FACULTY OF PHARMACEUTICAL SCIENCES

Intelligently Designed Electrochemical Platform For The Detection Of Food Contaminants

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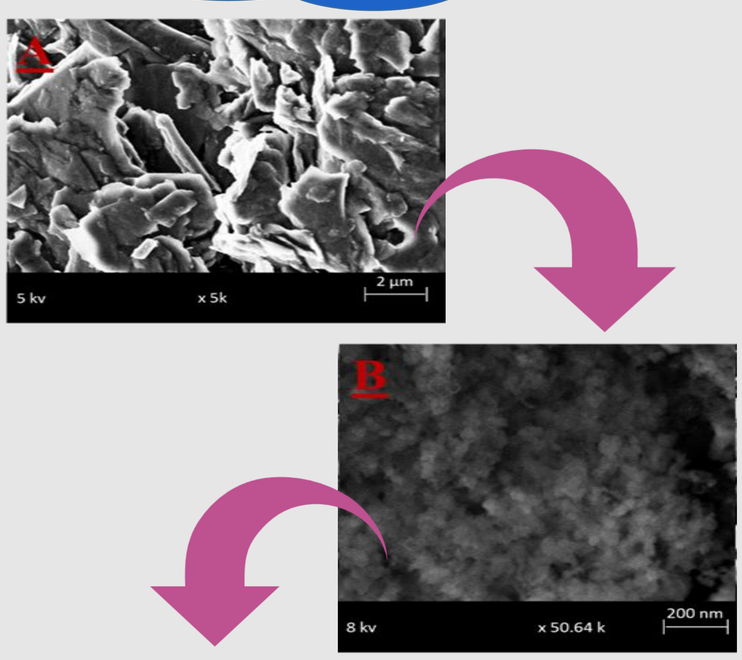
Introduction

Food safety is a challenge to human health worldwide and specifically in developing countries. Continuous monitoring of food contaminants through novel and sensitive analytical techniques is a must to ensure food safety. Among these contaminants are veterinary drugs broadly used by veterinarians to control farm animal diseases. In the present work, we demonstrate a novel electrochemical sensor fabrication technique for trace determination of diminazene (DIM), a veterinary drug commonly used in dairy animals and present in their milk. DIM residues accumulation in food can lead to the emergence of bacterial resistance. The MRL set by the EU for the presence of this compound in milk is 150 µg/L . The new sensor has been fabricated using nickel ferrite nanoparticles ($NiFe_2O_4$) modifying the carbon paste electrode (CPE), together with an ionic liquid. The modified CPE showed a synergic effect toward the oxidation of DIM. The prepared nanoparticles were investigated and characterized and the described voltammetric technique was optimized and validated. Under optimal conditions, the sensor showed a sensitive response to DIM over a wide linear range (0.02 -18 µM). Finally, the developed method was used to quantify traces of DIM in milk samples.

Results and Discussion

Characterization of bare and modified electrodes

Hydrothermally prepared nanoparticles



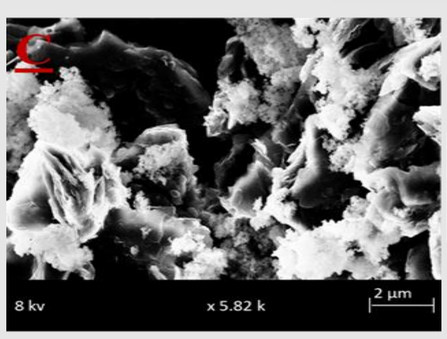


Fig 1. SEM images of (A) CPE, (B) $NiFe_2O_4$ and (C) $NiFe_2O_4$-IL/CPE

The SEM of CPE, $NiFe_2O_4$ and $NiFe_2O_4$-IL/CPE are shown in Fig. 1. Significant differences in the surface structure of CPE, $NiFe_2O_4$ and $NiFe_2O_4$-IL/CPE were observed. The surface of CPE was predominated by isolated and irregularly shaped graphite flaks and separately layers were noticed (Fig 1 A).

Electrochemical behavior of DIM

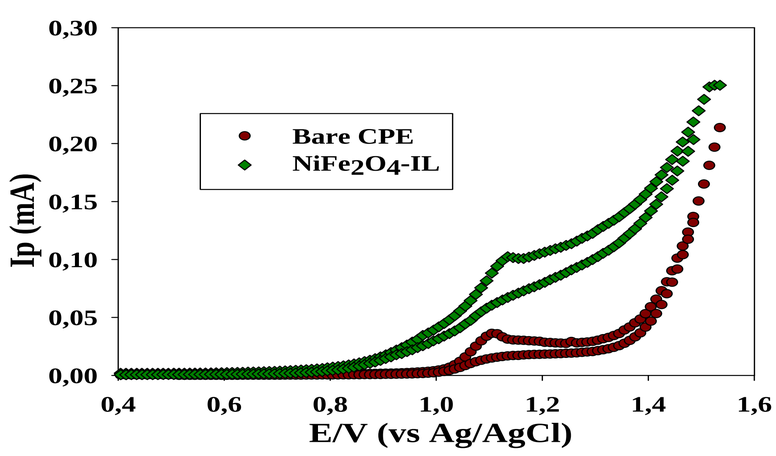


Fig 2. Cyclic voltammogrames of 1.0 mM DIM in B-R buffer (pH 2.0) at a scan rate of 100 mV s^{-1} recorded at CPE and $NiFe_2O_4$-IL/CPE electrodes

Preliminary investigation using CV shows an irreversible oxidation of 1.0 x 10-3 M of DIM in Britton-Robinson buffer pH 2 at scan rate 100 mVs−1 and no cathodic peak in the reverse scan. The CV was carried out in positive direction with applied potential range 0 to + 1.5 V at room temperature at bare CPE and modified $NiFe_2O_4$-IL/CPE (Fig 2). The oxidation peak currents are 105.34 µA and 37.4 µA for modified and bare CPE, respectively. The anodic process has been attributed in literature to the oxidation of primary amine group.

Influence of pH on the anodic peak current

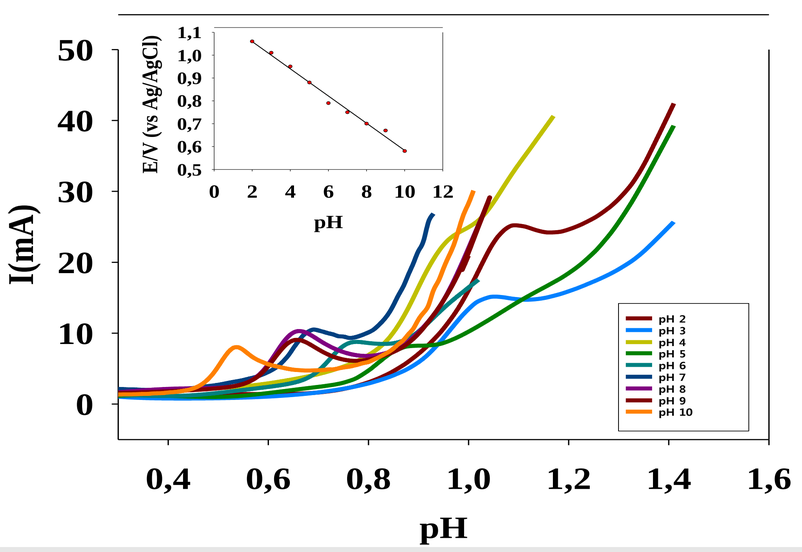


Fig 3. Square wave voltammetric responses of 1.0 × 10^{-5} M DIM at different pH values using $NiFe_2O_4$-IL/CPE sensing platforms. Scan rate: 100 mV s^{-1}. Inset: plot of anodic peak potential of DIM versus pH

Effect of pH on square wave voltammograms of the oxidation peak currents of DIM in Britton–Robinson buffer with different pH values (2 → 10) and scan rate 100 mV s-1 was investigated. The peak potential of DIM shifted negatively with increase in pH. This indicates that the oxidation of the drug in the solution is pH dependent. The highest current is obtained at pH 2. The relationship between the anodic peak potential and the solution pH (2– 10) could be fit to the linear regression equation of Epa (V) = 1.1781 - 0.0595 pH, with a correlation coefficient of r = 0.9903. The slope was found to be -59.5 mV/pH units over the pH range from 2 to 10, which is close to the theoretical value of -59 mV. This indicates that the number of protons and electrons transferred involved in the oxidation mechanism is equal.

Square wave voltammetry (SWV) studies

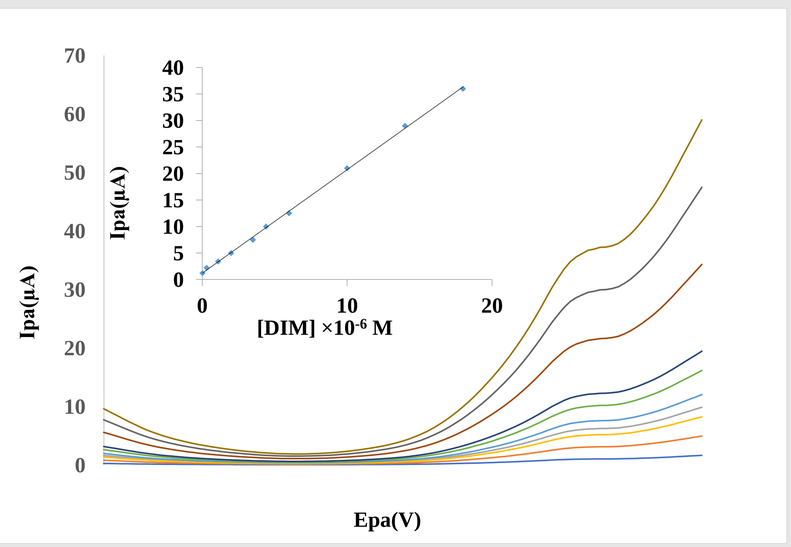


Fig 4. SWV of DIM at $NiFe_2O_4$-IL /CPE in B–R buffer pH 2.0 at a scan rate of 100 mV s^{-1} solution containing different concentrations. Insets: the plot of the peak current as a function of DIM in concentration range 2 × 10^{-8}– 1.8 × 10^{-5} M

Table 1. Determination of DIM in milk and pharmaceutical preparation using the proposed sensing protocol

Sample	Amount added standard (µM)	Amount found (µM)	Apparent recovery%
Milk	2.00	1.96	98.00
	4.00	3.98	99.50
	10.00	9.91	99.10
Recovery%±R.S.D			98.87±0.28
Dimazin©	2.00	2.04	102.00
	4.00	4.06	101.50
	10.00	10.10	101.00
Recovery%±R.S.D			101.5±0.50

Conclusion

1. The new sensor has been fabricated using $NiFe_2O_4$ modifying the CPE, together with an ionic liquid.
2. The modified CPE showed a synergic effect toward the oxidation of DIM.
3. The prepared nanoparticles were investigated and characterized and the described voltammetric technique was optimized and validated.
4. Under optimal conditions, the sensor showed a sensitive response to DIM over a wide linear range (0.02 -18 µM).
5. The developed method was used to quantify traces of DIM in milk samples.

References

1. Hao, C., Zhou, T., Liu, S., Wang, L., Huang, B., Kuang, N., & He, Y. (2016). Dual-channel optical sensing platform for detection of diminazene aceturate based on thioglycolic acid-wrapped cadmium telluride/cadmium sulfide quantum dots. *Journal of Colloid and Interface Science*, *472*, 76–83.
2. Ensafi, A. A., Arashpour, B., Rezaei, B., & Allafchian, A. R. (2014). Voltammetric behavior of dopamine at a glassy carbon electrode modified with NiFe2O4magnetic nanoparticles decorated with multiwall carbon nanotubes. *Materials Science and Engineering C*, *39*(1), 78–85.
3. Lv, M., Liu, Y., Geng, J., Kou, X., Xin, Z., & Yang, D. (2018). Engineering nanomaterials-based biosensors for food safety detection. *Biosensors and Bioelectronics*, *106*(January), 122–128.

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