

1 **Determination of ultra-trace amounts of neonicotinoid insecticide imidacloprid by cyclic**
2 **and square wave voltammetric methods using pretreated glassy carbon electrode**

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6 **Abstract**

7 Pesticide production and application have progressively increased worldwide during recent
8 decades. Among these compounds, imidacloprid (IMD) is a widely used insecticide in
9 agriculture, and more particularly to control sucking insects in crops. The aim of this work is
10 to develop rapid, simple and sufficiently sensitive cyclic voltammetry (CV) and square wave
11 voltammetry (SWV) for the detection and quantification of this insecticide in water and
12 agriculture samples. Pretreated glassy carbon electrode (PGC) was employed as working
13 electrode. Aqueous solutions were prepared with Confidor 200-SL commercial formulation of
14 IMD. Each voltammogram was characterized by a well-defined single irreversible cathodic
15 peak at approximately -1.38 V/SCE. The electrode reaction is mainly a diffusion controlled
16 process. The optimization of experimental parameters such as IMD initial concentration,
17 potential scan rate, pH and temperature was carried out by CV, and then a comparative study
18 was conducted by SWV. For the detection and quantification of IMD, the results obtained by
19 SWV showed higher sensibility and accuracy than that by CV. The developed methods were
20 successfully used to determine IMD in real samples, namely plum and peach juice.

21
22 *Keywords:* Neonicotinoid; Cyclic voltammetry; Square wave voltammetry; Pretreated glassy
23 carbon electrode; Detection; Quantification.

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1 **1. Introduction**

2 The neonicotinoid 1[(6-chloro-3-pyridinyl) methyl]-N-nitro-2-imidazolidinimine is one of the
3 most commonly used neonicotinoids for crop protection worldwide due to its low soil
4 persistence and high insecticidal activity at very low application rate [1]. It acts as antagonist
5 by binding to postsynaptic nicotinic receptors in the insect's central nervous system resulting
6 in the paralysis and death of insects [2]. IMD is the active substance of many commercial
7 insecticides such as Confidor, Gaucho, Prestige, Admire, and Provado [3].

8 However, the intensive use of such insecticide in agriculture and the improper storage or
9 disposal of obsolete insecticides is a source of environmental contamination. Many studies
10 have demonstrated the existence of these insecticides and their residues in fruits and
11 vegetables [4–8]. For these reasons, several analytical techniques and treatment processes
12 have been reported for the detection and the removal of IMD and its residues from water.
13 High performance liquid chromatography (HPLC) [4,5,7–10], gas chromatography–mass
14 spectrometry (GC–MS) [11] and liquid chromatography–mass spectrometry (LC–MS)
15 [6,12–14] are commonly used methods for the detection of IMD. Photochemical-fluorimetric
16 method [15,16] and enzyme-linked immunosorbent assay [17] were also utilized. These
17 instrumental methods are accurate but expensive and time consuming, requiring lengthy
18 sample extraction and cleanup procedures.

19 Various electrochemical methods have been proposed for the determination of IMD,
20 including square wave adsorptive stripping voltammetry (SWASV) [18] cyclic voltammetry
21 (CV) [19–23], differential pulse voltammetry (DPV) [20,23–25] and differential pulse
22 polarography (DPP) [26]. Different electrode materials such as glassy carbon, carbon paste,
23 carbon ceramic and mercury were used as cathodes for the determination of IMD. This
24 determination can be based on the irreversible reduction of the electroactive nitro group to
25 hydroxylamine and amine. The limit of detection (LOD) of this pesticide is dependent on the

1 electrode materials and the electrochemical techniques. The lower LOD measured is about
2 0.01 μM at mercury electrode using DPP method [26]. However, for environmental concerns
3 the use of mercury electrode is not advisable. At a glassy carbon electrode, LOD is about 30
4 μM using the cyclic voltammetric technique [19]. This value is too high for carrying out trace
5 analysis. However, because of its high electrical conductivity, impermeability to gases, high
6 chemical resistance, reasonable mechanical and dimensional stability and widest potential
7 range of all carbonaceous electrodes [27]. We have chosen this electrode to minimize the
8 LOD of IMD by the optimization of several experimental parameters.

9 Cyclic and Square-wave voltammetry are among the most effective techniques for
10 development of analytical procedures for several routine applications. These techniques are
11 used for both quantitative and qualitative chemical analysis. They have several distinct
12 advantages including a high sensitivity and rapidity of data acquisition. Furthermore, the
13 analysis of the characteristic parameters of these techniques provides information on the
14 mechanism, kinetics and thermodynamics of chemical reactions.

15 This paper describes fully validated, simple, rapid, selective and sensitive procedures for the
16 determination of IMD employing SWV and CV at PGC electrode.

17 **2. Material and methods**

18 **2.1. Reagents**

19 All solutions containing different amounts of IMD taken from an emulsifiable concentrate
20 (Confidor 200 SL Bayer Crop Science) containing 200 g L^{-1} IMD were prepared using water
21 purified in Milli-Q Millipore system. These solutions were kept in the dark at 4°C. The
22 supporting electrolyte is sodium sulfate (Na_2SO_4) 2 g L^{-1} provided by Biochem. Sulfuric acid
23 and sodium hydroxide were supplied by Merck and added to the required pH values covering
24 the pH range of 3–11. Prior to measurements, the reduction of the dissolved oxygen at the
25 electrode was eliminated by purging solutions with nitrogen for 5 min.

1 **2.2. Apparatus**

2 Cyclic and Square-wave voltammograms were performed using a potentiostat-galvanostat
3 (VoltaLab PST050). A conventional three-electrode, a pretreated glassy carbon disk (PGC: 3
4 mm diameter, Tacussel) was used as working electrode. A platinum foil and saturated calomel
5 electrodes were employed as counter and reference electrodes, respectively. The pH of the
6 solution was measured with a Hanna digital pH meter 301 with combination glass electrode.

7 **2.3. Pretreatment of the glassy carbon electrode**

8 Prior to each measurement, the PGC disk was mechanically polished with fine alumina
9 powder (0.05 μm) and washed with bidistilled water to remove any residual polish before
10 transferring to the cell. In order to obtain an active surface and reproducible electrochemical
11 response, the PGC electrode was subjected to potential cycling conditions in 2 g L⁻¹ sodium
12 sulfate between -2.0 and +2.0 V at a higher scan rate of 5.0 V s⁻¹ for 120 s.

13 **2.4. Procedure for the determination of IMD in fruits samples**

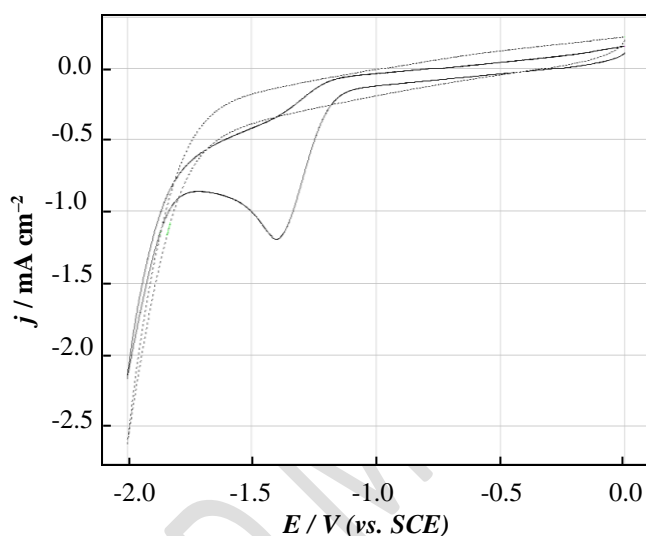
14 Plum and peach samples at the stage of maturation were obtained from the local market of
15 Sfax City, Tunisia. These fruits were put into plastic bags and transported to the laboratory
16 where they were immediately subjected to analysis. 200 g of samples were washed in
17 ultrapure water, chopped into small pieces and pressed mechanically by braun MP-80
18 multipress juice extractor. The suspension was filtered through a 0.45 mm milli-pore filter
19 (Watman filter paper), centrifuged for 20 min until a clear sample, then, the obtained juice
20 was fortified by the IMD. The amount of IMD in the plum and peach juice was evaluated by
21 the standard addition method. The IMD content in the fruits juice was determined from the
22 calibration curve of IMD concentration vs. peak current. The pH of the juice extracted was
23 modified to 7.0 with appropriate volumes of NaOH solution. Finally, 20 mL of the filtrate
24 juice was added to the supporting electrolyte solution (0.05 mol L⁻¹) in the voltammetric cell
25 for measurement. All tests cited in this work were performed at 25°C.

1 3. Results and discussion

2 3.1. Cyclic Voltammetry investigation

3 Figure 1 shows the cyclic voltammogram of IMD recorded at a concentration of 0.5 g L^{-1} in 2
4 g L^{-1} Na_2SO_4 solution. A single cathodic peak appears at about -1.38 V (vs. SCE).

5 In the reverse scan, there is no oxidation peak in the selected potential range in accordance
6 with an irreversible electrochemical process.



16 **Figure 1:** Voltammograms of the first cycle of the PGC electrode immersed in 2.0 g L^{-1}
17 Na_2SO_4 solution without (dotted curve) and with (solid curve) 0.5 g L^{-1} IMD. $\text{pH} = 7$, $\nu = 100$
18 mV s^{-1} and $T = 25^\circ\text{C}$.

19

20 Moreover, successive cycles (Fig. 2) keep the same shape indicating that the reaction
21 intermediates are not electroactive in the available potential range. Only a decrease in the
22 peak current is observed. This can be attributed to the adsorption of molecules on a portion of
23 the electrode surface which becomes inactive. This phenomenon is often present on
24 voltammograms of redox active organic compounds.

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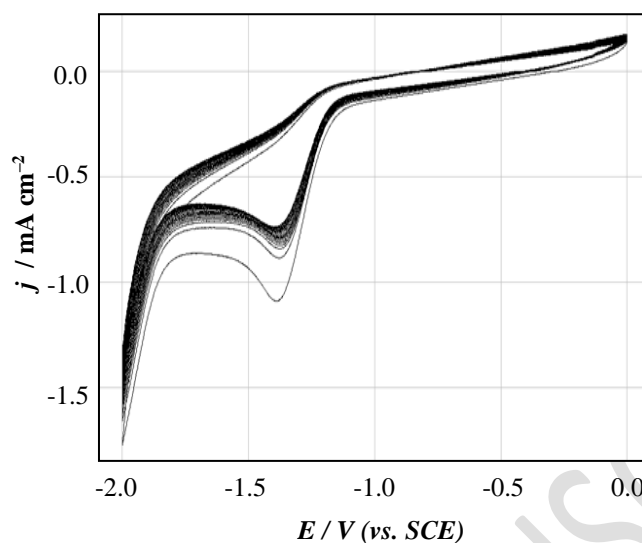


Figure 2: Repetitive cyclic voltammograms of the PGC electrode immersed in a solution containing $2.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.5 \text{ g L}^{-1} \text{ IMD}$. $\text{pH} = 7$, $v = 100 \text{ mV s}^{-1}$ and $T = 25^\circ\text{C}$.

3.1.1. Effect of potential scan rate

The cyclic voltammogram of IMD solution was recorded at different scan rates Fig. 3. As the scan rate increased from 10 to 500 mV s^{-1} , the peak current increased. A linear relationship was obtained between the logarithm of the peak current and the logarithm of the scan rate (eq. (1)) with a slope of 0.48 (inset of Fig. 3). This value indicates that the IMD reaction is purely diffusion-controlled [28].

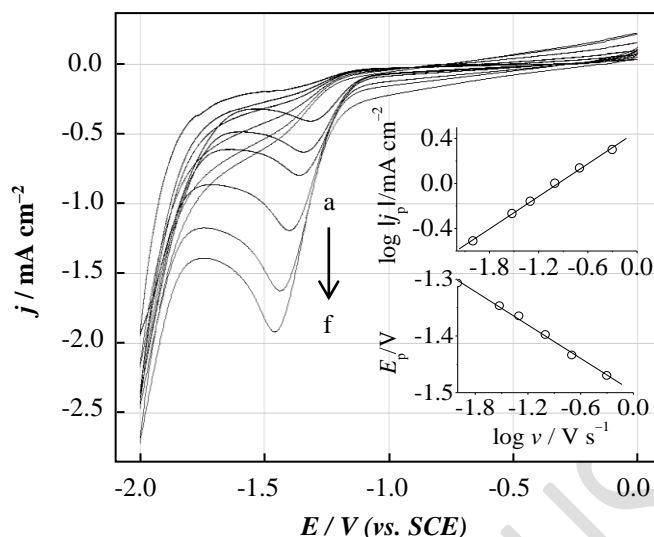
$$\log |j_p| (\text{mA cm}^{-2}) = 0.48 \log v (\text{V s}^{-1}) + 0.46 \quad (r = 0.998) \quad (1)$$

For an irreversible reduction process, the theoretical relationship between the peak current (j_p) and the voltage scan rate (v) is given by the following equation [29]:

$$j_p = -2.99 \cdot 10^5 n (\alpha n_a)^{1/2} c (D)^{1/2} (v)^{1/2} \quad (2)$$

where, j_p is the cathodic peak current (A cm^{-2}), n is the number of electron equivalents exchanged during the reduction reaction, α is the charge-transfer coefficient, n_a the number of electrons involved in the rate-determining step of the electrode process, D the diffusion

1 coefficient ($\text{cm}^2 \text{s}^{-1}$), c is the bulk concentration of the diffusing species (mol cm^{-3}) and v is
 2 the potential scan rate (V s^{-1}).



12 **Figure 3:** Voltammograms of the first redox cycle of the PGC electrode immersed in a solution
 13 containing $2.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.5 \text{ g L}^{-1} \text{ IMD}$ recorded at different scan rates. (a) 10; (b); 30
 14 (c) 50; (d) 100; (e) 200 and (f) 500 mV s^{-1} . The inset panels show the plot of $\log |j_p|$ and E_p as
 15 a function of $\log v$. $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

16
 17 In addition, the peak potential E_p is shifted to more negative values with increasing the scan
 18 rates, confirming the irreversible nature of the reduction process (Fig. 3).

19 For an irreversible electrode process, E_p can be defined by the following equation at 25°C
 20 [30].

$$21 \quad E_p = E^\circ - 2.3 \frac{RT}{\alpha n_a F} \left[\log \left(\frac{D^{1/2}}{k^\circ} \right) + \log \left(\frac{\alpha n_a F v}{RT} \right)^{1/2} + 0.34 \right] \quad (3)$$

22 where, E_p is the peak potential (V), E° is the standard potential (V), R is the gas constant
 23 ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (K), F is the Faraday constant ($96,485 \text{ C mol}^{-1}$) and
 24 k° is the standard rate constant of the electrochemical reaction.

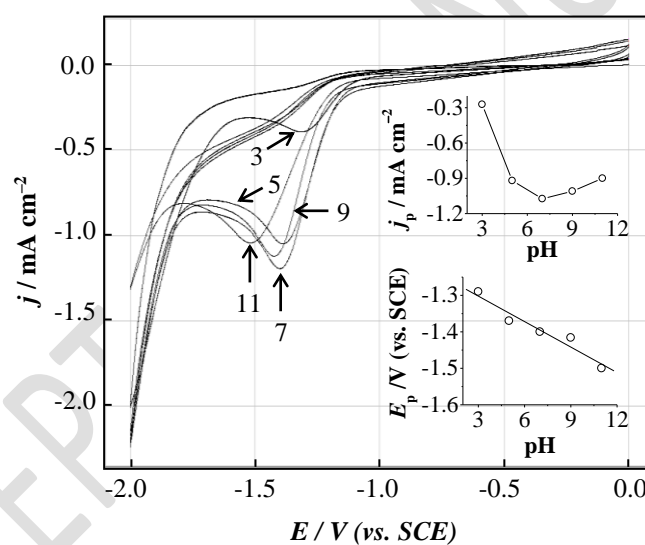
1 The inset of Fig. 3 displays a linear relationship between E_p and logarithm of scan rate (eq.
2 (4)).

$$3 \quad E_p(\text{V}) = -0.08 \log v (\text{V s}^{-1}) - 1.49 \quad (r = 0.997) \quad (4)$$

4 Moreover, It is known that a rate-determining electron transfer is always a one-electron
5 process ($n_a = 1$) and α generally varies between 0.3 and 0.7 [31,32]. From the slope of eq. (4),
6 the charge transfer coefficient $\alpha = 0.37$ suggests that the reduction process is irreversible.

7 3.1.2. Effect of pH

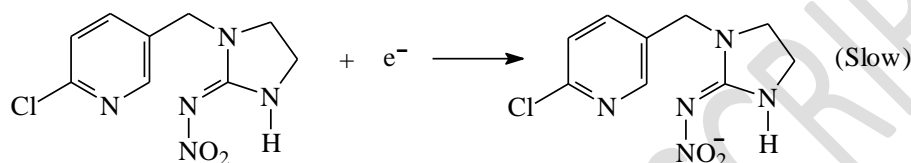
8 The effect of the solution pH on the electrochemical reduction of 0.5 g L^{-1} IMD was studied
9 in the pH range of 3–11 at the PGC electrode. The results reveal that all voltammograms
10 demonstrate a single cathodic peak regardless of pH (Fig. 4).



19
20 **Figure 4:** Voltammograms of the first redox cycle of the PGC electrode immersed in a solution
21 containing $2.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.5 \text{ g L}^{-1}$ IMD recorded at different pH (indicated). $v = 100$
22 mV s^{-1} and $T = 25^\circ\text{C}$.

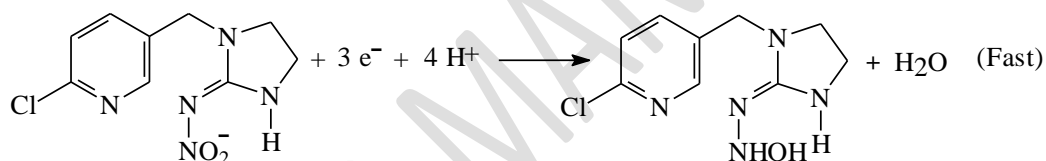
23
24 However, the absolute value of the current of this peak increased significantly with increasing
25 the pH value from 3 to 7. It reached a maximum level at pH 7 and then decreased gradually
26 above pH 7. This result is in good agreement with other studies on the determination of the

1 nitro group containing neonicotinoid insecticides [19,24,26]. Thus, considering the sensitivity
 2 of the determination of IMD, pH 7 was selected for the succeeding analytical experiments.
 3 In accordance with the literature [33–35], the electrochemical reduction of nitro-substituted
 4 compounds, in acid, neutral or basic medium, involves four electrons to give the
 5 corresponding hydroxylamine on two steps. The first reaction is slow (rate-determining step)
 6 and undergoes one-electron transfer ($n_a = 1$).

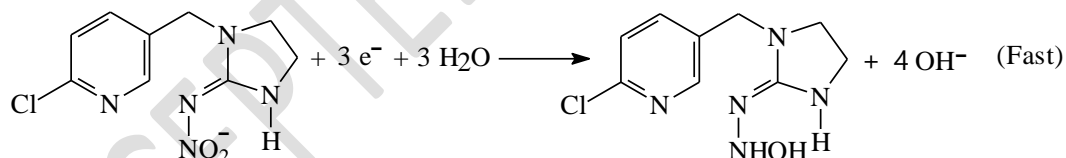


7
 8 The second step is fast and involves three electrons and pH-dependent.

9 In acidic medium:



10
 11 In neutral or basic medium:



12
 13 Moreover, increasing pH results in a negative shift of the peak potential (E_p) (inset of Fig. 4).

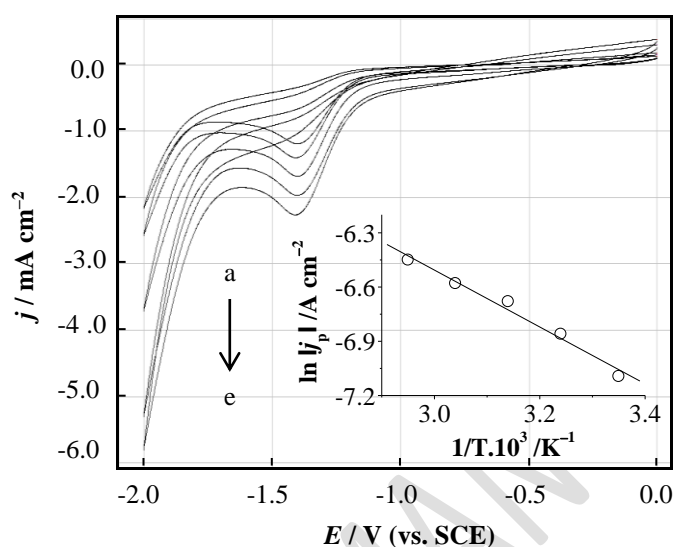
14 A linear relationship between E_p and pH was obtained. This linear relation can be expressed
 15 by (Eq. (5)).

$$16 \quad E_p(\text{V}) = -0.057 \text{ pH} - 1.241 \quad (r = 0.968) \quad (5)$$

17 The E_p values are shifted by increasing the pH by about 57 mV per pH unit in the pH range 3–
 18 11, indicate that the ratio of the exchanged electrons and protons is most probably one.

19 3.1.3. Effect of temperature

1 The effect of temperature on the electrochemical behavior of IMD was studied in 2.0 g L⁻¹
 2 Na₂SO₄ containing 0.5 g L⁻¹ IMD between -2.0 and 0.0 V at a scan rate of 100 mV s⁻¹ and at
 3 temperatures between 25 and 60°C. Cyclic voltammograms (Fig. 5) show that the cathodic
 4 peak current increased with the increase of temperature.



14 **Figure 5:** Voltammograms of the first redox cycle of the PGC electrode immersed in a
 15 solution containing 2.0 g L⁻¹ Na₂SO₄ + 0.5 g L⁻¹ IMD at different temperatures. The inset
 16 panel shows the Arrhenius-type plot of the peak current density. (a) 25, (b), 35 (c) 45, (d) 55
 17 and (e) 65°C. pH = 7 and $\nu = 100$ mV s⁻¹.

18 The natural logarithm of the peak current increased linearly with the inverse of the
 19 temperature (Eq. (6)) as shown in the inset of Fig. 5.

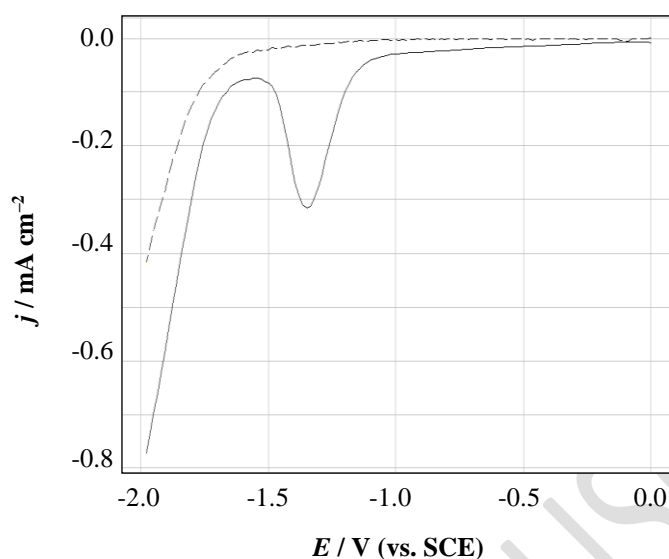
$$20 \quad \ln |j_p| = -1.57 \frac{1}{T} - 1.78 \quad (r = 0.994) \quad (6)$$

21 According to the Arrhenius equation, the activation energy E_a was found to be 13 kJ mol⁻¹.
 22 This value is less than 40 kJ mol⁻¹, and thus confirms the fact that the electro-reduction of
 23 IMD on the electrode is diffusion-controlled [36].

24 3.2. Square wave voltammetric investigation

25 SWV technique was employed to understand the electrochemical process of IMD occurring at
 26 PGC electrode. Fig. 6 exhibits the square wave voltammograms recorded in the absence and

1 presence of 0.5 g L^{-1} IMD in a solution of 2.0 g L^{-1} Na_2SO_4 . It is clear that, during the
 2 cathodic scan, a single reduction peak was observed at a potential of -1.35 V (vs. SCE).



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 13 **Figure 6:** Square wave voltammograms of the PGC electrode immersed in a 2 g L^{-1} Na_2SO_4
 14 solution without (dotted curve) and with 0.5 g L^{-1} IMD (solid curve). $f = 100 \text{ s}^{-1}$, $\Delta E_a = 50$
 15 mV , $\Delta E_i = 10 \text{ mV}$, $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

16
 17 The optimization of the analytical method involved a systematic study of the experimental
 18 parameters that affect the SWV response, namely frequency (f), pulse amplitude (ΔE_a) and
 19 scan increment (ΔE_i).

20 *3.2.1. Effect of square wave frequency*

21 This parameter is important in SWV because it determines the intensity of the signal and, in
 22 turn, the sensitivity of the analytical methodology. Fig. 7 illustrates the SW voltammograms
 23 obtained for different frequency values in the range of 20 to 100 s^{-1} .

24 The cathodic peak current increases by increasing the frequency value. The inset of Fig. 7
 25 shows a linear relationship between the logarithm of the peak current and the logarithm of the
 26 frequency with a slope of 0.51 (Eq. (7)). This value indicates that the IMD reaction is purely
 27 diffusion-controlled [39].

$$\log |j_p| = 0.51 \log f - 1.56 \quad (r = 0.998) \quad (7)$$

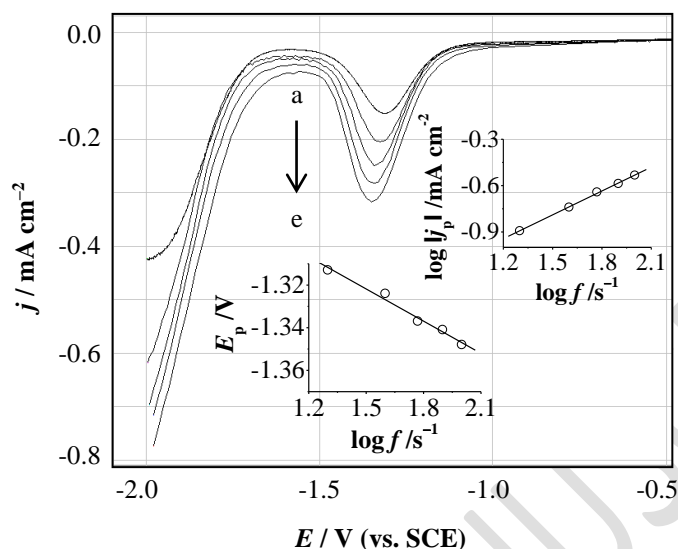


Figure 7: Square wave voltammograms of the PGC electrode immersed in a solution containing $2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.5 \text{ g L}^{-1} \text{ IMD}$ recorded at different frequency. f : (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 s^{-1} . $\Delta E_a = 50 \text{ mV}$; $\Delta E_i = 10 \text{ mV}$; $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

Moreover, a linear relationship was obtained between the peak potential and the logarithm of the frequency (Eq. 8).

$$E_p = -0.05 \log f - 1.25 \quad (r = 0.991) \quad (8)$$

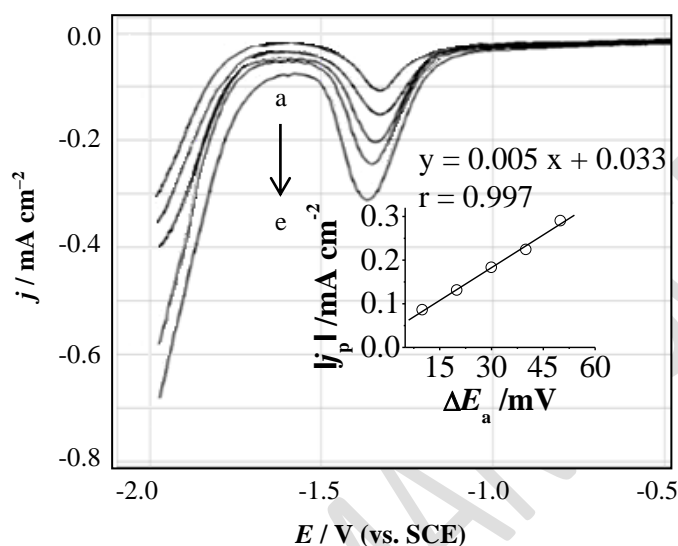
The slope of this straight line has been used to calculate αn value for the electrochemical reaction by means of Eq. (9) which is equal to 0.05.

$$\frac{\Delta E_p}{\Delta \log f} = -\frac{2.3 RT}{\alpha n F} \quad (9)$$

It is clear from the literature that the number of electrons exchanged by the molecule of IMD has been assumed to be $n = 4$ to give hydroxylamine. Therefore, the charge transfer coefficient $\alpha = 0.29$ suggests that the reduction process is irreversible.

3.2.2. Effect of pulse amplitude

1 Another important parameter involved in SWV is the pulse amplitude (ΔE_a). The effect of
 2 pulse amplitude on the reduction peak current of 0.5 g L^{-1} IMD in 2.0 g L^{-1} Na_2SO_4 of $\text{pH} = 7$
 3 was studied by different values of pulse amplitudes from 10 mV to 50 mV at a frequency of
 4 100 s^{-1} (Fig. 8).



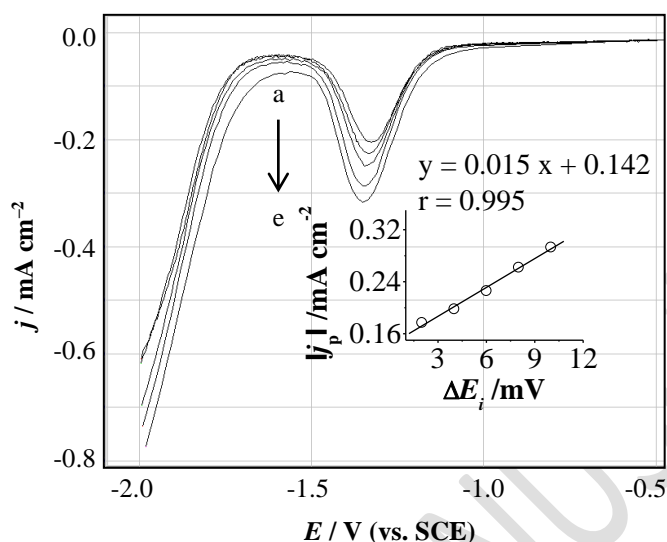
17 **Figure 8:** Square wave voltammograms of the PGC electrode immersed in a solution
 18 containing 2 g L^{-1} Na_2SO_4 + 0.5 g L^{-1} IMD recorded at different pulse amplitude. ΔE_a : (a)
 19 10, (b) 20, (c) 30, (d) 40 and (e) 50 mV. $f = 100 \text{ s}^{-1}$, $\Delta E_i = 10 \text{ mV}$, $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

21 The results indicated that the peak current increased when the pulse amplitude increased from
 22 10 to 50 mV. Therefore, at pulse amplitude of 50 mV, the peak current was found to be much
 23 sharper and defined.

26 3.2.3. Effect of scan increment

27 This parameter, which allows determining the amount of potential changes between two data
 28 points in the experiment, was investigated. The effect of the scan increment (ΔE_i) on the
 29 electrochemical reduction of IMD by SWV was studied in the range of 2 to 10 mV on the

1 PGC electrode in the presence of 0.5 g L^{-1} IMD. Fig. 9 reveals that the peak current enhanced
 2 upon the increase of scan increment (2–10 mV). Therefore, a scan increment of 10 mV was
 3 preferable in the present study.



14 **Figure 9:** Square wave voltammograms of the PGC electrode immersed in a solution
 15 containing $2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + 0.5 \text{ g L}^{-1}$ IMD recorded at different scan increment. ΔE_i : (a) 2,
 16 (b) 4, (c) 6, (d) 8 and (e) 10 mV. $f = 100 \text{ s}^{-1}$, $\Delta E_a = 50 \text{ mV}$, $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

17 3.3. Calibration curve

18 After selecting the most suitable conditions, the determination of IMD concentration using
 19 PGC electrode was performed with CV and SWV techniques. Figs. 10 and 11 display the
 20 cyclic and the square wave voltammograms obtained for different concentrations of IMD in
 21 $2.0 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ at $\text{pH} 7$.

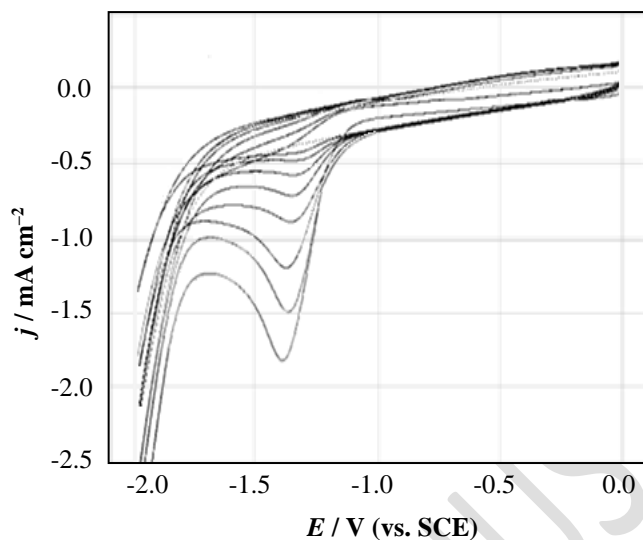
22 A well-defined single irreversible cathodic peak, proportional to the concentration of the
 23 IMD, was observed. A linear relationship between the reduction current and the IMD
 24 concentration was obtained for both methods. LOD and LOQ of IMD were calculated from
 25 the calibration curve using the following equations:

26 The LOD and LOQ were calculated using the following equations [37].

$$27 \text{ LOD} = \frac{3s}{m} \quad (10)$$

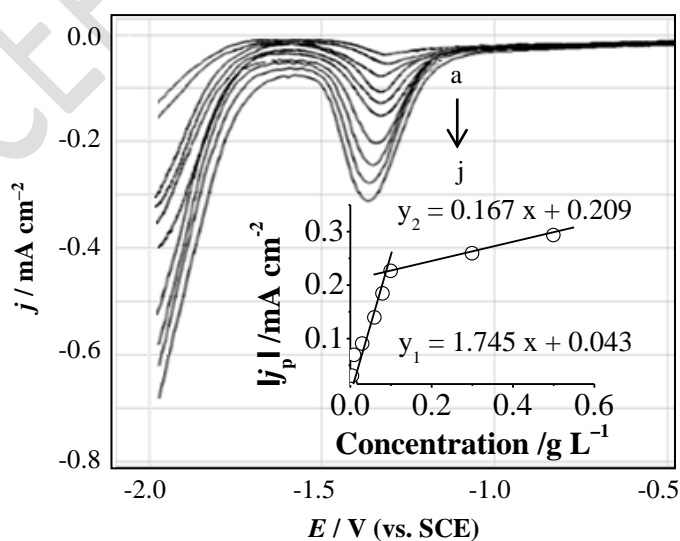
$$1 \quad \text{LOQ} = \frac{10s}{m} \quad (11)$$

2 where s is the standard deviation of the intercept and m is the slope of the calibration curve.



13
14 **Figure 10:** Voltammograms of the first redox cycle of the PGC electrode immersed in a
15 solution containing $2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + \text{IMD}$ at different concentrations. IMD: (a) 5, (b) 20, (c)
16 50, (d) 90, (e) 150, (f) 250, (g) 350, (h) 500 mg L^{-1} , $\nu = 500 \text{ mV s}^{-1}$, $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

17 The LOD and the LOQ were, respectively, 8.7 and 29.1 mg L^{-1} for CV. By SWV, a linear
18 relationship between the SWV current and IMD concentration was obtained covering two
19 linear ranges from $1.25\text{--}100 \text{ mg L}^{-1}$ and $100\text{--}500 \text{ mg L}^{-1}$.



1 **Figure 11:** Square wave voltammograms of the PGC electrode immersed in a solution
 2 containing $2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4 + \text{IMD}$ at different concentrations. IMD: (a) 1.25×10^{-3} , (b) 2.5×10^{-3} ,
 3 (c) 5×10^{-3} , (d) 10^{-2} , (e) 3×10^{-2} , (f) 6×10^{-2} , (g) 8×10^{-2} , (h) 0.1, (i) 0.3, (j) 0.5 g L^{-1} . $f = 100 \text{ s}^{-1}$,
 4 $\Delta E_a = 50 \text{ mV}$, $\Delta E_i = 10 \text{ mV}$, $\text{pH} = 7$ and $T = 25^\circ\text{C}$.

5 The lower linear range was used for calculating the LOD and the LOQ, which were equal to
 6 2.8 and 9.3 mg L^{-1} , respectively. This result indicates that the SWV technique has relatively
 7 better sensitivity for detecting the IMD than the CV technique (Table 1).

8 **Table 1:** Determination of IMD by CV and SWV techniques.

Parameter	Techniques	
	CV (PGC)	SWV (PGC)
Linearity range (mg L^{-1})	5–500	1.25–100
Intercept (mA cm^{-2})	0.093	0.043
SD of intercept (mA cm^{-2})	0.00832	0.00162
Slope ($\text{mA cm}^{-2} \text{ L mg}^{-1}$) $\times 10^3$	2.868	1.745
Regression coefficient	0.999	0.998
Number of data points	8	10
LOD (mg L^{-1})	8.7	2.8
LOQ (mg L^{-1})	29.1	9.3

9 On the other hand, table 2 compares the performance of the proposed approaches with several
 10 voltammetric electrochemical methods reported in the literature for IMD determination.

11 **Table 2.** Comparison of the efficiency of some voltammetric methods in the determination of
 12 IMD.

Electrode	Methods	Range (mg L^{-1})	LOD (mg L^{-1})	LOQ (mg L^{-1})	References
BDD	SWV	7.6–51	2.2	7.3	[38]
CPE	DPV	1.7–30	0.52	1.73	[24]
PGC	SWV	1.25–100	2.8	9.3	Present work
PGC	CV	5–500	8.7	29.1	Present work
GCE	CV	2.7–500	7.6	25.9	[19]
BiFE	DPV	2.5–51	2.9	–	[39]
nAg _n /nTiO ₂ n _f /GCE	CV	0.25–1.7	0.01	0.05	[20]
	DPV	0.12–0.85	0.006	0.021	

1 Abbreviations: GCE, Glassy carbon electrode; CPE, Carbon-paste electrode;
2 nAg_{nf}/nTiO₂_{nf}/GCE, nanosilver Nafion®/nanoTiO₂ Nafion® modified glassy carbon
3 electrode; BiFE, Bismuth-film electrode; BDD, Boron-Doped Diamond.

4 As can be seen from this table, the proposed approaches are the most sensitive method that
5 used a bare electrode; however, it is less sensitive only than the methodologies that used
6 complex and modified electrodes.

7 The repeatability and reproducibility of results are excellent. In fact, to evaluate these
8 properties, two IMD solutions (5 and 20 mg L⁻¹) were tested four times by CV and SWV
9 techniques. With respect to the CV technique, the repeatability of the current measurement
10 was 1.12% RSD for 5 mg L⁻¹ and 1.21% RSD for 20 mg L⁻¹. However, by using the SWV
11 technique the repeatability was 1.3% RSD for 5 mg L⁻¹ and 1.5% RSD for 20 mg L⁻¹.

12 The reproducibility of the current measurement was also calculated 0.97% RSD for 5 mg L⁻¹
13 and 0.88% RSD for 20 mg L⁻¹ by CV technique. When using the SWV, the RSD were 0.93%
14 for 5 mg L⁻¹ and 1.1% for 20 mg L⁻¹. The low values of relative standard deviation (RSD)
15 indicate good precision and reproducibility of the proposed CV and SWV methods for the
16 assay of IMD.

17 The recovery efficiencies (R %) for the different systems under investigation were calculated
18 using equation (11):

$$19 \quad R(\%) = \frac{[IMD]_{\text{found}}}{[IMD]_{\text{added}}} \times 100 \quad (12)$$

20 The analysis of the peak current showed that the obtained values of recovery ranged from
21 95.4% to 100.1% by CV technique and 100.22% to 100.4% by SWV. These average percent
22 recoveries obtained indicate the good accuracy of these methods.

23 **3.4. Determination of IMD in plum and peach fruits**

24 The applicability of the CV and SWV methods was tested by determining the IMD in real
25 samples namely plum and peach juices. The IMD content in the fruit juice samples were

1 determined by measuring the peak current from the calibration curves in Fig. 10 and Fig.11.
 2 The amounts of this pesticide were added to yield concentrations in the range between 5 mg L⁻¹
 3 and 20 mg L⁻¹. As can be seen from Table 3, the obtained recovery was in the range
 4 97.9–102.4% by CV and 101.8%–118% by SWV which indicates that the developed methods
 5 can be applied for quantitative determination of IMD in fruit juices.

6 **Table 3:** Analytical parameters obtained at a PGC for the determination of IMD in plum and
 7 peaches juices using CV and SWV techniques.

Methods	Juice	Added amount (mg L ⁻¹)	Found amount (mg L ⁻¹)	Recovery (%)	RSD (%)
CV	Plum	20	20.48	102.4	0.98
		10	9.86	98.6	0.87
		5	4.97	99.5	1.03
	Peaches	20	19.72	98.6	1.05
		10	9.79	97.9	0.99
		5	5.05	101	1.10
SWV	Plum	20	21.28	106.4	1.04
		10	11.3	113	0.96
		5	5.35	107	1.21
	Peaches	20	20.36	101.8	0.96
		10	10.3	103	1.24
		5	5.90	118	1.33

8
 9 The RSD ranged from 0.87%–1.1% and 0.96%–1.33%, respectively, by CV and SWV. The
 10 low values of RSD indicate good precision and reproducibility of the CV and SWV methods
 11 and the average percent recoveries obtained were quantitative, indicating good accuracy of the
 12 methods.

14 4. Conclusion

15 CV and SWV methods have been proved to be very sensitive for the determination of organic
 16 molecules including IMD. This work is the basis for the development of voltammetric
 17 methods for the determination of IMD in commercial formulations. All experimental and
 18 instrumental parameters were optimized as their values strongly affect the sensitivity of the

1 voltammetric methods. The LOD and LOQ values obtained by these methods were
2 determined and the result has found that the SWV is more sensitive than the CV. It was also
3 demonstrated that these methods were satisfactorily applied to the determination of IMD in
4 real samples such as plum and peach juice.

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