

Full Paper

Fabrication of a Nanostructure Voltammetric Sensor for Carmoisine Analysis as a Food Dye Additive

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Abstract- In this study, fabrication of carbon paste electrode amplified with CdO/CNTs nanocomposite and 1-ethyl-3-methylimidazolium tetrafluoroborate (CdO/CNTs/1-E-3-MITFBr/CPE) for determination of carmoisine was investigated. The electro-oxidation of carmoisine occurs at a potential about 680 mV at a surface of CdO/CNTs/1-E-3-MITFBr/CPE and this mount is less positive than the bare carbon paste electrode at the optimized condition. The square wave voltammograms (SWV) peak currents of carmoisine show good linear dynamic range (0.1-700 μ M) with a detection limit of 40.0 nM. Finally, the CdO/CNTs/1-E-3-MITFBr/CPE was used as highly selective sensor for determination of carmoisine in real samples.

Keywords- Carmoisine analysis, CdO/CNTs nanocomposite, Voltammetry, 1-ethyl-3-methylimidazolium tetrafluoroborate

1. INTRODUCTION

Carmoisine is a synthetic azo dye with wide application in the food industry [1]. The application of azo dyes in food production increased in the recent years due to their color variation and cheapness. A lot of Azo dyes input on the prohibited substances list due to many side effects of them [2]. According to International Agency for Research on Cancer

(IARC) reported some of azo dyes can be increased the risk of cancer [2]. Therefore, determinations of this type of food additives are very important in food products. In the Europe, carmoisine is authorized for use in certain foods and beverages, such as cheeses, dried fruit, and some alcoholic beverages and is permitted for use as an excipient in medications [3]. Although high-performance liquid chromatography and spectrophotometry were used for analysis of food additive from many years ago [4-7], electrochemical sensors showed many advantages for analysis of food compounds due to fast response [8-11]. High oxidation/reduction over-potential and low sensitivity of electro-active compounds at as surface of unmodified electrodes are major problems for trace level analysis of them [12-21]. Therefore, modified electrodes were suggested as highly powerful tools for trace level analysis of electro-active compounds [22-29]. According to the previous published papers, the room temperature ionic liquids and nano-materials can be improved sensitivity of electrochemical sensors for analysis of electro-active materials [30-35]. Therefore, in the presence study, we fabricated a highly sensitive voltammetric sensor based on carbon paste electrode modified with CdO/CNTs nanocomposite and 1-ethyl-3-methylimidazolium tetrafluoroborate for analysis of carmoisine in food samples. The fabricated sensor showed good electrical conductivity compared to unmodified electrode and improved the quality of carbon paste electrode for analysis of carmoisine in food samples.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

The entire reagent that used in this research such as carmoisine, sodium hydroxide, phosphoric acid, paraffin oil were purchased from Merck and Sigma-Aldrich Company. CdO/CNTs synthesized according to recommend procedure by Cheraghi et al. reported paper [11]. Phosphate buffer solutions (PBS) with different pH values were used during the experiment. A μ -Autolab system (Netherland) that connected to the computer with NOVA software included three electrochemical cells included CdO/CNTs/1-E-3-MITFBr/CPE (as working electrode), Ag/AgCl/KCl sat (as references electrode) and Pt wire (as a counter electrode) was used for electrochemical investigation.

2.2. Preparation of CdO/CNTs/1-E-3-MITFBr/CPE

At first we mixed 0.28 g 1-ethyl-3-methylimidazolium tetrafluoroborate as an ionic liquid and 0.72 g of the paraffin oil and 0.94 g graphite powder with 0.12 g CdO/CNTs very well for 30 min to obtain a wetted paste. Then we separate a portion of the mixture then filled it in to the glass tube to prepare the navel sensor CdO/CNTs/CPE as o working electrode in this work.

2.3. Real samples preparation

Fruit juices were purchased from local market as real samples. The purchasing samples homogenized, centrifuged, and filtered through a 0.25 μm filter membrane and were used directly in electrochemical cell.

3. RESULTS AND DISCUSSION

3.1. Characterization of CdO/CNTs nanocomposite

Figure 1 showed SEM image of CdO/CNTs nanocomposite. As can be seen, the spherical particles of CdO incorporated at a surface of carbon nanotubes.

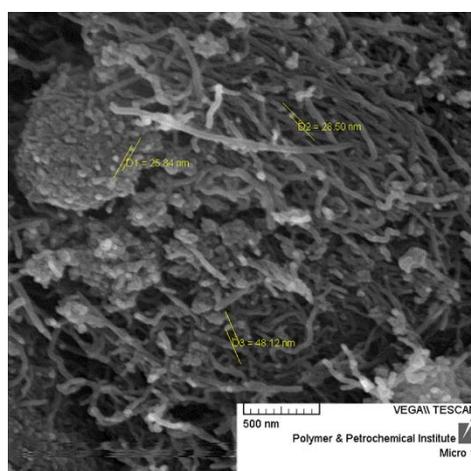
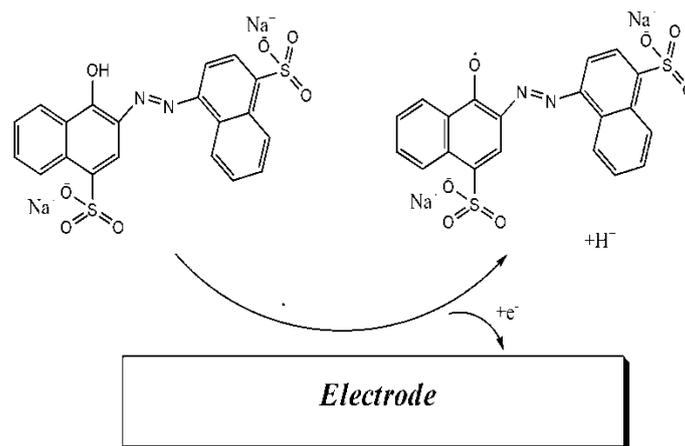


Fig. 1. SEM image of CdO/CNTs nanocomposite uses in this work

3.2. Voltammetric Investigation

In this work, we investigate the electro-oxidation behavior of carmoisine with linear sweep voltammetry at a different pH values. Carmoisine can be oxidized at positive potential and the potential depends on the kind of electrode and different solution pH value (Scheme 1).

In order to this, the voltammetric response of carmoisine (250 μM) at a surface of CdO/CNTs/1-E-3-MITFBr/CPE was recorded in the solution with different pH value from 5.0-9.0. The result confirm our thought, the peak potential of the redox couple was pH dependent with a slope of -55.9 mV/pH unit at 25 $^{\circ}\text{C}$ which was equal to the Nernstian value for a one-electron, one-proton electrochemical reaction. Voltammetric result show, at pH 7.0 we have that the maximum value of current and lees value of potential Fig. 2, so this pH was selected as an optimized condition during the work.



Scheme 1. The mechanism for electro-oxidation of carmoisine

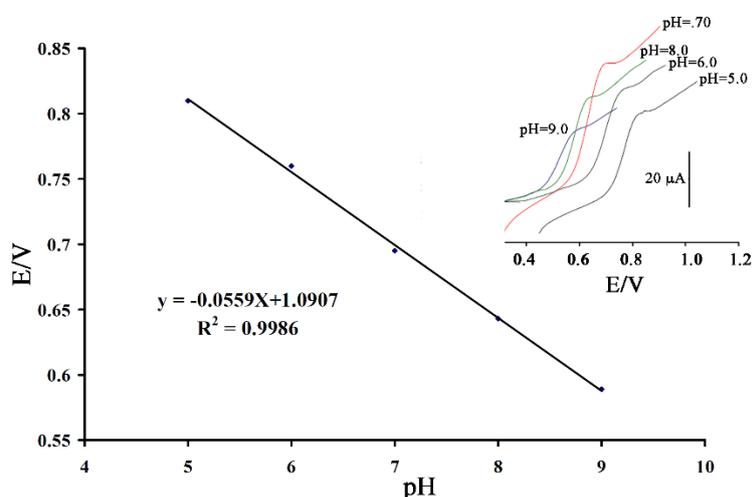


Fig. 2. Plot of potential and E_p , vs. pH for the electro-oxidation of 250 μM carmoisine at CdO/CNTs/1-E-3-MITFBr/CPE Inset: influence of pH on linear sweep voltammetric response at a surface of the modified electrode

Linear sweep voltammograms of 200 μM carmoisine with scan rate of 100 mV s^{-1} at the surface of different electrodes is recorded. Result showed carbon paste electrode modified with CdO/CNTs and 1-E-3-MITFBr has a significant oxidation peak current around 680 mV with the peak current of $55.3 \mu\text{A}$ (Fig. 3, curve d). In addition carbon paste electrode modified with 1-E-3-MITFBr (curve c; $E_{pa}=690 \text{ mV}$; $I_{pa}=41.2 \mu\text{A}$) or modified with CdO/CNTs (curve b; $E_{pa}=693 \text{ mV}$; $I_{pa}=21.8 \mu\text{A}$) have the lowest value of current peak with more value of over-potential.

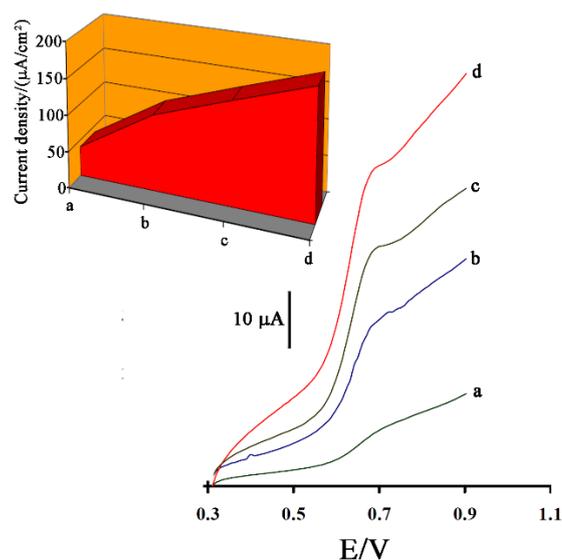


Fig. 3. Linear sweep voltammograms of 200 μM carmoisine at a surface of (a) CPE; (b) CdO/CNTs/CPE; (c) 1-E-3-MITFBr/CPE and (d) CdO/CNTs/1-E-3-MITFBr/CPE at pH 7.0, respectively. Insert; Current density diagrams relative to linear sweep voltammograms presence in figure 3

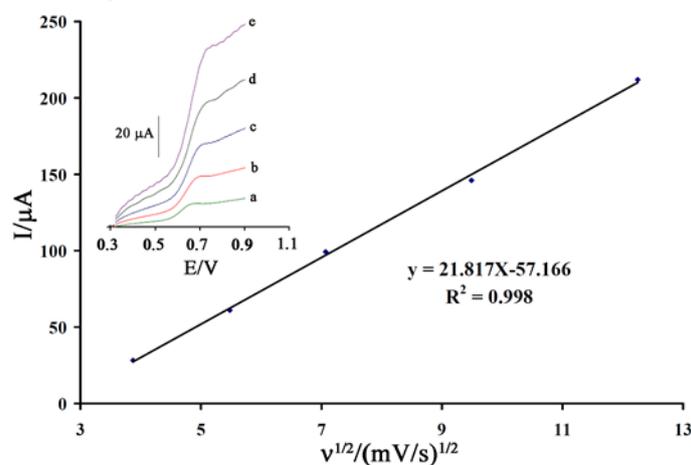


Fig. 4. Plot of I_{pa} vs. $v^{1/2}$ for the oxidation of carmoisine at CdO/CNTs/1-E-3-MITFBr/CPE. Inset shows linear sweep voltammograms of carmoisine at a surface of CdO/CNTs/1-E-3-MITFBr/CPE at different scan rates of a) 15, b) 30, c) 50, d) 90, e) 150 mV/s

In addition, the oxidation of carmoisine showed low oxidation current 9.99 μA with potential ~ 710 mV (curve a). When we used 1-E-3-MITFBr and CdO/CNTs the peak current of carmoisine increased that confirmed good electrical conductivity of mediators. Also, the current density investigation in figure 3 insert confirmed electrical conductivity of mediators at as surface of electrode.

The effect of scan rate (v) on the oxidation current of carmoisine was also examined (Figure 4). The results showed that the peaks current increased linearly with increasing the square root of scan rate that ranged from 15 to 150 mVs^{-1} . There is a relationship between the peak current (i_p) and $v^{1/2}$ regarding the equation that show the diffusion-controlled process for the electro-oxidation of carmoisine on the surface of (CdO/CNTs/1-E-3-MITFBr/CPE) in this work.

It is necessary to know the rate-determination step. So the Tafel plot was drawn and the slope of this plot equal to $2.3 RT/n(1-\alpha)F$ to obtain the value of α , which is equal to 0.76.

Chronoamperometric measurements of carmoisine at CdO/CNTs/1-E-3-MITFBr/CPE were examined by setting the working electrode potential at 700 mV vs. Ag/AgCl/KCl_{sat} for the two various concentration 100 and 200 μM of carmoisine (Figure 5A). The plots of I vs. $t^{-1/2}$ were presence in figure 5B. From these slopes and Cottrell equation, value of the D was found to be $5.6 \times 10^{-6} \text{ cm}^2/\text{s}$.

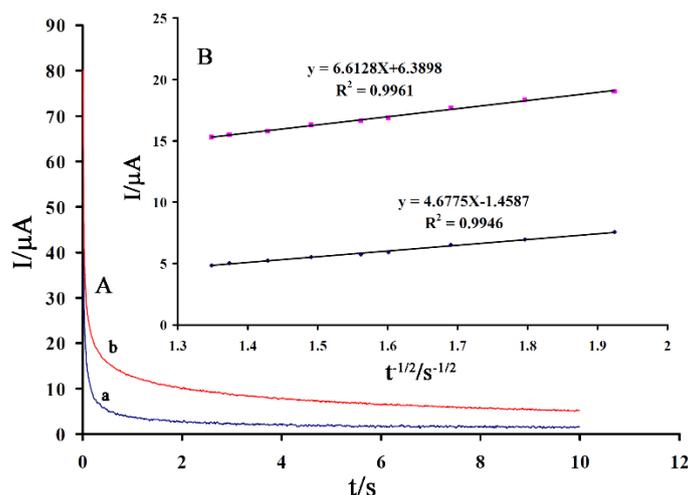


Fig. 5. Chronoamperograms obtained at a surface of CdO/CNTs/1-E-3-MITFBr/CPE in the presence of (a) 100, (b) 200 μM carmoisine in the buffer solution (pH7.0)

3.3. LOD and LDR Determination

Square wave voltammetry (SWV) was used to determine the linear dynamic ranges of carmoisine concentration (figure 6). Different concentration of electro-active material prepared and examined. The conclusion of this investigation showed the linear relation between oxidation current and carmoisine concentration from 0.1-700.0 μM with the limit of detection 0.04 μM by SWV.

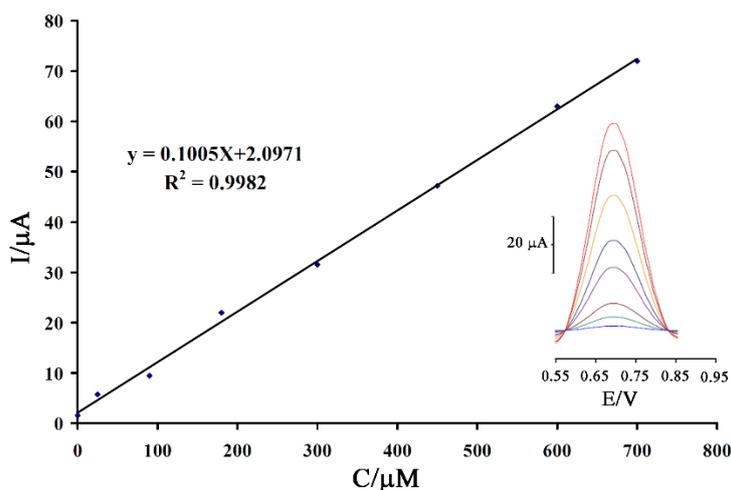


Fig. 6. Linear relation between oxidation peak current and concentration of carmoisine at a surface of CdO/CNTs/1-E-3-MITFBr/CPE Square wave voltammograms of CdO/CNTs/1-E-3-MITFBr/CPE containing different concentrations of carmoisine in the range 0.1-700 μM

3.4. Interference Study

For evaluation the selectivity of proposed sensor, the interference of different foreign species that is usual in fruit juices samples was investigated in the present of 20 μM carmoisine. Tolerance limit was evaluated as the maximum concentration of foreign substances with an approximate relative error of $\pm 5\%$. The results are shown in Table 1 and confirm good selectivity of sensor for analysis of carmoisine.

Table 1. Interference study for the determination of 20.0 μM carmoisine

Species	Tolerante limits ($W_{\text{Substance}}/W_{\text{Analytes}}$)
Li^+ , F^- , Br^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^-	800
Starch	Saturation
glucose, tryptophan, isolucin, thiamine, pantothenic acid	250

3.5. Real Sample Analysis

In order to evaluate the applicability of CdO/CNTs/1-E-3-MITFBr/CPE, it was applied for analysis of real samples such as orange and lemon juices. The measurements data present in table 2 that confirm good ability of proposed sensor for real sample analysis.

Table 2. Determination of carmoisine in food samples (n=5)

Sample	Added carmoisine	Expected carmoisine	Found carmoisine	Recovery for carmoisine (%)
Orange juice ^a	---	---	---	---
	5.00	5.00	4.87±0.56	97.4
Lemon juice ^a	---	---	---	---
	10.00	10.00	10.28±0.45	102.8

^aThe obtained results according to (mg/L)

3.6. Stability of sensor

The stability of CdO/CNTs/1-E-3-MITFBr/CPE was investigated by recorded electrochemical responses of 25.0 μ M carmoisine over a period of 45 days. Compared to its first signal, only 2.9% deviation was recorded when CdO/CNTs/1-E-3-MITFBr/CPE was used daily and stored in the laboratory. This suggests that CdO/CNTs/1-E-3-MITFBr/CPE possesses long-term stability.

4. CONCLUSION

In this paper, we fabrication carbon paste electrode modified with CdO/CNTs and 1-ethyl-3-methylimidazolium tetrafluoroborate as highly sensitive sensor for carmoisine analysis. Voltammetric behavior of carmoisine was investigated and square wave voltammograms display good linear dynamic ranges with a good limit of detection (40.0 nM) at a surface of CdO/CNTs/1-E-3-MITFBr/CPE. The application of CdO/CNTs/1-E-3-MITFBr/CPE is acceptable in real samples and the statistic calculations confirm the accuracy and validity of the sensor.

REFERENCES

- [1] K. Hunger, P. Mischke, W. Rieper, R. Raue, K. Kunde, and A. Engel, "Azo Dyes" Ullmann's Encyclopedia of Industrial Chemistry. Weinheim (2005) doi:10.1002/14356007.a03_245.
- [2] M. Elyasi, M. A. Khalilzadeh, and H. Karimi-Maleh, Food Chem. 141 (2013) 4311.
- [3] J. G. Millichap, and M. M. Yee, Pediatrics 2 (2012) 330.
- [4] S. P. Alves, D. M. Brum, É. C. Branco de, A. A. D. P. Netto, Food Chem. 107 (2008) 489.
- [5] K. S. Minioti, C. F. Sakellariou, and N. S. Thomaidis, Anal. Chim. Acta 583 (2007) 103.
- [6] H. M. Merken, and G. R. Beecher, J. Agric. Food Chem. 48 (2000) 577.

- [7] A. A. Ensafi, B. Rezaei, and S. Nouroozi, *Anal. Sci.* 20 (2014) 1749.
- [8] A. A. Ensafi, M. Taei, and T. Khayamian, *Int. J. Electrochem. Sci.* 5 (2010) 116.
- [9] A. A. Ensafi, and R. Hajian, *Electroanalysis* 18 (2006) 579.
- [10] H. Asari-Bami, M. A. Khalilzadeh, and H. Karimi-Maleh, *Anal. Bioanal. Electrochem.* 8 (2016) 1033.
- [11] S. Cheraghi, M. A. Taher, and H. Karimi-Maleh, *J. Food Compos. Anal.* 62 (2017) 254.
- [12] B. J. Sanghavi, and A. K. Srivastava, *Electrochim. Acta* 56 (2011) 4188.
- [13] B. J. Sanghavi, and A. K. Srivastava, *Anal. Chim. Acta* 706 (2011) 246.
- [14] Y. L. Su, and S. H. Cheng, *Anal. Chim. Acta* 901 (2015) 41.
- [15] L. Daneshvar, G. Rounaghi, Z. E'shaghi, M. Chamsaz, and S. Tarahomi, *J. Mol. Liq.* 215 (2016) 316.
- [16] X. Qiu, L. Lu, J. Leng, Y. Yu, W. Wang, M. Jiang, and L. Bai, *Food Chem.* 190 (2016) 889.
- [17] B. J. Sanghavi, P. K. Kalambate, S. P. Karna, and A. K. Srivastava, *Talanta* 120 (2014) 1.
- [18] X. Cao, H. Xu, S. Ding, Y. Ye, X. Ge, and L. Yu, *Food Chem.* 194 (2016) 1224.
- [19] M. Parsaei, Z. Asadi, and S. Khodadoust, *Sens. Actuators B* 220 (2015) 1131.
- [20] E. Er, H. Celikkan, and N. Erk, *Sens. Actuators B* 224 (2016) 170.
- [21] S. Cheraghi, M. A. Taher, and H. Karimi-Maleh, *Electroanalysis* 28 (2016) 366.
- [22] A. A. Ensafi, M. M. Abarghoui, and B. Rezaei, *Sens. Actuators B* 196 (2014) 398.
- [23] A. A. Ensafi, and H. Karimi-Maleh, *Drug testing and analysis* 3 (2011) 325.
- [24] A. A. Ensafi, S. Dadkhah-Tehrani, and H. Karimi-Maleh, *Anal. Sci.* 27 (2011) 409.
- [25] A. A. Ensafi, M. Taei, and T. Khayamian, *Int. J. Electrochem. Sci.* 5 (2010) 116.
- [26] A. A. Ensafi, M. Taei, H. R. Rahmani, and T. Khayamian, *Electrochim. Acta* 56 (2011) 8176.
- [27] A. A. Ensafi, and H. Karimi-Maleh, *Int. J. Electrochem. Sci.* 5 (2010) 392.
- [28] M. Sheikhshoaie, H. Karimi-Maleh, I. Sheikhshoaie, and M. Ranjbar, *J. Mol. Liq.* 229 (2017) 489.
- [29] M. Bijad, H. Karimi-Maleh, M. Farsi, and S. A. Shahidi, *Food Anal. Methods* 10 (2017) 3773.
- [30] M. Baghayeri, H. Veisi, H. Veisi, B. Maleki, H. Karimi-Maleh, and H. Beitollahi, *RSC Adv.* 4 (2014) 49595.
- [31] M. R. Akhgar, H. Beitollahi, M. Salari, H. Karimi-Maleh, and H. Zamani, *Anal. Methods* 4 (2012) 259.
- [32] H. Karimi-Maleh, A. A. Ensafi, H. Beitollahi, V. Nasiri, M. A. Khalilzadeh, and P. Biparva, *Ionics* 18 (2012) 687.
- [33] A. Baghizadeh, H. Karimi-Maleh, Z. Khoshnama, A. Hassankhani, and M. Abbasghorbani, *Food Anal. methods* 8 (2015) 549.

- [34] H. Yaghoobian, H. Karimi-Maleh, A. M. Khalilzadeh, and F. Karimi, *J. Serbian Chem. Soc.* 74 (2009) 1443.
- [35] H. Karimi-Maleh, K. Ahanjan, M. Taghavi, and M. Ghaemy, *Anal. Methods* 8 (2016) 1780.