



Original scientific paper

## An electrochemical sensor for detection of vanillin in food samples using $\text{CuFe}_2\text{O}_4$ nanoparticles/ionic liquids modified carbon paste electrode

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### Abstract

A highly selective electrochemical sensor modified with  $\text{CuFe}_2\text{O}_4$  nanoparticles and the ionic liquid was constructed for the detection of vanillin. The sensor could recognize vanillin from its analogs and possible coexistent substances. The response peak current and vanillin concentration showed a good linear relationship in the range of 0.01 - 300.0  $\mu\text{M}$ , with a sensitivity of 0.0923  $\mu\text{A } \mu\text{M}^{-1}$ . The detection limit was 0.008  $\mu\text{M}$  ( $S/N = 3$ ). Besides, the reproducibility and stability measurements were also evaluated. It was applied to the determination of vanillin in real samples with satisfactory results.

### Keywords

Voltammetric sensor;  $\text{CuFe}_2\text{O}_4$  nanoparticles; vanillin; modified electrode

### Introduction

Vanillin ( $\text{C}_8\text{H}_8\text{O}_3$ ), (4-hydroxy-3-methoxybenzaldehyde) is a phenolic aldehyde derived from vanilla bean or pod of the tropical vanilla plant that contains Vitamin-B, potassium, calcium, thiamin, riboflavin, and iron [1,2]. Vanillin has been an indispensable smell additive in most beverages and desserts such as candies, biscuits, cakes, pudding, chocolate, ice creams, and wine which attract a large number of people, especially at young ages. In mM range of concentration (more than 75 mg/body weight), vanillin has toxic effects and can lead to dangerous consequences to consumers because it can affect the liver and kidney functions, producing headaches, nausea and vomiting. Due to the side effects of vanillin, it is forbidden in infant food [3-5]. Therefore, the quantitative determination of vanillin in foods and beverages has significant importance, especially for growing children.

Several determination methods of vanillin were introduced, including chromatography, spectroscopy and capillary electrophoresis [6-12]. Most of these methods provide very effective information for identification, quantification and selectivity, but they are time-consuming and complicated in sample pretreatment processes and thus require highly sophisticated instruments.

In recent years, electroanalytical methods have been used for the determination of target species as an alternative analytical method, thanks to their low cost, fast response, simple operation, high

sensitivity and online detection ability [13-38]. In addition, because the vanillin molecules can be oxidized, the usage of electrochemical sensors is an ideal technique for the detection of vanillin. However, the determination of vanillin on the bare solid electrode is a relatively high overpotential with low reproducibility is a major problem. This is due to the contamination effect that causes poor selectivity and sensitivity. To overcome these obstacles, the modification of the electrode surface is an effective way [39-41].

Electrochemical studies of the intrinsic properties of ionic liquids (ILs) have also been reported and the electrochemical window of ionic liquids can be as wide as 4.5 V compared with 1.2 V in most aqueous electrolytes. Properties such as non-flammability, high ionic conductivity, electrochemical and thermal stability of ionic liquids make them ideal electrolytes in electrochemical devices like in batteries, capacitors, fuel cells, photovoltaics, actuators and electrochemical sensors [42-46].

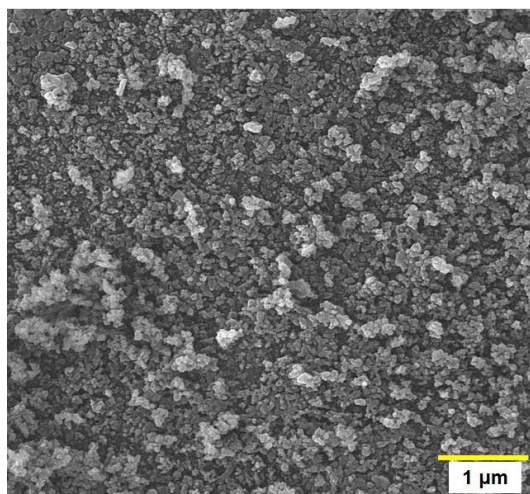
Nanostructured materials have been the subject of scientific research because of their unique electrical, thermal, chemical and physical properties. Nanomaterials and especially metal nanoparticles (NPs) of a variety of shapes, sizes and compositions are changing nowadays in electrochemical measurement [47-62].

In this research,  $\text{CuFe}_2\text{O}_4$  nanoparticles ( $\text{CuFe}_2\text{O}_4$ -NPs) were prepared using co-precipitation reaction. The electrochemical behavior of vanillin at a modified and unmodified carbon paste electrode (CPE) was investigated. The obtained results show the advantage of  $\text{CuFe}_2\text{O}_4$ -NPs/ILs/CPE to the bare carbon paste electrode in terms of better reversibility and higher sensitivity. The proposed voltammetric sensor is highly selective and sensitive enough for the determination of vanillin in the real samples.

## Experimental

### *Apparatus and chemicals*

All the electrochemical measurements were carried out on a PGSTAT302N potentiostat/galvanostat Autolab consisting of a traditional three-electrode system: a bare or modified CPE as the working electrode, an Ag/AgCl as the reference electrode and a Pt wire as a counter electrode. Solution pH values were determined using a 713 pH meter combined with a glass electrode (Metrohm, Switzerland). Vanillin and other chemicals used were analytical grade and were purchased from Merck. Ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) was purchased from Sigma Aldrich co.  $\text{CuFe}_2\text{O}_4$  nanoparticles were synthesized in our laboratory and a typical SEM is shown in Figure 1.



**Figure 1.** SEM image of  $\text{CuFe}_2\text{O}_4$  nanoparticles

### Preparation of $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$

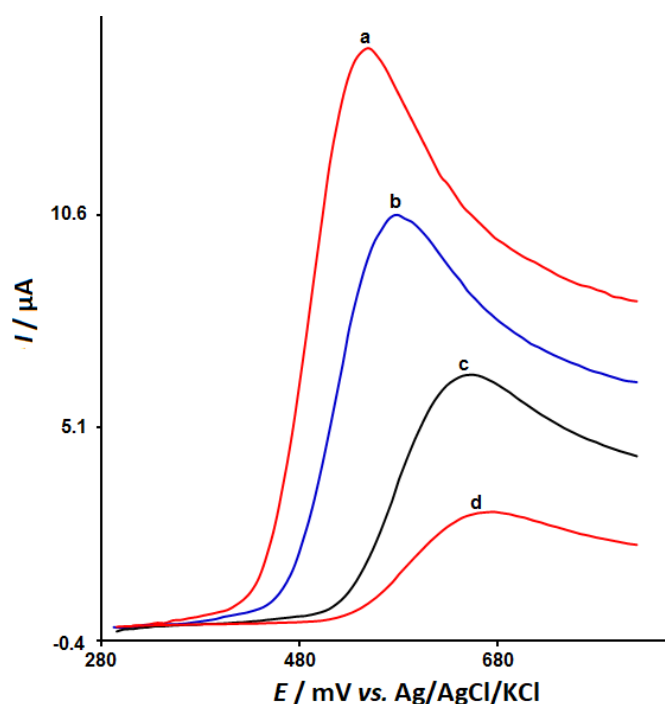
$\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  was prepared by mixing 0.04 g of  $\text{CuFe}_2\text{O}_4\text{-NPs}$  with 0.96 g graphite powder and approximately  $\sim 0.8$  mL of ionic liquids with a mortar and pestle. The paste was then packed into the end of a glass tube ( $\sim 3.4$  mm inner diameter and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact. For comparison, ionic liquids/carbon paste electrode (IL/CPE) in the absence of  $\text{CuFe}_2\text{O}_4\text{-NPs}$ , ( $\text{CuFe}_2\text{O}_4\text{-NPs/CPE}$ ) consisting of  $\text{CuFe}_2\text{O}_4\text{-NPs}$  powder and paraffin oil, and bare carbon paste electrode (CPE) consisting of graphite powder and paraffin oil were also prepared in the same way. The surface areas of the  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  and the unmodified SPE were obtained by cyclic voltammetry using 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  at various scan rates. Using the Randles–Sevcik equation for  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$ , the electrode surface was found to be  $0.373 \text{ cm}^2$  which was about 4.14 times greater than un-modified SPE.

## Results and discussion

### Electrochemical behavior of vanillin at the surface of various electrodes

The mechanism of the vanillin oxidation on  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  is based on the relationship between the oxidation potential and pH of the supporting electrolyte. The effect of the electrolyte pH on the oxidation of  $40.0 \mu\text{M}$  vanillin was investigated at  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  using differential pulse voltammetry (DPV) measurements in the phosphate buffer solution (PBS) in the pH range from 2.0 to 9.0. According to the results, the oxidation peak current of vanillin depends on the pH value and increases with increasing pH until it reaches the maximum at pH 7.0, and then decreases with higher pH values. The optimized pH corresponding to the higher peak current was 7.0, indicating that protons are involved in the reaction of vanillin oxidation.

The electrochemical behavior of vanillin was investigated by differential linear sweep voltammetry (LSV). The differential pulse voltammograms obtained using the bare CPE (Curve d), ILs/CPE (Curve c),  $\text{CuFe}_2\text{O}_4\text{-NPs/CPE}$  (Curve b) and  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  (Curve a) in 0.1 M PBS (pH 7.0) in the presence of  $65.0 \mu\text{M}$  vanillin are shown in Figure 2.

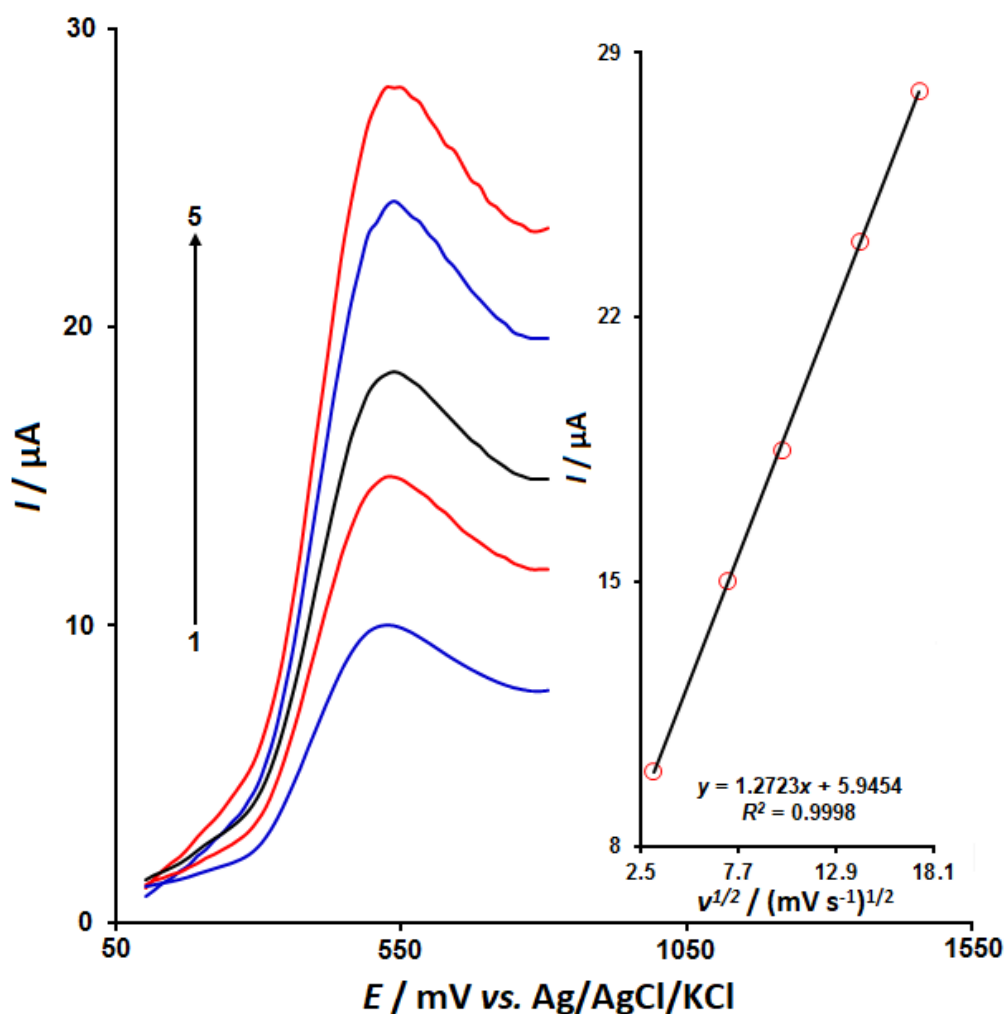


**Figure 2.** The linear sweep voltammograms of (a)  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$ , (b)  $\text{CuFe}_2\text{O}_4\text{-NPs/CPE}$ , (c) ILs/CPE and (d) bare CPE in 0.1 M PBS (pH 7.0) in the presence of  $150.0 \mu\text{M}$  vanillin at the scan rate  $50 \text{ mVs}^{-1}$

On a bare CPE, an irreversible signal with a low oxidation current of  $\sim 2.9 \mu\text{A}$  was obtained with a peak potential of  $\sim 680 \text{ mV}$ . After modifying the electrode with ILs/CPE, and  $\text{CuFe}_2\text{O}_4\text{-NPs/CPE}$ , the peak current increased up to  $\sim 6.5$  and  $\sim 10.6 \mu\text{A}$ , respectively. In contrast,  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  exhibited an enhanced sharp anodic peak current ( $I_{\text{pa}} = 14.9 \mu\text{A}$ ) at a much lower overpotential  $E_p = 550 \text{ mV}$ . These results confirmed that the  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs}$  improved the sensitivity of the modified electrode by enhancing peak current and decreasing the overpotential of the oxidation of vanillin.

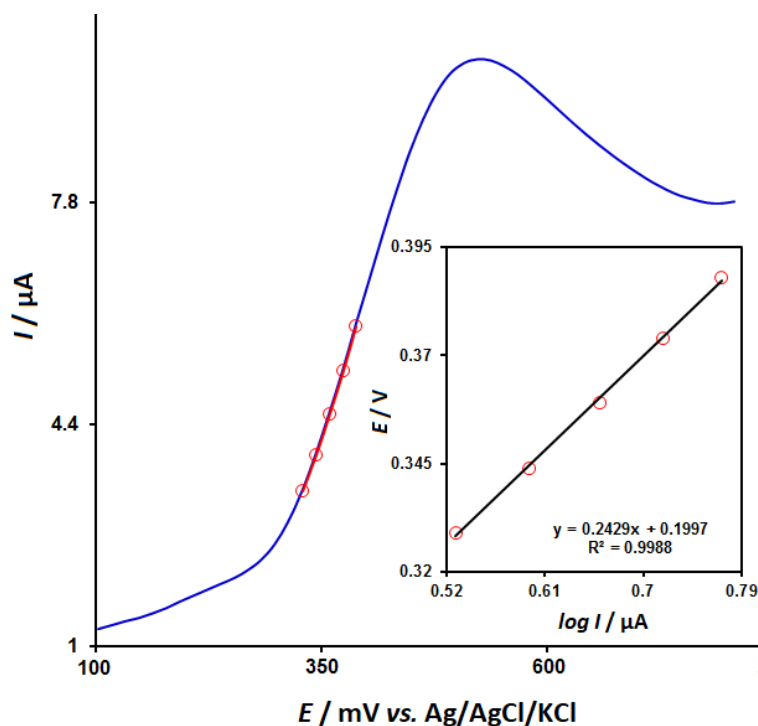
#### Effect of scan rate on the determination of vanillin at $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$

The influence of the scan rate ( $\nu$ ) on the peak currents ( $I_{\text{pa}}$ ) of vanillin at  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  was investigated by LSV. Figure 3 shows the voltammetric response of  $150.0 \mu\text{M}$  vanillin at  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  at different scan rates in the range of 10 to  $300 \text{ mV/s}$ . The oxidation peak current of vanillin increases linearly with increasing scan rate. Linear regression equation was obtained from the plot  $I_{\text{pa}}$  vs.  $\nu^{1/2}$  as follows:  $I_{\text{pa}} / \mu\text{A} = 1.2723 \nu^{1/2} / \text{mV}^{1/2} \text{ s}^{-1/2} + 5.9454$  ( $R^2 = 0.9998$ ) for the oxidation process, which indicates that the reaction of vanillin at  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  is diffusion controlled.



**Figure 3.** Linear sweep voltammograms of  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  in  $0.1 \text{ M PBS}$  ( $\text{pH } 7.0$ ) containing  $150.0 \mu\text{M}$  vanillin at various scan rates; 1-5 correspond to  $10, 50, 100, 200$  and  $300 \text{ mV s}^{-1}$ , respectively. Inset: variation of anodic peak current vs.  $\nu^{1/2}$

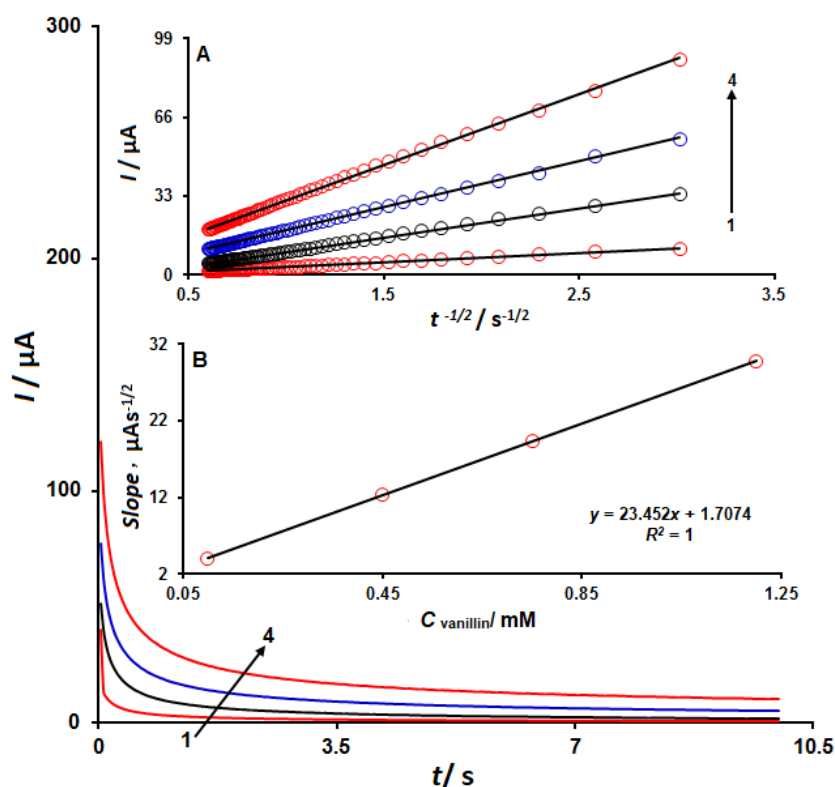
In addition, the plot of  $\log I$  vs.  $E$  (Tafel plot) is linear, having the following regression equation:  $\log I = 0.2429 E + 0.1997$  ( $R^2 = 0.9988$ ) (Figure 4). Assuming that  $n_\alpha = 1$ , the value of  $\alpha$  was calculated as  $\sim 0.76$ .



**Figure 4.** Tafel plot for  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  in 0.1 M PBS (pH 7.0) in the presence of 150.0  $\mu\text{M}$  vanillin and scan rate  $10 \text{ mV s}^{-1}$

#### Chronoamperometric analysis

The analysis of chronoamperometry for vanillin samples was performed by use of  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE vs. Ag/AgCl/KCl}$  (3.0 M) at 0.6 V. Chronoamperometric results of different concentrations of vanillin in PBS (pH 7.0) are demonstrated in Figure 5.



**Figure 5.** Chronoamperograms obtained at  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  in 0.1 M PBS (pH 7.0) for different concentrations of vanillin; 1-4 correspond to 0.1, 0.45, 0.75 and 1.2 mM of vanillin. Insets: (A) plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 1-4. (B) plot of the slope of the straight lines against vanillin concentration

The Cottrell equation for the chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as in equation (1):

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (1)$$

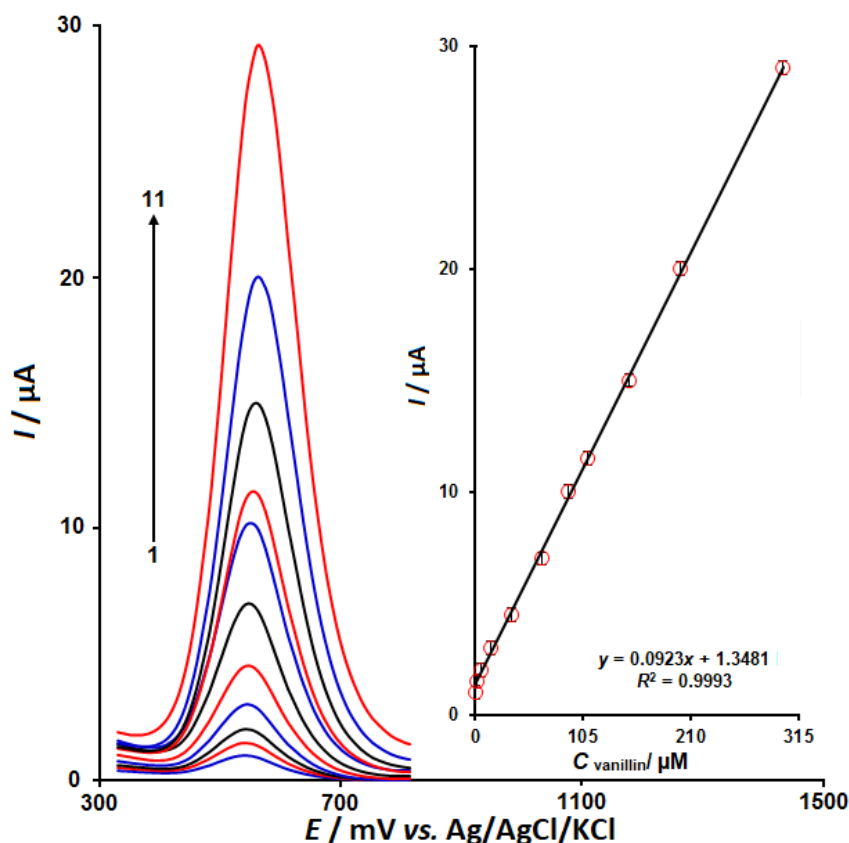
where  $D$  represents the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), and  $C_b$  is the applied bulk concentration ( $\text{mol cm}^{-3}$ ). Experimental results of  $I$  vs.  $t^{-1/2}$  were plotted in Figure 5A, with the best fits for different concentrations of vanillin. The resulted slopes corresponding to straight lines in Figure 5A, were then plotted against the concentration of vanillin (Figure 5B). The mean value of  $D$  was determined to be  $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  according to the resulting slope and Cottrell equation.

#### Calibration curve

Because DPV commonly has a higher sensitivity than cyclic voltammetry technology, the DPV technique was applied for the quantitative detection of vanillin. Figure 6 shows the differential pulse voltammograms of vanillin at various concentrations using  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  (Step potential of 0.01 V and pulse amplitude of 0.025 V). As seen, the oxidation peak currents of vanillin enhance gradually by increasing its concentration. The oxidation peak currents ( $I_{pa}$ ) show a good linear relationship with the concentrations of vanillin ranging from 0.01 M to 300.0  $\mu\text{M}$ . The linear equation is  $I_{pa} / \mu\text{A} = 0.0923C_{\text{vanillin}} / \mu\text{M} + 1.3481$  ( $R^2 = 0.9993$ ) (Figure 6 (inset)). Also, the limit of detection,  $C_m$ , of vanillin was calculated using the equation (2):

$$C_m = 3S_b/m \quad (2)$$

where  $m$  is the slope of the calibration plot ( $0.0923 \mu\text{A} / \mu\text{M}$ ) and  $S_b$  is the standard deviation of the blank response obtained from 15 replicate measurements of the blank solution. The detection limit for the determination of vanillin using this method  $0.008 \mu\text{M}$  was obtained.



**Figure 6.** DPVs of  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  in 0.1 M (pH 7.0) containing different concentrations of vanillin. 1–11 correspond to 0.01, 1.0, 5.0, 15.0, 35.0, 65.0, 90.0, 110.0, 150.0, 200.0 and 300.0  $\mu\text{M}$  of vanillin. Inset: plot of the electrocatalytic peak current as a function of  $C_{\text{vanillin}}$  in the range of 0.01–300.0  $\mu\text{M}$ .

The performance of this sensor is compared with some of the recently reported electrodes for vanillin quantification (see Table 1) [63–66].

**Table 1.** Comparison of the sensing performances toward the detection of vanillin between the existing modified electrodes and the proposed  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$

Electrochemical sensor	Method	Linear range	LOD	Ref.
Anodically pre-treated boron-doped diamond electrode	Square-wave voltammetry	3.3–9.8 $\mu\text{M}$	0.167 $\mu\text{M}$	[63]
nitrogen-doped graphene/carbon nanotubes/glassy carbon electrode	Square-wave voltammetry	0.01–10.0 $\mu\text{M}$	0.0033 $\mu\text{M}$	[64]
Cationic cetylpyridium bromide /carbon nanofibers/ glassy carbon electrode	DPV	0.5–750.0 $\mu\text{mol dm}^{-3}$	0.14 $\mu\text{mol dm}^{-3}$	[65]
Cellulose diacetate/Au–Ag nanoparticles/ glassy carbon electrode	Amperometry	0.2–50.0 $\mu\text{mol dm}^{-3}$	0.04 $\mu\text{mol dm}^{-3}$	[66]
$\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$	DPV	0.01–300.0 $\mu\text{M}$	0.008 $\mu\text{M}$	This work

#### Stability and reproducibility of the modified electrode

The long-term stability test of the  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  sensor using DPV was performed at room temperature. The results exhibited that the peak current of 40.0  $\mu\text{M}$  vanillin at the  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  stayed at 94.9 % of its primary current after 7 days, 92.4 % after 14 days, and 90.7 % after 21 days, indicating the superior long-term stability of the proposed sensor.

For reproducibility,  $\text{CuFe}_2\text{O}_4\text{-NPs/ILs/CPE}$  was stored for 7, 14, and 21 days at room temperature. Voltammetry measurements were performed in PBS (0.1 M, pH 7.0) containing 40.0  $\mu\text{M}$  vanillin.

The results showed that CuFe<sub>2</sub>O<sub>4</sub>-NPs/ILs/CPE response did not change with time. Hence, the developed electrode provides good reproducibility for the determination of vanillin.

### Analysis of real samples

The real samples for the analysis were prepared and quantified by DPV method. The developed sensor was applied to detect vanillin in chocolate and coffee milk samples. The results are summarized in Table 2. Each measurement was repeated five times. The recovery and relative standard deviation (RSD) values confirmed that the CuFe<sub>2</sub>O<sub>4</sub>-NPs/ILs/CPE sensor has great potential for analytical application.

**Table 2.** Application of CuFe<sub>2</sub>O<sub>4</sub>-NPs/ILs/CPE for determination of vanillin in real samples (n = 3)

Sample	Concentration, $\mu\text{M}$		Recovery, %	RSD, %
	Spiked	Found		
Chocolate	0.0	2.7	-	3.2
	2.0	4.6	97.9	1.9
	4.0	6.9	102.9	2.8
Coffee milk	0.0	4.0	-	1.8
	1.0	5.1	102.0	2.3
	3.0	6.8	97.1	3.3

### Conclusion

A sensitive electrochemical sensor for the detection of vanillin was developed based on CuFe<sub>2</sub>O<sub>4</sub> nanoparticles and ionic liquid. CuFe<sub>2</sub>O<sub>4</sub> nanoparticles can provide a larger specific surface and excellent electrical conductivity for the sensor. This sensitive electrochemical sensor showed that the concentration of vanillin presented a linear correlation range from 10 to 300.0  $\mu\text{M}$  and the limit of detection was 0.008  $\mu\text{M}$ . The diffusion coefficient for vanillin using CuFe<sub>2</sub>O<sub>4</sub>-NPs/ILs/CPE,  $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  was obtained. The designed sensor has a good recovery in two real samples of tap water and orange juice, indicating it can be used as an alternative detection method via comparison with other detection methods. The sensor displayed a promising possibility in actual monitoring.

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