the concentration of $\text{K}_4\text{Fe}(\text{CN})_6$ solution, n is one for the compound under investigation and D_R is $7.60 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for water medium at 25°C . The active surface area of the $\text{SC}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$ composite (0.112 cm^2) was found to be the greatest compared to the other electrodes (0.066 cm^2 , 0.068 cm^2 , 0.071 cm^2 and 0.090 cm^2 for CPE, TiO_2/CPE , MWCNT/CPE and SC/CPE , respectively).

Electrochemical impedance spectroscopy (EIS) is a powerful method of analyzing the electrical resistance of a system. The radius of the circular part of the Nyquist plot is equal to the charge transfer resistance of the electrode surface for the electrochemical reaction concerned.^{30,31} The impedance measurements were also made use of to compare the surface areas of the five electrodes. The same redox couple was used as the standard analyte. Fig. 1B displays the Nyquist plots obtained with the five electrodes. The spectra in Fig. 1B clearly show that among the five electrodes the $\text{SC}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$ composite electrode displays the smallest electrical resistance which is indicative of the relatively higher surface area.

As a first trial to see whether the $\text{SC}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$ composite was also a good electrode material for the electrochemical investigation of VAN, current responses of the five electrodes in the electrochemical oxidation of $1.0 \times 10^{-3} \text{ M VAN}$ were compared. The voltammograms were obtained in 0.04 molL^{-1} BR buffer (pH 7.0) at a scan rate of 0.10 V/s (Fig. 2). As can be seen from Fig. 2, the $\text{SC}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$ composite produces the best current response (curve e). Electrodes produced from similar compositions were also reported in the literature to be effective in the voltammetric analysis of other compounds.^{17,32}

Optimum composition for the modified electrode

The composition of the modified electrode ($\text{SC}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$) was found to have a significant effect on the voltammetric response of the modified electrodes by means of changing its sensitivity and selectivity.³³ For this propose, the electrodes were prepared with the different combinations containing 3.0% and 13.0% in respect to sepiolite clay, TiO_2 , MWCNT graphite powder and mineral oil, so the voltammetric responses of the modified electrodes were studied by CV technique in the presence of $1.0 \times 10^{-3} \text{ molL}^{-1}$ VAN at BR buffer solution (data not shown). Herein, the optimal modified electrode composition for the $\text{SC}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$ was found as 6.67% clay, 5.0% TiO_2 , 3.33% MWCNT, 85% graphite powder and $10 \mu\text{L}$ mineral oil.

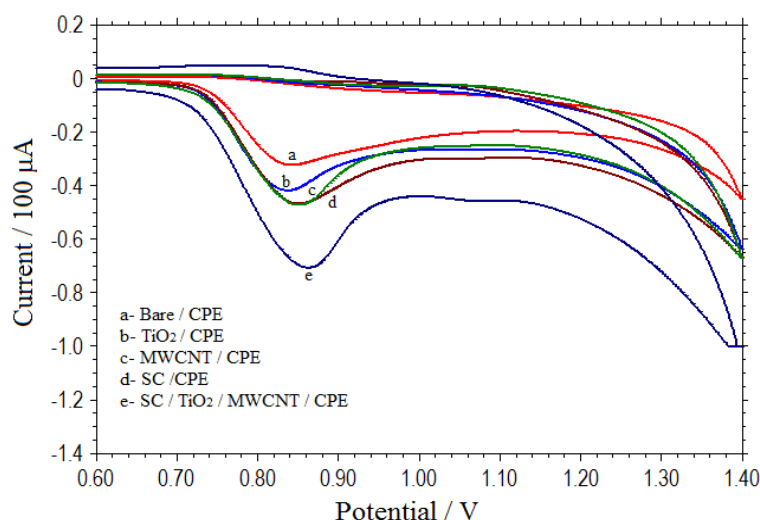


Fig. 2 – Cyclic voltammograms of $1.0 \times 10^{-3} \text{ molL}^{-1}$ VAN at (a) Bare CPE, (b) TiO_2/CPE , (c) MWCNT/CPE , (d) Sep/CPE and (e) $\text{Sep}/\text{TiO}_2/\text{MWCNT}/\text{CPE}$ in the BR buffer, pH 2.0, scan rate 0.100 V .

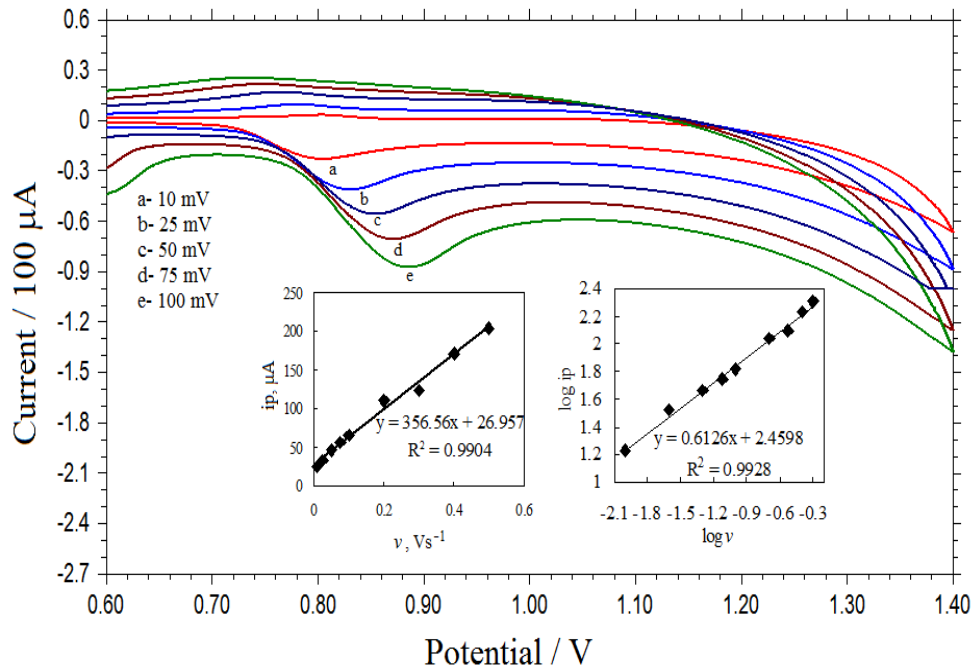


Fig. 3 – Cyclic voltammograms of VAN at different scan rates at Sep/TiO₂/MWCNT/CPE (inserts are the plot of i_p vs v and $\log i_p$ vs $\log v$) (C_{VAN} : 1.0×10^{-3} molL⁻¹ in BR buffer, pH 2.0).

Optimization of pH, accumulation potential and accumulation time

The effects of pH, accumulation time and accumulation potential on the peak current obtained with the same concentration of VAN were also investigated. AdsSW voltammograms were made use of for this purpose. Samples in the pH range 1.0–12.0 (with 1.0 unit increments) were tested for choosing the best pH. Accumulation potentials were changed in the range (–0.30) – (+0.80 V) with 0.10 V increments. Accumulation times were in the range 0.0 – 150 s (30 s increments). The results are summarized in Fig. 4. The graphs

show that the optimum pH, accumulation potential and accumulation time are 7.0, 0.0 V and 60 s, respectively.

The electrochemical behaviour of vanillin on the SC/TiO₂/MWCNT/CP electrode

The electrochemical behaviour of VAN on the SC/TiO₂/MWCNT/CP electrode of the optimum composition (to be called *the electrode* hereafter) was studied. The voltammograms of 1.0×10^{-3} molL⁻¹ VAN solution at different scan rates are shown in Fig. 4.

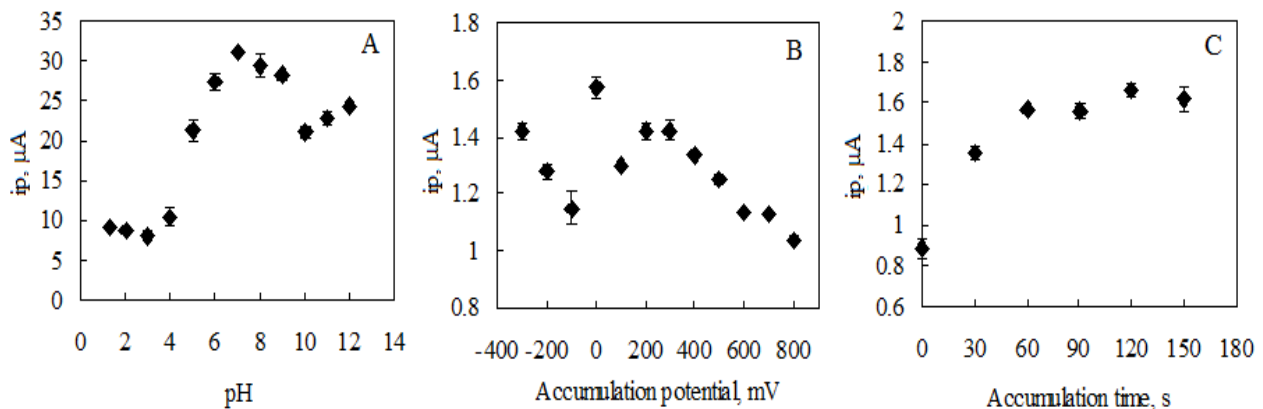


Fig. 4 – Peak currents obtained from AdsSW voltammograms to analyse the effect of pH (A), accumulation potential (B) and accumulation time (C) (C_{VAN} : 1.0×10^{-3} molL⁻¹, Sep/TiO₂/MWCNT/CPE).

It is well known that the relationship between the peak currents / potentials and the scan rate gives some important clue about the electrochemical mechanism.³³ We investigated the change of peak potentials and peak currents at different scan rates. Using the data extracted from Fig. 4, the linear relationship ($i_p = 3.57 \times 10^{-4}v + 2.70 \times 10^{-5}$) was found between i_p and v , with a correlation coefficient of $R^2 = 0.9904$. That the i_p - v correlation is linear indicates an adsorption-controlled process. The function correlation $\log i_p$ and $\log v$ ($\log i_p = 0.61 \log v + 2.46$) is also linear and the slope of the straight line is 0.61 (between 0.5 and 1.0), which is another indication of an adsorption controlled process.³⁴

With increasing scan rates, the peak potentials (E_p) tend to shift to more anodic values. The linear dependence of the peak potential upon logarithm of scan rate can be expressed as E_p (V) = 0.089 $\log v$ (Vs⁻¹) + 0.674 (with $R^2 = 0.9903$).

Voltammetric theory predicts that the slope of the straight line E_p vs. $\log v$ (Vs⁻¹) should be equal to $0.0296 / (an)$, where n is the number of electrons in the rate determining step and α is the charge transfer coefficient.^{35,36} Using this relation, the term (an) was found to be 0.33.

The square wave voltammetric studies were also done and the effect of the frequency of the excitement signal (f , s⁻¹) on the peak potentials

was analyzed. The data extracted from the square wave voltammograms indicate that the peak potentials shift to more positive values with increasing excitement frequency. The corresponding linear equation correlating the peak potential (E_p) and $\log f$ is as follows: E_p (V) = 0.091 $\times \log f$ + 0.44 ($R^2 = 0.9952$). On the other hand, n' being the number of electrons transferred in the overall reaction, the corresponding theoretical relation between E_p and $\log f$ is "slope = 0.059 / $n\alpha$ ".³⁶ The evaluation of the empirical and theoretical equations yields a value of 0.65 for the term ($n'\alpha$). Dividing $n'\alpha$ by $n\alpha$ gives a ratio of 1.97. We take this quantity to be 2.0, and tentatively suggest that the number of electrons transferred in the rate determining step and the overall reaction are 1.0 and 2.0, respectively. This conclusion is an agreement with the literature reports.³⁷

The number of protons involved in the electrochemical process was also sought for using CV runs at different pH values. E_p values were measured in the pH range of 2.0 – 12.0 with one pH unit increments. We found that the empiric relation between E_p and pH is E_p (V) = 0.055 \times pH + 0.99 ($R^2 = 0.9975$). The theoretical counterpart of this relation is as follows:³⁸

$$E_p = \partial RT / nF \times \text{pH} + (E^0 + RT / nF \times \ln [\text{Ox}] / [\text{Red}]) \quad (2)$$

here ∂ is the number of protons and E^0 is the standard peak potential. By equating the term $\partial RT / nF$ to 0.055 and taking the value of n as 2.0. We found the number of protons (∂) involved in the overall reaction to be 1.0.

Voltammetric determination of VAN

Analytical characteristics

Standard series of VAN in the concentration range of 1.0×10^{-8} – 1.0×10^{-4} molL⁻¹ were prepared and AdsSW voltammograms were recorded using optimum pH, accumulation potential and accumulation time. The calibration curve was plotted by regressing the concentration against the peak current (Fig. 5). As can be seen in the insert of Fig. 5, the oxidation peak current was proportional to vanillin concentration in the range of 3.0×10^{-7} – 9.0×10^{-5} molL⁻¹. The linear regression equation correlating the peak current (i_p) and concentration (M) is as follows:

$$(A) = 0.1047c \text{ (M)} - 0.5746 \times 10^{-6} \text{ (R}^2 = 0.995) \quad (3)$$

Reproducibility, repeatability and stability studies

To characterize the reproducibility, 1.0×10^{-5} molL⁻¹ vanillin solution was measured by examining three independent SC/TiO₂/MWCNT/CP modified sensors by three repeated measurements. The oxidation peak current has no apparent decrease with a RSD of 2.94%, revealing excellent reproducibility and the peak potential was found to be 0.74% (Table 1). The values found indicate a good precision for the newly developed method.

The repeatability of the SC/TiO₂/MWCNT/CPE was evaluated by measuring of 1.0×10^{-5} molL⁻¹ vanillin solution for 10 times with the same electrode under the optimum conditions. The satisfying results were obtained for the repeatability of the peak current and of the peak potential with RSD below 2.55% and 0.70%, respectively.

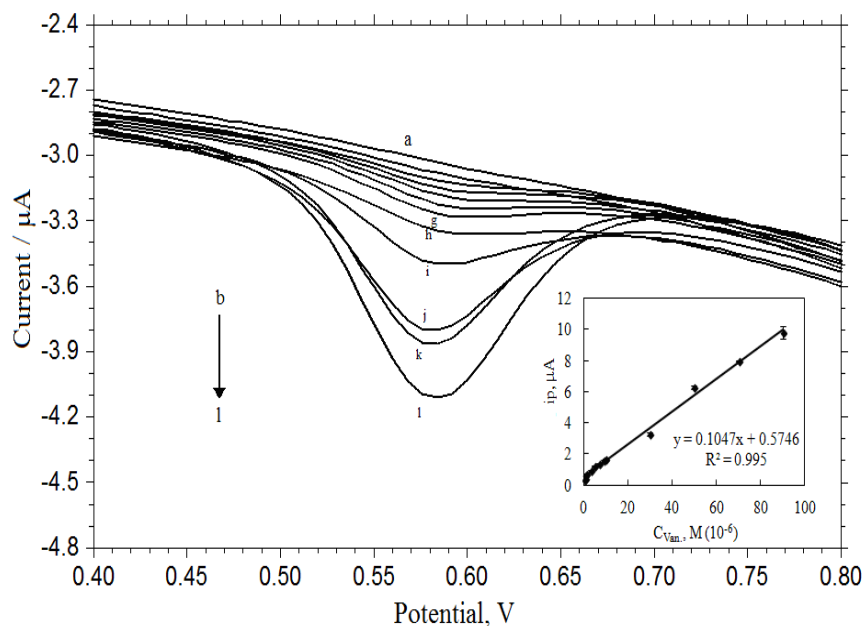


Fig. 5 – AdsSW voltammograms of the different concentrations of vanillin at the modified electrode (a) BR buffer, (b–l): 3.0×10^{-7} , 1.0×10^{-6} , 3.0×10^{-6} , 5.0×10^{-6} , 7.0×10^{-6} , 9.0×10^{-6} , 1.0×10^{-5} , 3.0×10^{-5} , 5.0×10^{-5} , 7.0×10^{-5} , 9.0×10^{-5} molL⁻¹, respectively (pH 7.0, E_{acc.}: 0.0 V, t_{acc.}: 60 s), (insert: calibration curve of vanillin).

Table 1

The statistical results of regression analysis

Method	AdsSWV
Peak potential, mV	590
Slope, molL ⁻¹ (A.L/mol)	0.1047
Regression coefficient, R ²	0.995
Working range, µmolL ⁻¹	0.3 – 90.0
LOD, µmolL ⁻¹ *	0.0226
LOQ, µmolL ⁻¹ *	0.753
Reproducibility of peak current, RSD %	2.94
Reproducibility of peak potential, RSD %	0.74
Repeability of peak current, RSD %	2.55
Repeability of peak potential, RSD %	0.70

* In the confidence limit of 95 %, $t = 2.57$ for $N = 5$ for the determination of limit of quantification, and limit of detection RSD is the relative standard deviation of five replications.

The stability of the sensor made up of SC/TiO₂/MWCNT/CP composite was evaluated by comparing current responses obtained weekly on 1.0×10^{-5} molL⁻¹ VAN solution for a period of two months. The tip of the electrode was inserted into a plastic vial; wrapped with a paraffin tape so as to isolate from the room atmosphere and the sensor was kept at room temperature as such. AdsSWVs of the VAN solution were recorded at the end of each week and the peak currents were compared. After eight weeks, the peak current on the voltammogram of the vanillin solution was found to have retained 90% of its original value.

Limit of detection (LOD) and limit of quantification (LOQ) values were calculated using

the relations $LOD = 3 s/m$ and $LOQ = 10 s/m$, s being the standard deviation with the selected working concentration and m , the slope of calibration curve. LOD and LOQ values were found to be $0.0226 \mu\text{molL}^{-1}$ and $0.753 \mu\text{molL}^{-1}$, respectively.

The working range and the LOD of the quantitative voltammetric method developed here were compared with the electrochemical literature concerning the analysis of VAN. The comparison is given in Table 2. The table indicates that the measurements done with the electrode system developed is among the best ones (the lowest LOD values). The linear working range is also among the widest ones.

Table 2

Comparison of the performances of different electrochemical sensors for the determination of VAN

Method	Electrode	Medium	Working Range (μmolL^{-1})	LOD (μmolL^{-1})	Applications	Ref.
SWV	Cylindrical CFME	Ethyl acetate	10–700	4.2	Dehydrated pudding powder	13
Amperometric	PVC/graphite electrode	NaOH–KCl pH 13.0	660–9200	290	Food samples	14
Sono-SWV	GCE	Ethyl acetoacetate (0.1 molL^{-1} TBAN)	50–300	16.0	Natural Vanilla Extract	15
SWV	Screen-printed sensor	PBS pH 7.4	5.0–400	0.40	Yoghurt, compote	16
SWV	MWCNTTAPcCo/GCE	NR	4.2–5000	0.44	NR	17
Amperometric	CDA/Au–AgNP/GCE	PBS pH 2.0	0.2–50	0.04	Vanilla bean, vanilla tea	18
AddPV	Graphene/GCE	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ - $\text{C}_6\text{H}_8\text{H}_2\text{O}$, pH 7.0	0.6–48	0.056	Biscuits samples	34
AdsSWAV	Boron-doped diamond electrode	PBS, pH 2.5	3.3–98	0.16	Turkish milk pudding with almond flour <i>Vanilla planifolia</i> extract and commercial vanilla flavor	37
DPV	LCPE	0.1 molL^{-1} PBS, pH 7.0	10–100	2.88	Ice cream, Biscuit, Beverage	39
DPV	Arg–G modified GCE	HAc–NaAc buffer, pH 5.0	2.0–70	1.0	Biscuits	40
SWV	Ag NP/GN/GCE	0.1 molL^{-1} PBS, pH 6.98	2.0–100	0.332	Vanilla bean, vanilla tea, biscuit	41
LSV	AuPd/GCE	0.1 molL^{-1} PBS buffer, pH 7.0	0.1–7.0 and 10–40	0.02	Chocolate cookie, milk tea	42
SWV	NGR–NCNT	0.01 molL^{-1} H_2SO_4	0.01–10	0.003	Biscuit, chocolate, jelly, juice	43
DPV	MFG/GCE	BR Buffer pH 1.8	0.03–8.0	0.0015	Infant formula	44
CV	Poly valine modified electrode	BR buffer, pH 7.0	0.096–66.1	1.0	Biscuits, Chocolates	45
DPV	EMDG	PBS buffer, pH 7.0	0.1–45	0.032	Spiked water sample	46
DPV	GO/CCNT/IL/AuNP/MIP	PBS buffer, pH 7.0	0.01–2.5	0.0062	Food samples	47
CV	AgPd/GO composite	PBS pH 6.0	0.02–45	0.005	Food samples	48
Second-order derivative linear scan voltammetry	GR–PVP/ABPE	0.1 molL^{-1} H_3PO_4	0.02–2.0 and 2.0–40 and 40–100	0.01	Commercial samples	49
SWV	AuNP–PAH/GCE	0.2 molL^{-1} Acetate buffer pH 5.0	0.9–15	0.055	Chocolate and biscuit samples	50
LSV	TBAC–900 modified GCE	PBS buffer (0.1 molL^{-1}), pH 7.0	5.0–1150	6.80	Food stuff	51
DPV	CPB/CNF/GCE	BR buffer, pH 2.0	0.5–75 and 75–750	0.14	Energy drink and vanilla sugar	52
SWV	Poly(ARS)/GCE	Acetate buffer, pH 4.0	0.001–10	0.80	Biscuit, soybean milkpowder, vanilla tea	53
DPV	1–MA–3Al–Br–VA–MIP–SWNT–COOH/GCE	PBS buffer (0.1 molL^{-1}), pH 7.0	0.4–8.0, and 10–140	0.20	Vanilla sugar and vanilla pudding	54
AdsSWV	SC/TiO ₂ /MWCNT/CP E	BR buffer pH 7.0	0.3–90	0.0226	This study	This study

CV: Cyclic voltammetry, AdDPV: Adsorptive differential pulse voltammetry, PBS: Phosphate buffer solution, CFME: Cylindrical carbon fiber microelectrode, NR: Not Reached, AdsSWAV: Adsorptive stripping square wave anodic voltammetry, CDA: Cellulose diacetate, TBAN: tetrabutylammonium nitrate, LCPE: Lysine modified carbon paste electrode, EMDG: Electrolytic manganese dioxide-graphene composite film electrode, CSCB/CN/GCE: GCE modified with carbon nanofibers and cationic surfactant cetylpyridinium bromide, GO/CCNT/IL/AuNP/MIPs: Graphene oxide/carboxylated multiwalled carbon nanotube/ionic liquid/gold, nanoparticle/molecularly imprinted polymers composite electrode, CPB/CNF/GCE: Cationic cetylpyridinium bromide carbon nanofibers glassy carbon electrode, Ag NP/GN/GCE: Ag nanoplate graphene glassy carbon electrode. AuNP-PAH: allylamine hydrochloride), NGR-NCNT: Nitrogen-doped graphene/carbon nanotube, MFG/GCE: GCE modified by GO-MnO₂ nanocomposites, AuPd/GCE: AuPd-graphene hybrid based electrode, LSV: Linear sweep voltammetry, GR-PVP/ABPE: graphene-polyvinylpyrrolidone composite film modified acetylene black paste electrode, AgPd/GO: Ag-Pd bimetallic nanoparticles-decorated graphene oxide, AuNP-PAH/GCE: Gold nanoparticles stabilized in poly(allylamine hydrochloride) glassy carbon electrode. TBAC: Cajuput tree bark derived activated carbon, Poly(ARS)/GCE: Poly(Alizarin Red S) modified glassy carbon electrode. 1-MA-3AI-Br-VA-MIP-SWNT-COOH/GCE: 1-(α -methylacrylate)-3-allylimidazolium bromide vanillin, molecularly imprinted ionic liquid polymer-carboxyl single-walled carbon nanotube composite coated glassy carbon electrode.

Table 3

Mean recovery results and the relative standard deviation

Sample	Sample value, (μmolL^{-1})	Found, (μmolL^{-1})	*Mean recovery, %	*RSD, %
Dr. Oetker Vanilla Sugar	6.0	6.0 \pm 0.017	101.84	0.95
Dr. Oetker Vanilla Pudding	6.0	5.75 \pm 0.09	105.85	0.92

* In the confidence limit of 95 %, $t = 2.57$ for $N = 5$ for the determination of mean recovery and RSD of five replications.

Interference studies

Possible interferences were explored by adding common chemical agents into the BR buffer (pH 7.0) containing 1.0×10^{-5} molL⁻¹ vanillin, 1000-fold concentrations of Na⁺, Cl⁻, Ca²⁺, Mg²⁺, NO₃⁻, citric acid; 500-fold concentrations of Al³⁺, K⁺, 100-fold concentrations of glucose, Fe²⁺, Cu²⁺, Zn²⁺, Pb²⁺; and 10-fold concentration of ascorbic acid were tried. At these levels, all the chemical species were found to have statistically insignificant effect on the intensity of the peak currents (relative errors < 5.0%).

Analytical application

Using the electrode developed, two different commercial samples (vanilla sugar and vanilla pudding of Dr. Oetker) were analyzed in relation to vanillin contents. The accuracy of the method was tested by analyzing the commercial food samples enriched with known amounts of vanillin. The mean recovery results and the relative standard deviations are listed in Table 3. The recovery data indicate that the method proposed can be used safely in food samples with high carbohydrate content.

CONCLUSION

A simple sensor made up of SC/TiO₂/MWCNT/CPE has been developed for the voltammetric

(AdsSWV) determination of vanillin in food samples. The sensor has the advantages of ease of preparation, good stability, practical surface regeneration, high precision, low cost, wide linear range and low detection limit. The electrode proved to be applicable to vanillin assay in real samples.

Acknowledgments: This research has been supported by the Ankara University Scientific Research projects Coordination Unit, Project Nos. 13J4240009 and 2005-07-05-094.

REFERENCES

1. R. Rana, A. Mathur, C. K. Jain, S. K. Sharma and G. Mathur, *Int. J. Biotech. Bioeng. Res.*, **2013**, *4*, 227–234.
2. P. Barghini, D. Di Gioia, F. Fava and M. Ruzzi, *Microb. Cell Fact.*, **2007**, *6*, 1–11.
3. N. J. Walton, M. J. Mayer and A. Narbad, *Phytochem.*, **2003**, *63*, 505–515.
4. L. M. Han, Q. R. Shen, H. Y. Ju, S. Yan and F. Yan, *Acta Ecol. Sin.*, **2002**, *22*, 1425–1432.
5. F. Garcia Sanchez, C. Carnero Ruiz, J. C. Marquez Gomez and M. Hernandez Lopez, *Analyst*, **1990**, *115*, 1121–1123.
6. T. Sostaric, M. C. Boyce and E. E. Spickett, *J. Agric. Food Chem.*, **2000**, *48*, 5802–5807.
7. L. S. D. Jager, G. A. Perfetti and G. W. Diachenko, *Food Chem.*, **2008**, *107*, 1701–1709.
8. S. Sujalmi, S. Suharso, R. Supriyanto and Buchari, *Indo. J. Chem.*, **2005**, *5*, 7–10.
9. K. N. Waliszewski, V. T. Pardio and S. L. Ovando, *Food Chem.*, **2006**, *101*, 1059–1062.
10. S. Minematsu, G. S. Xuan and X. Z. Wu, *J. Environ. Sci. (China)*, **2013**, *25*, S8–S14.

11. M. Ohashi, H. Omae, M. Hashida, Y. Sowa and S. Imai, *A. J. Chromat.*, **2007**, *1138*, 262–267.
12. S. Erden, Z. Durmuş and E. Kılıç, *Electroanal.*, **2011**, *23*, 1967–1974.
13. L. Agui, J. E. Lopez-Guzman, A. Gonzalez-Cortes, P. Yanez-Sedeno and J. M. Pingarron, *Anal. Chim. Acta*, **1999**, *385*, 241–248.
14. M. Luque, E. Luque-Pérez, A. Ríos and M. Valcárcel, *Anal. Chim. Acta*, **2000**, *410*, 127–134.
15. J. L. Hardcastle, C. J. Paterson and R. G. Compton, *Electroanal.*, **2001**, *13*, 899–905.
16. F. Bettazzi, I. Palchetti, S. Sisalli and M. Mascini, *Anal. Chim. Acta*, **2006**, *555*, 134–138.
17. D. J. Kong, S. F. Shen, H. Y. Yu, J. D. Wang and N. S. Chen, *Chinese J. Inorg. Chem.*, **2010**, *26*, 817–821.
18. D. Y. Zheng, C. G. Hu, T. Gan, X. P. Dang and S. S. Hu, *Sens. and Actuat. B*, **2010**, *148*, 247–252.
19. M. Quinto, S. A. Jenekhe and A. J. Bard, *Chem. Mater.*, **2001**, *13*, 2824–2832.
20. K. Gong, S. Chakrabarti and L. Dai, *Angew. Chem. Int. Ed.*, **2008**, *47*, 5446–5450.
21. M. Pumera, *Electrochem. Comm.*, **2013**, *36*, 14–18.
22. Z. Quan, E. Ni, Y. Ogasawara and N. Sonoyama, *Solid State Ionics*, **2014**, *262*, 128–132.
23. L. E. Davis, *Clays and Clay Technology Bull.*, **1955**, *169*, 47–53.
24. Z. Navratilova and P. Kula, *Electroanal.*, **2003**, *15*, 837–846.
25. I. K. Tonle, E. Ngameni and A. Walcarius, *Electrochim. Acta*, **2004**, *49*, 3435–3443.
26. D. E. Bayraktepe, Z. Yazan and K. Polat, *J. Electroanal. Chem.*, **2016**, *780*, 38–45.
27. O. A. Farghaly, R. S. Abdel Hameed and A. A. H. Abu-Nawwas, *Int. J. Electrochem. Sci.*, **2014**, *9*, 3287–3318.
28. L. Zhang and J. Lian, *J. Electroanal. Chem.*, **2007**, *611*, 51–59.
29. H. Beitollah, M. Goodarzian, M. A. Khalilzadeh, H. Karimi-Maleh, M. Hassanzadeh and M. Tajbakhsh, *J. Mol. Liq.*, **2012**, *173*, 137–143.
30. E. P. Randviir and C. E. Banks, *Anal. Methods*, **2013**, *5*, 1098–1115.
31. F. E. Salih, A. Ouarzane and M. El Rhazi, *Arabian J. Chem.*, **2017**, *10*, 596–603.
32. S. Erden, D. E. Bayraktepe, Z. Yazan and E. Dinç, *Ionics*, **2016**, *22*, 1231–1240.
33. S. A. Chermini, H. Krimi, M. Keyvanfard and K. Alizad, *Iranian J. Pharm. Res.*, **2016**, *15*, 107–117.
34. J. Peng, C. Hou and X. Hu, *Int. J. Electrochem. Sci.*, **2012**, *7*, 1724–1733.
35. X. Y. Wang, H. T. Shi, Q. Ma and Q. F. Zhang, *Z. Naturforsch.*, **2010**, *65B*, 32–36.
36. M. Duran, Z. Durmuş, İ. H. Taşdemir and E. Kılıç, *Curr. Pharm. Anal.*, **2012**, *8*, 28–36.
37. Y. Yardım, M. Gulcan and Z. Senturk, *Food Chem.*, **2013**, *14*, 1821–1827.
38. F. Öztürk, İ. H. Taşdemir, Z. Durmuş and E. Kılıç, *Collect. Czech. Chem. Commun.*, **2010**, *75*, 685–702.
39. B. K. Chethana, S. Basavanna and Y. Arthoba Naik, *J. Chem. Pharm. Res.*, **2012**, *4*, 538–545.
40. Y. Zhao, Y. Du, D. Lu, L. Wang, D. Ma, T. Ju and M. Wu, *Anal. Methods*, **2014**, *6*, 1753–1758.
41. L. Huang, K. Hou, X. Jia, H. Pan and M. Du, *Mat. Sci. and Eng. C*, **2014**, *38*, 39–45.
42. L. Shang, F. Zhao and B. Zeng, *Food Chem.*, **2014**, *151*, 53–57.
43. L. Jiang, Y. Ding, F. Jiang, L. Li and F. Mo, *Anal. Chim. Acta*, **2014**, *833*, 22–28.
44. T. Gan, Z. Shi, Y. Deng, J. Sun and H. Wang, *Electrochim. Acta*, **2014**, *147*, 157–166.
45. M. A. Xinying, *Int. J. Electrochem. Sci.*, **2014**, *9*, 3181–3189.
46. Y. Liu, Y. Liang, H. Lian, C. Zhang and J. Peng, *Int. J. Electrochem. Sci.*, **2015**, *10*, 4129–4137.
47. X. Wang, C. Luo, L. Li and H. Duan, *RSC Advances*, **2015**, *5*, 92932–92939.
48. J. Li, H. Feng, J. Li, J. Jiang, Y. Feng, L. He and D. Qian, *Electrochim. Acta*, **2015**, *176*, 827–835.
49. P. Deng, Z. Xu, R. Zeng and C. Ding, *Food Chem.*, **2015**, *180*, 156–163.
50. T. R. Silva, D. Brondani, E. Zapp and I. C. Vieira, *Electroanal.*, **2015**, *27*, 465–472.
51. V. Veeramani, R. Madhu, S.-M. Chen, P. Veerakumar, J.-J. Syua and S.-B. Liu, *New J. Chem.*, **2015**, *39*, 9109–9115.
52. G. Ziyatdinova, E. Kozlova, E. Ziganshina and H. Budnikov, *Monatsh. Chem.*, **2016**, *147*, 191–200.
53. H. Filik, A. A. Avan and Y. Mümin, *Food Anal. Methods*, **2016**, DOI: 10.1007/s12161-016-0545-z.
54. W. Wu, H. Wang, L. Yang, F. Zhao and B. Zeng, *Int. J. Electrochem. Sci.*, **2016**, *11*, DOI: 10.20964/2016-0703.