SİDAS MEDYA
Akademik Gıda®
ISSN Online: 2148-015X
http://www.academicfoodjournal.com

Akademik Gıda 17(1) (2019) 1-8, DOI: 10.24323/akademik-gida.543981

Research Paper / Araştırma Makalesi

Voltammetric Determination of Vanillin Using a Pretreated Pencil Graphite Electrode

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Received (Geliş Tarihi): 21.02.2019, Accepted (Kabul Tarihi): 07.03.2019

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ABSTRACT

In this study, a sensitive voltammetric method for the determination of vanillin in commercial food products was proposed using a pencil lead as an electrode material. In the cyclic voltammograms of vanillin recorded in pH 8.0 Britton Robinson buffer at the pre-oxidized pencil graphite electrode (p-PGE), a sharp peak was observed at about 520 mV (vs. Ag / AgCl electrode) attributed to the oxidation of vanillin. Subsequently, the voltammetric determination of vanillin based on its oxidation at p-PGE was carried out using the differential pulse voltammetry (DPV) technique under optimized conditions. DPV results showed that the oxidation peak current of vanillin increased linearly in the concentration range of 0.5 to 10.0 μM vanillin with a detection limit of 0.16 μM (based on $3S_b$). In the final step, this voltammetric method was applied to the determination of vanillin in vanilla syrup samples. Results were in good agreement with the values indicated on the labels of samples.

Keywords: Pencil graphite electrode, Vanillin, Voltammetric determination, Differential pulse voltammetry

Koşullandırılmış Kalem Grafit Elektrot Kullanılarak Vanilinin Voltammetrik Tayini

ÖZ

Bu çalışmada, bir elektrot malzemesi olarak kurşun kalem ucu kullanılarak ticari gıda ürünlerinde vanilin tayini için hassas bir voltammetrik yöntem önerilmiştir. Vanilinin, önceden oksitlenmiş grafit kalem elektrotu (pre-oxidized pencil graphite electrode, p-PGE) kullanılarak pH 8.0 Britton Robinson tampon çözeltisinde kaydedilen döngüsel voltammogramlarında, yaklaşık 520 mV'da (Ag/AgCl elektroduna karşı) vanilinin yükseltgenmesine atfedilen keskin bir pik gözlenmiştir. Daha sonra, vanilinin p-PGE'de yükseltgenmesine dayalı voltammetrik vanilin tayini, optimize koşullar altında diferansiyel puls voltammetri (DPV) tekniği kullanılarak gerçekleştirildi. DPV sonuçları, vanilinin yükseltgenmesine ait pik akımının, 0,16 μM ($3S_b$'ye dayanarak) gözlenebilme sınırı ile birlikte 0,5-10,0 μM vanilin derişim aralığında doğrusal olarak arttığını göstermektedir. Çalışmanın son aşamasında, bu voltammetrik yöntem vanilya şurubu örneklerinde vanilin tayinine uygulanmıştır. Elde edilen sonuçların numune şişesindeki etiketli değerler ile iyi bir uyum içinde olduğu tespit edilmiştir.

Anahtar Kelimeler: Kalem grafit elektrot, Vanilin, Voltammetrik tayin, Diferansiyel puls voltammetri

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INTRODUCTION

Vanillin is a natural flavor and aroma substance used worldwide and commonly found in many plant species. Vanillin named 4-hydroxy-benzaldehyde by IUPAC has been widely used in various areas such as in confectionery, perfumery, beverages, and food and pharmaceutical products. Moreover, vanillin exhibits biological and therapeutic activities such as anticancer, antioxidant, antimicrobial, antimutagenic, hypolipidemic, antisickling activities etc. [1-3]. Its therapeutic potential in cancer treatment and prevention is explained by its inhibiting activity towards the free radicals responsible for tumor development [2]. Vanillin is naturally found and generally extracted from the cured beans of the vanilla plant: *V. planifolia* and *V. tahitensis* as well as it is synthetically produced by various chemical and also biotechnological methods [4]. Hence the determination of vanillin in the foods and beverages, pharmaceutical, nutritional and cosmetic products and its production steps has a great importance.

In the determination of vanillin a variety of methods have been developed using chromatographic [5-8], spectroscopic [3, 9, 10] and electroanalytical techniques [11-26]. Although chromatographic methods such as GC and HPLC with various detectors (especially MS detector) have been widely used for the selective and reliable detection of vanillin [5-8], they have some drawbacks such as time consuming sample pretreatment procedures, high cost, expensive devices, high consumption of organic solvent, needs highly trained personal etc. On the other hand, low sensitivity and selectivity in spectrophotometric methods and lack of finding fluorophore compounds in fluorimetric studies can restrict to use spectroscopic methods. Among them electroanalytical methods have recently been found much attention, because these methods have some advantages such as low cost, simplicity, better sensitivity, wide linear concentration range and fast response [11-26].

In the electrochemical determination of vanillin, various types of electrodes and modified electrodes have been successfully used. For example, gold nanoparticle-modified screen-printed carbon electrode modified with graphene quantum dots and Nafion [12], overoxidized poly(pyrrole) film-modified glassy carbon electrode [13], Aluminum doped TiO_2 nanoparticles-modified screen printed carbon electrode [14], AuPd nanoparticles-graphene composite modified electrode [23] and screen printed graphite electrode [26] have been used for the determination of vanillin using differential pulse or square wave voltammetric techniques. However, our literature search showed that recently often preferred pencil graphite electrode (PGE) has not been used for the determination of vanillin. The reason of the widely using of PGE in electrochemical sensor studies is that this electrode has many advantages such as disposable, low costs, commercial availability etc. [27-33]. In addition there is no time consuming polishing and modification procedure in the PGE compared with other high costs common solid electrodes [33]. In this study, the differential pulse voltammetric determination of vanillin has been carried out using PGE. Thus, disposable, low cost, sensitive and selective method for the electrochemical determination of vanillin has been proposed. The applicability of the proposed methods was tested by determination of vanillin in the vanilla syrups.

MATERIALS and METHODS

Reagents and Apparatus

Vanillin standard was obtained from Sigma Aldrich and all other chemicals were of analytical grade. A stock solution of vanillin was prepared as 0.10 M in ultra-pure water. The diluted vanillin solution was prepared from this stock solution. Britton-Robinson buffer solutions (BRBS) used voltammetric studies were prepared in the pH range of 2.0 to 10.0 by proper mixture of 0.04 M H_3PO_4, 0.04 M H_3BO_3, 0.04 M CH_3COOH and 0.20 M NaOH containing 0.10 M KCl.

All cyclic and differential pulse voltammetric measurements were carried out using a Compactstat Electrochemical Interface (Ivium Technologies, Eindhoven, the Netherlands). The measurement of pH of solutions was performed using A HI 221 Hanna pH-meter with a combined glass electrode (Hanna HI 1332). Elga Option Q7B water purification system (18.2 MΩ cm) was used to supply ultra-pure water. An electrochemical cell including an auxiliary electrode (a platinum wire), a reference electrode (an Ag/AgCl/sat. KCl) and a working electrode (PGE) were used to perform voltammetric studies. The PGE obtained by insertion of pencil leads of 60 mm with a diameter of 0.5 mm (Ultra-Polymer, 2B, Tombow, Japan) into a mechanical pencil (Rotring, Germany). A 1.0 cm of length of pencil lead (geometric surface area is 15.9 mm^2) was immersed into supporting electrolyte solution.

Voltammetric Studies

PGEs were used with and without using a pre-oxidation procedure in which pencil leads were pre-anodized at +1.45 V for 60 s in 0.10 M pH 7.0 phosphate buffer solution with 0.10 M KCl (p-PGE). In the first step of voltammetric experiments, cyclic voltammograms (CVs) of 0.5 mM vanillin at p-PGE were recorded in the BRBS in the pH range of 2.0-10.0 including 0.10 M KCl at a scan rate of 50 mV/s using a potential range from -0.3 to 1.2 V. In the second step, CVs of 0.5 mM vanillin at p-PGE were recorded at various scan rates changed in the range from 10 to 400 mV/s in the pH 8.0 BRBS. To compare electrochemical behavior of vanillin at p-PGE, CVs of vanillin were also recorded by using GCE and bare PGE in the pH range of 8.0 BRBS including 0.10 M KCl at a scan rate of 50 mV/s using a potential range from -0.3 to 1.2 V. Before use, GCE (BASi MF-2012 model, Ø =3 mm, geometric surface area = 7.1 mm^2) was polished with alumina slurry on the polishing cloth, washed with deionized water and sonicated with ethanol and water in an ultrasonic bath, respectively.

In the final step, electrochemical determination of vanillin was carried out by recording differential pulse voltammograms (DPVs) of vanillin at p-PGE in the pH 8.0 BRBS containing 0.10 M KCl in a potential range of -0.3 to 1.2 V at a scan rate of 50 mV/s using optimized pulse amplitude (15 mV) and pulse time (2 ms).

Analysis of Vanilla Syrups

Applicability of the proposed voltammetric method was tested for the determination of vanillin in two different vanilla syrups which were purchased from a local market in Turkey. The samples with light yellow and brown (including caramel) colors were identified Sample 1 and Sample 2, respectively. Before analysis Sample 1 and Sample 2 were diluted to 20 and 100 folds with pH 8.0 BRBS containing 0.10 M KCl, respectively. An aliquot volume (about 20 µL) of these diluted syrup samples was added into the electrochemical cell that contained 5.0 mL of pH 8.0 BRBS containing 0.10 M KCl and then the DPVs were recorded under above mentioned conditions. The standard addition method was applied by adding successive aliquots of 0.10 mM vanillin standard solution to the electrochemical cell. After each addition, the DPVs were recorded. The recoveries were calculated by evaluating the peak current obtained from standard addition method. To compare results obtained from proposed electrochemical method, vanillin in vanilla syrups was also determined by using a known spectrophotometric method [34]. For this purpose, 1 mL of vanilla syrup added to 20 ml of ultra-pure water in the separation funnel, and then vanillin was extracted to total 60 mL of chloroform using three sequential extractions with 20 mL. In the second extraction step, vanillin in chloroform was extracted to total 150 mL of 0.1 M NaOH using three sequential extractions with 50 mL and then each extracted solutions was diluted to 250 mL with 0.1M NaOH. Then, the absorbance of extracted solutions was measured with standard solutions of vanillin (1, 2, 3, 4 and 5 ppm vanillin prepared in 0.1 M NaOH) at 347 nm using a spectrophotometer.

RESULTS and DISCUSSION

Voltammetric Behavior of Vanillin on PGE

To investigate electrochemical behavior of vanillin, CVs of vanillin were recorded at bare PGE, p-PGE and bare GCE. CVs of 0.5 mM vanillin at these three electrodes recorded in pH 8.0 BRBS including 0.10 M KCl at 50 mV/s are shown in Figure 1. In the CV of 0.5 mM vanillin at the bare PGE, a well-defined anodic peak at +520 mV was observed (Figure 1b). The current density of this peak increased about twice in the case of using p-PGE (Figure 1a), because pre-anodization of the bare PGE offers an affective electrode surface area by functionalization of electrode. When the GCE was used, the current density of the anodic peak decreased significantly and its peak potential shifted to more positive direction (+600 mV) (Figure 1c). The reason of these adverse events to be observed at the GCE can be attributed to the sluggish electron transfer and the passivation of electrode surface due to the adsorption of oxidation products on the electrode surface. It can be concluded that the electro-active surface of the PGE is higher than the GCE. Thus p-PGE facilitates the electron transfer between electrode and vanillin and the remarkable enhancement in the peak current were obtained.

Figure 2 shows CVs of the p-PGE in the presence of 0.5 mM vanillin recorded at various scan rates. It can be seen that oxidation peak of vanillin at +520 mV increased by increasing scan rate. The plot of peak current versus square root of the scan rate given in the inset of Figure 2 shows that currents increased linearly with the square root of the scan rate in a range from 10 to 400 mV/s. This linear change indicates that oxidation of vanillin at the p-PGE was controlled with a diffusion process.

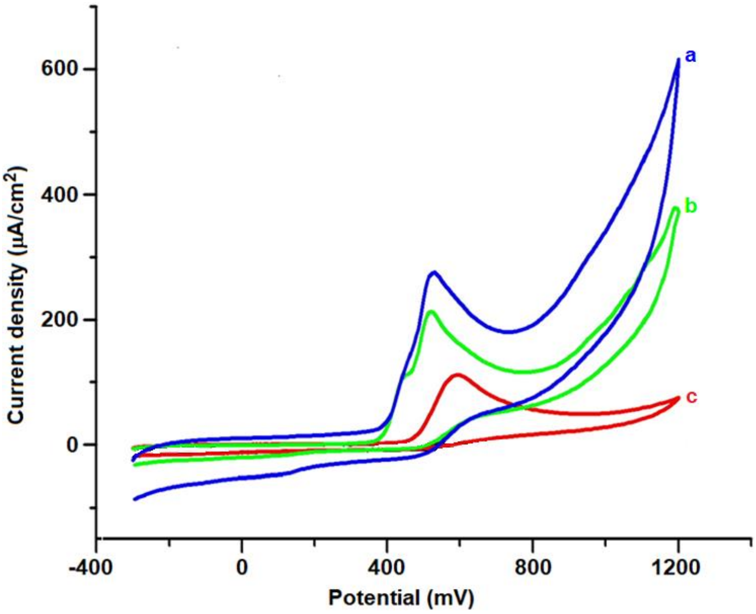

Figure 1. CVs of p-PGE (a), bare PGE (b) and bare GCE (c) in the presence of 0.5 mM vanillin in the pH 8.0 BRBS at a scan rate of 50 mV/s.

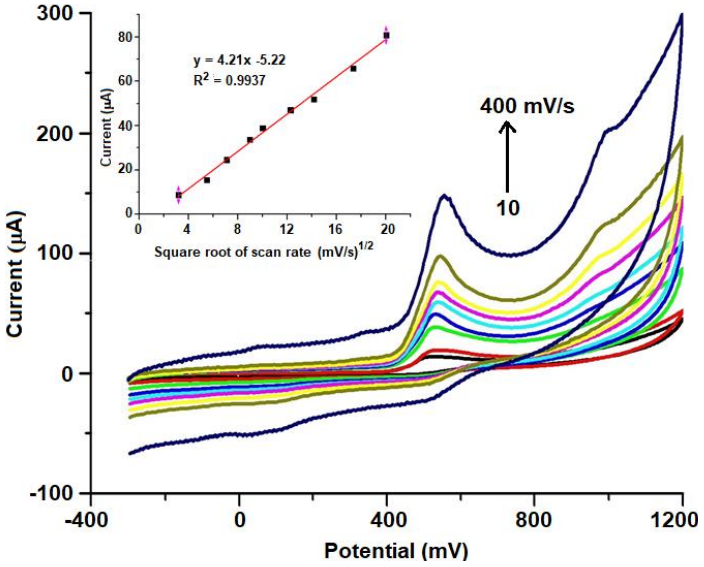

Figure 2. CVs of 0.5 mM vanillin in pH 8.0 BRBS containing 0.10 M KCl at p-PGE at various scan rate (mV/s) Inset: Plot of peak current versus square root of scan rate.

To see the effect of the pH on the oxidation peak of vanillin, the DPVs of 0.1 mM vanillin at the p-PGE were also recorded in the BRBS containing 0.10 M KCl with various pHs in the range from 2.0 to 10.0 at a scan rate of 50 mV/s (Figure 3A). Oxidation peak potential of vanillin shifted to negative direction with an increase of pH. Moreover, the plot of peak potential of vanillin versus pH given in Figure 3B shows that peak current increased linearly with increasing of pH from 2.0 to 8.0 based on the linear equation of E_p (mV) = -58pH + 955(R^2 = 0.991). The obtained slope is very close to the anticipated Nernstian value of -59.16 mV for equal numbers of electrons and protons process. Thus, hydroquinone groups in the vanillin oxidized to quinine groups by giving two electrons and two protons which was in good agreement with those reported for electrooxidation of vanillin at various types of electrodes in the literature [16, 17, 24, 25].

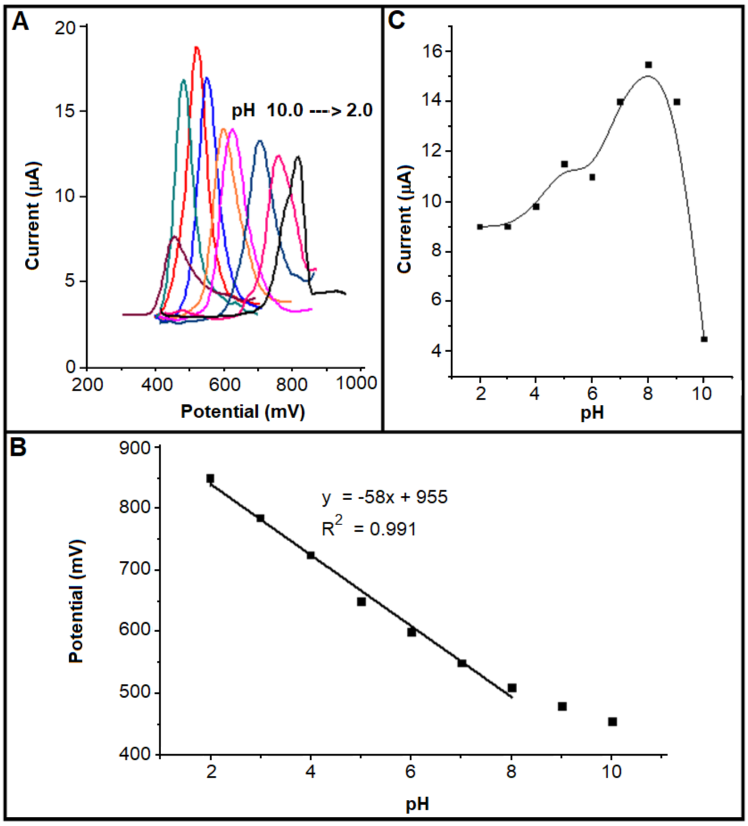

Figure 3. **A)** DPVs of p-PGE in the presence of 0.10 mM vanillin at various pH values (from 2.0 to 10) of BRBSs, **B)** A plot of oxidation peak potential of vanillin versus pH and **C)** A plot of peak current versus pH.

Differential Pulse Voltammetric Determination of Vanillin

To obtain the highest current for differential pulse voltammetric determination of vanillin, some parameters were optimized. Figure 3C shows the effect of pH on the peak current of 0.10 mM vanillin at the p-PGE. It can be seen that the highest peak current was observed in the case of using pH 8.0 BRBS as supporting electrolyte. Therefore, optimization of some parameters such as pulse time, pulse amplitude and scan rate were carried out by recording DPVs of 0.10 mM vanillin at the p-PGE in pH 8.0 BRBS. The differential pulse voltammetric studies show that pulse time, pulse amplitude and scan rate were optimized as 2 msec, 15 mV and 50 mV/s, respectively.

The oxidation peak current of vanillin depending on increased vanillin concentration was investigated by recording DPVs under optimal experimental conditions. Figure 4A shows DPVs of the p-PGE recorded in pH 8.0 BRBS containing different concentration of vanillin ranging from 0 to 100 μM. The curve of peak current versus concentration of vanillin given in Figure 4B shows that oxidation current of vanillin increased linearly with vanillin concentration between 0.5 and 10.0 μM based on equation of Ip (μA) = 0.79C(μM) + 0.26, R^2 = 0.9949). To find limit of detection (LOD), DPVs of lowest vanillin concentration which can be detectable were recorded for five times and standard deviation (sd) of the means accepted as the sd of blank (S_b) was estimated from the results. LOD was found to be 0.16 μM using the equations of LOD = 3 S_b/m, where m is the slope of the calibration plot (0.79 μA μM^{-1}).

The DPVs of 5.0 μM of vanillin under optimal experimental conditions were also recorded by using five individual p-PGEs thus repeatability of proposed electrode was investigated by evaluation of obtained peak currents. The relative standard deviation of 3.0 % (n=5) implies that the p-PGE offers a substantial repeatability for vanillin determination.

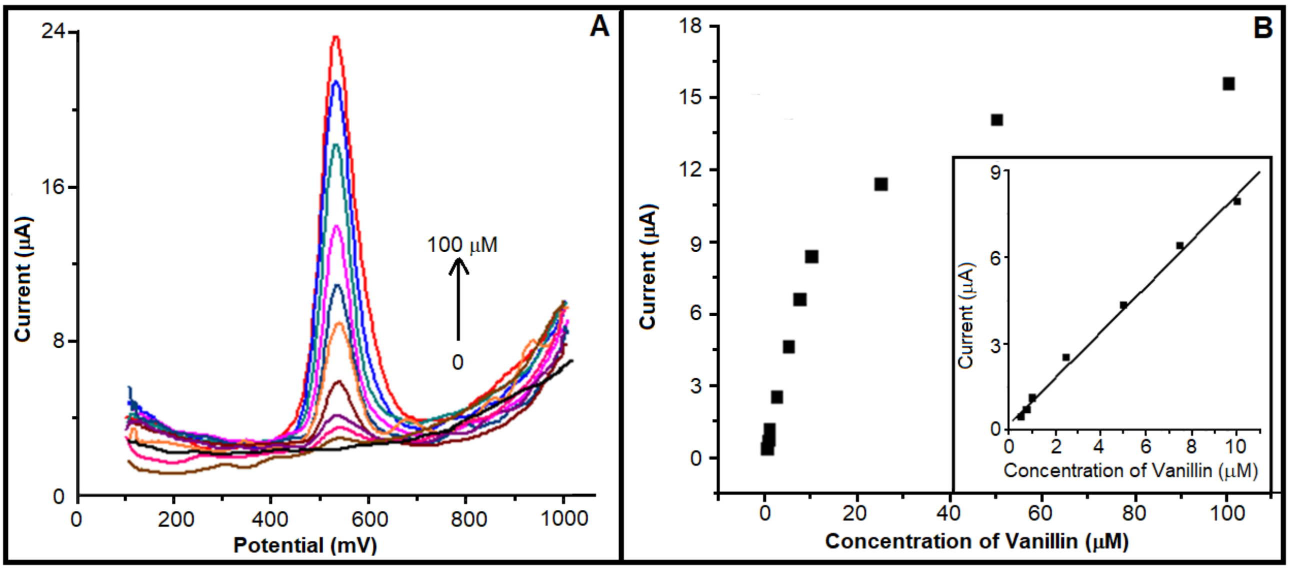

Figure 4. **A)** DPVs of vanillin in the increased concentration (from 0 to 100 μM) at p-PGE and **B)** The plot of peak current versus concentration of vanillin Inset: Linear calibration curve of vanillin

A comparison of the analytical performance of proposed electrode with that some other electrodes reported in the literature is given Table 1. It can be seen that the p-PGE offers a lower LOD, a higher sensitivity with a reasonable wide linear range than some previously published paper. Table 1 shows that various types of modified electrodes have been successfully used for the sensitive and selective determination of vanillin. However, these electrodes have some disadvantages compared with the PGE such as lower reproducibility, time consuming polishing and also modification steps, expensive electrode materials.

Interference Study

To test the interference effect of some substances on the voltammetric response of vanillin at proposed electrode, DPVs of 5.0 μM vanillin were recorded in the absence and presence of some cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cu^{2+} Zn^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}), some anions (Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}) and some organic molecules (glucose, sucrose, ascorbic acid (AA), dopamine (DA) and uric acid (UA)) under optimal experimental conditions. The results demonstrated that the oxidation peak of 5.0 μM vanillin was not significantly influenced by a 1000-fold concentration of interferences. Especially, oxidation peak of vanillin was not influenced by electroactive AA, DA and UA interferents. Since the oxidation peaks of AA, DA and UA were observed at 125, 155 and 250 mV, respectively, while vanillin oxidized at 520 mV. Results obtained from interference experiments indicated that p-PGE might be suitable for selective determination of vanillin in real samples.

Table 1. Comparison of analytical performance of proposed electrode with some previous reported electrodes for vanillin determination.

Electrode	Technique	Supporting Electrolyte	LR (µM)	LOD (µM)
AuNPs-modified SPCE modified with GQD and Nafion[12]	DPV	0.025 M H_2SO_4	0.66-0.33	0.32
	LSV	0.025 M H_2SO_4	13-660	3.9
Overoxidized poly(pyrrole) film-modified GCE [13]	DPV	ABS pH 5.2	0.032-1.50	0.012
Aluminium doped TiO_2 Nanoparticles-modified SPCE [14]	LSV	0.1 M H_3PO_4	0.07-20	0.02
GCE modified with Cu_2O-electrochemically RGO nanocomposite film [15]	SOD-LSV	0.1 M H_2SO_4	0.1-10 and 10-100	0.01
CPE modified with CdO/SWCNTs and ionic liquid [16]	SWV	0.1 M PBS, pH 6.0	0.03-800	0.009
CoS nanorods@Nafion modified GCE [17]	DPV	0.05 M PBS, pH 7.2	0.5- 56	0.07
MgO/SWCNTs and ionic liquid modified CPE[19]	SWV	0.1 M PBS, pH 7.0	0.02-800	0.008
AuNP-PAH/GCE [21]	SWV	0.2 M ABS pH 5.0	0.90-15.0	0.055
AuPd nanoparticles-graphene composite modified GCE [23]	DPV	0.1 M PBS, pH 7.0	0.1-7 and 10-40	0.02
Arginine functionalized graphene nanocomposite modified GCE [24]	DPV	ABS pH 5.2	2.0-70.0	1.0
This work (p-PGE)	DPV	BRBS pH 8.0	0.5-10	0.16

LR: Linearity range, LOD: Limit of detection, AuNPs: Gold nanoparticles, SPCE: Screen printed carbon electrode, GQD: Graphene quantum dots, DPV: Differential pulse voltammetry, LSV: Linear sweep voltammetry, SOD-LSV: Second order derivative linear sweep voltammetry, GCE: Glassy carbon electrode, RGO: Reduced graphene oxide, SWCNT: Single walled carbon nanotube, CPE: Carbon pasta electrode, PAH: poly(allylamine hydrochloride), PBS: Phosphate buffer solution, ABS: Acetate buffer solution, SWV: Square wave voltammetry, p-PGE: Pre-anodized pencil graphite electrode

Analytical Application

The proposed voltammetric procedure using p-PGE was applied to the determination of vanillin in two different vanilla syrups (Sample 1 and Sample 2). DPVs of p-PGE were recorded based on standard addition procedure which was described as detail in experimental section. The content of vanillin in these samples was also determined with a known spectrophotometric method [34]. The obtained results presented in Table 2 show that vanillin in the real samples can accurately determine with proposed voltammetric method using p-PGE. As shown in Table 2, the results obtained for vanillin determination by proposed method was found in good agreement with those by spectrophotometric method.

CONCLUSION

In this study, differential pulse voltammetric determination of vanillin was proposed using p-PGE that has some advantages such as sensitive response, a disposable, low cost and commercial available electrode material. CVs of vanillin showed that vanillin oxidized at about +520 mV in the pH 8.0 BRBS with a sharp peak at p-PGE. On the other hand, it was observed that vanillin also oxidized at the bare PGE and the bare GCE under same conditions. However, the peak currents of vanillin at bare PGE and especially bare GCE was found to be lower than that of p-PGE as well as peak potential shifted to a little bit positive direction. These results showed that p-PGE shows electrocatalytic activity toward oxidation of vanillin due to the porous surface of PGE and functionalization of PGE with pre-oxidation procedure. Proposed voltammetric method using the p-PGE has a good liner response toward vanillin in the concentration range from 0.5 to 10.0 µM with a detection limit of 0.16 µM. This proposed method has also been successfully applied to the determination of vanillin in two different vanilla syrups. Finally, it can be concluded that a sensitive, selective, disposable, low cost and simple voltammetric method has been developed for the determination of vanillin using a very useful electrode, PGE.

Table 2. Determination of vanillin in real samples (n=3).

Syrup Samples	Obtained results (mol L^{-1})	
	Proposed Method (DPV)	Spectrophotometric Method [34]
Sample 1(with light yellow color)	$4.5x10^{-2} \pm 1.0x10^{-3}$	$4.6x10^{-2} \pm 2.0x10^{-3}$
Sample 2 (with brown color)	$5.9x10^{-3} \pm 2.7x10^{-4}$	$6.2x10^{-3} \pm 3.1x10^{-4}$

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