



Voltammetric determination of fenitrothion based on pencil graphite electrode modified with poly(Purpald®)

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Abstract

For the first time in this work, 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald®) polymer film on the surfaces of disposable pencil graphite electrodes (PGEs) were successfully electrosynthesized. The optimized conditions of electropolymerization of Purpald® film were also investigated. Electrochemical deposition was carried out by cyclic voltammetry (CV) in a potential range of 0.0–1.0 V at a scan rate of 25 mV s⁻¹ in 10 cycles. Polymer growth conditions were systematically investigated for determining optimal settings in developing the sensor. The recommended Purpald®-modified pencil graphite electrodes were used for the determination of fenitrothion. Under appropriate working conditions, the differential pulse voltammetric (DPV) current response of fenitrothion (FNT) oxidation was linear in the range of 25–200 μM (R^2 : 0.993) with a detection limit of 17.39 μM (S/N : 5). The recommended Purpald®-modified pencil graphite electrode was successfully applied to the detection of fenitrothion in apple juice and tap water.

Keywords Purpald® · Electropolymerization · Fenitrothion · Sensor · Pencil graphite electrode

Introduction

Pesticides are chemicals that are used against the target living organisms in agricultural struggle, and which are effective in destroying, blocking, removing from the environment and reducing (Yan et al. 2018). Today, pesticides have supported the increase in product quality and yield in agriculture by controlling agricultural pests and diseases caused by them. The use of pesticides is a necessity in getting food products that will meet the world population. Therefore, they are also vital for use not only for farmers but also for consumers. In addition, pesticides are used not only in the production but also in the post-harvest storage period, to prevent yield penalty (Pundir and Chauhan 2012; Songa and Okonkwo 2016; Eddleston et al. 2008).

On the one hand, the use of agricultural chemicals increases agricultural production; while on the other hand, the unconscious and wrong use of the end user can directly or indirectly threaten human and environmental health (Kumar et al. 2015; Long and Krupke 2016). In addition,

pesticides used in controlled quantities have the adverse effect on living organisms by causing accumulation in the tissues of plants in the food chain (Zhang et al. 2017; Xia et al. 2018).

Organophosphate compounds are the most widely used pesticide group in the world. Organophosphate insecticides with high insecticidal and acaricidal effects are mainly phosphoric, thiophosphoric and dithiophosphoric acid esters. Organophosphate insecticides are absorbed by the respiratory and digestive systems as well as by the skin. The main toxic mechanisms of action are due to the inactivity of the two very important enzymes, cholinesterase, and acetylcholinesterase. Thus, the breakdown of acetylcholinesterase in synapses is halted and acetylcholine, which is continuously synthesized in the organism, accumulates. As a result, endogenous acetylcholine poisoning occurs (Xia et al. 2018; Uniyal and Sharma 2018; Sgobbi and Machado 2018).

Fenitrothion, which we use in our work, is an organophosphate-derived insecticide that is no longer approved for use in the EU but in the current MRL values of European Union pesticide database indicates at a rate of 0.01–7.0 mg kg⁻¹ in some vegetables and fruits as the lower limit of analytical determination to fenitrothion. Fenitrothion has a low potential for leaching to groundwater and is not expected to be persistent in soil or water systems. It is highly toxic to birds,

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aquatic invertebrates and honeybees, but moderately toxic to fish, algae, earthworms, and mammals. Studies in the literature on this subject are mostly chromatographic and electrochemical studies, and these insecticides and fungicides have been shown to have adverse effects on humans and many experimental animals (Shamili et al. 2017, 2018; Park et al. 2018; Mahugija et al. 2018; Sun et al. 2018; Zhu et al. 2017; Takayasu et al. 2017; Kumar et al. 2018; Ensafi et al. 2017a, b; Surucu et al. 2016; Akyuz et al. 2017; Salehzadeh et al. 2016; Khan et al. 2017).

Due to the limited use of voltammetric electrodes, the working conditions have been improved by changing the chemical or electrochemical properties of the electrodes. The modifying by chemical may be prepared by chemical bonding to the electrode surface or by chemical adsorption. Polymer films based on modified electrodes have received extensive interest due to their broad scope of application in the chemical and biological sensor (Mantione et al. 2017; Gu et al. 2017). Such electrodes can also be prepared by electropolymerization at the surface of the electrode or by forming a polymer film directly on the electrode surface. Electropolymerization is a facile and rather of the effective approach for preparing polymer film-based electrodes. Electropolymerization process conditions (concentration, scan rate, the range of potential, etc.) can be easily changed and thus conductive films having different properties and functions are obtained (Dunst et al. 2017; Kim and Palmore, 2012; Chen et al. 2013; Correa et al. 2016). In this way, the electrochemical parameters can control thickness of film, interpenetration and charge transport characteristic. Due to their various electrochemical properties, conductive polymers have a wide range of applications when they showed electrical conductivity close to metals and can be easily processed. Especially, they are used in the construction of sensors, chargeable batteries, photochemical cells, electrochromic devices and ion selective electrode (Mangione et al. 2018; Castaneda et al. 2017; Boursicot et al. 2017; Wolfart et al. 2017; Devasurendra et al. 2017).

In the literature, there are many studies for electropolymerization of five- or six-membered heterocyclic compounds, such as pyrrole, *o*-phenylenediamine and thiophene (Si and Song, 2018; Azak et al. 2018; Shamsipur et al. 2018; Rao et al. 2018). At the same time, a restricted number of studies involving electropolymerization processes with thiazole and triazole-based monomers are existing.

Purpald[®] is a chemical material acting as a pigment and/or a color-exchanger agent used in the detection of aldehyde and aldehyde derivatives. Due to the S, C and N atoms present in the Purpald[®] structure, it shows an ideal ligand effect for metal complexes (Chu et al. 2018; do Carmo et al. 2015; Wondracek et al. 2016; Hill et al. 2009).

In this study, for the first time in the literature, the voltammetric detection of fenitrothion insecticide was performed

using disposable pencil graphite electrodes modified by Purpald[®]. Characterization of these polymer films was carried out using cyclic voltammetry. Working conditions are optimized for best voltammetric performance. The developed disposable Purpald[®]-modified pencil graphite electrodes were tested in apple juices as a real sample.

Materials and methods

Reagents and instruments

Purpald[®] ($\geq 99\%$), sodium hydroxide ($\geq 98\%$), glacial acetic acid (100%), boric acid ($\geq 99.5\%$), phosphoric acid ($\geq 85\%$), dimethyl sulfoxide ($\geq 99.9\%$) and fenitrothion (HPLC and GC grade) were purchased from Sigma–Aldrich. Britton–Robinson buffer solutions (BR) were prepared with H_3BO_3 , CH_3COOH and H_3PO_4 , and NaOH was added until the desired pH was reached. All used chemicals are of analytical purity and have not been subjected to any purification process. The chemical solutions used in the experiments were prepared with ultrapure water. All pH buffer solutions were stored at 4 °C. The analyte and monomer solutions were newly prepared each day. Tombow (HB, 0.5 mm) pencil graphite was purchased from stationery shop.

An IVIUM Compact Stat Plus Model electrochemical analyzer (The Netherlands) was used for cyclic voltammetry (CV), differential pulse voltammetry (DPV). The three-electrode system consisted of a pencil graphite electrode (PGE) as working (geometric area is 15 mm²), an Ag/AgCl (3.0 M KCl) electrode (BAS, Model RE-5B, W. Lafayette, USA) as reference, and a platinum wire (geometric area is 15 mm²) as auxiliary. Thermo Scientific Orion 4-Star plus pH/Conductivity Meter with combined glass electrode was used to determine the pH of buffer solutions. Ultrapure water was obtained from a LABCONCO WaterPro Water Purification Systems (Kansas City, USA).

Preparation of Purpald[®]-PGE

Electropolymerization of Purpald[®] onto the pencil graphite electrode was executed using cyclic voltammetry technique. For the fabrication of electrode, PGE was coated with the electrochemically synthesized polymer of Purpald[®]. Any pre-treatment procedure was not performed prior to modification to the PG electrode. Electrosynthesis solution consisted of 1×10^{-4} M Purpald[®] in 0.1 M H_2SO_4 and the potential of the PGE working electrode was cycled ten times between 0.0 and 1.0 V at scan rate of 25 mV s⁻¹. Then, PGE was removed from the synthesis solution and washed several times with ultrapure water to remove any residual compound left with the polymer matrix.

Results and discussion

Electrochemical behavior of Purplad®

The formation of poly(Purplad®) film on the electrode surface is demonstrated in Fig. 1a. The cyclic voltammogram was obtained during the electropolymerization of Purplad® performed using Britton–Robinson (BR) buffer pH 8. The figure indicates one irreversible oxidation peak, which is responsible from the electrochemical polymerization, at 0.280 V vs. Ag/AgCl (3.0 M KCl). As shown in Fig. 1a, Purplad® can easily be polymerized via potentiodynamic polymerization between (0.0) and (+0.6) V. After the first cycle, the oxidation peak current tended to decrease. This can be interpreted as:

The electroactivity of monomeric species is higher than that of the polymeric ones. The concentration of monomeric species decreases during the CV cycles. Furthermore, the redox reactions at the electrode surface where a new polymeric species is formed in each CV cycle are more difficult than the redox reactions on the bare electrode surface, and, therefore, a reduction in the peak current occurs in each CV cycle.

After completion of the electropolymerization process, the modified electrode was washed five times in the 0.1 BR (pH 8) buffer solution and left to dry.

The interfacial charge transfer resistance (R_{ct}) is related to interfacial processes of charge/ion transfer through the electrode/electrolyte interface. If the chemical system is kinetically slow going, it will show a large semicircle (R_{ct}), indicating that mass transfer, which is an important factor, is only effective in a very limited frequency range.

The smaller semicircle (R_{ct}) indicates the rapid transfer capability of the charge/ions.

According to Fig. 1b, the R_{ct} value of Purplad®-PGE is much higher than that of the bare electrode. This result shows that a polymeric structure that causes mass transfer on the electrode surface is formed, i.e., the Purplad® molecule is coated on the electrode surface by the electropolymerization process.

Determination of optimal electrochemical conditions for an effective Purplad® modification

Electrochemically prepared film properties depend on preparation parameters such as potential, temperature, concentrations, electrode materials, supporting electrolyte, current density, and the nature of anions incorporated into the polymer during the electrosynthesis. In electrochemical studies, the pH of the media performs a significant effect of the peak current, potential, and shape of the voltammograms. It is also useful in the assessment of proton–electron ratio related to electrode reaction. To produce fine and stable poly(Purplad®) films, it is necessary to first determine the electrosynthesis potential and the pH values of each solution in each electrolyte.

At first, 1×10^{-4} M Purplad® was inserted in different electrolyte solutions to deposit Purplad® on the PGE surface with cyclic voltammetry. The obtained voltammograms are shown in Fig. 2. As shown in Fig. 2, the voltammetric signals of the Purplad®, at different pH (between 2 and 8) BR buffer solutions and 0.1 M H_2SO_4 were examined by cyclic voltammetry between (0.0) and (+1.0) V.

pH of electrolyte and redox potential are important chemical parameters that could alter the reduction/oxidation potential of target compounds; since protons are involved

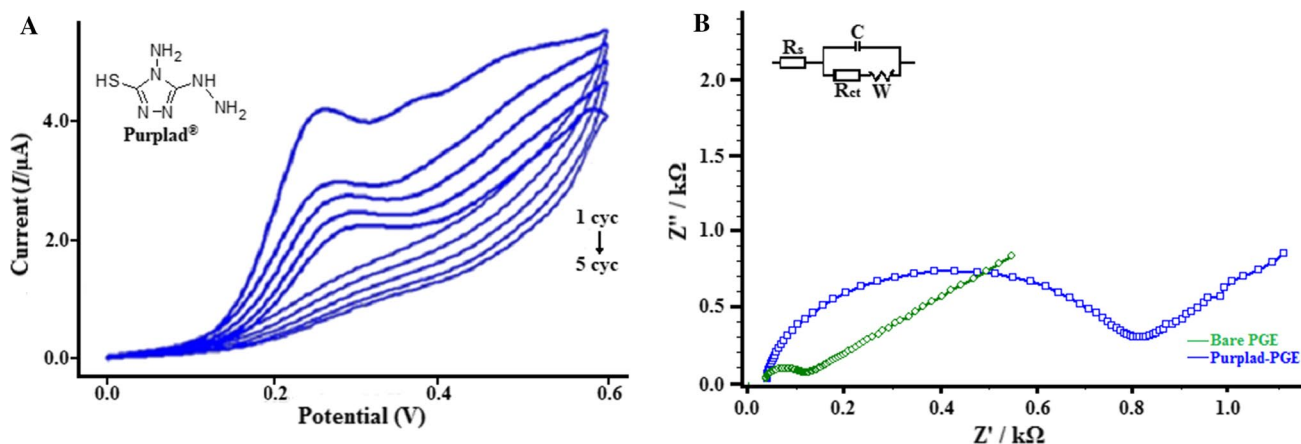


Fig. 1 a Electropolymerization of Purplad® (5 cycles) on the pencil graphite electrode. 0.1 mM Purplad® containing 0.1 M pH 8 BR. The potential sweeps applied between (0.0 V) and (+0.6 V) with

the scan rate of 25 mV s^{-1} . b The Nyquist plots of bare PGE and Purplad®-PGE in the $2.5 \text{ mM } [Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution

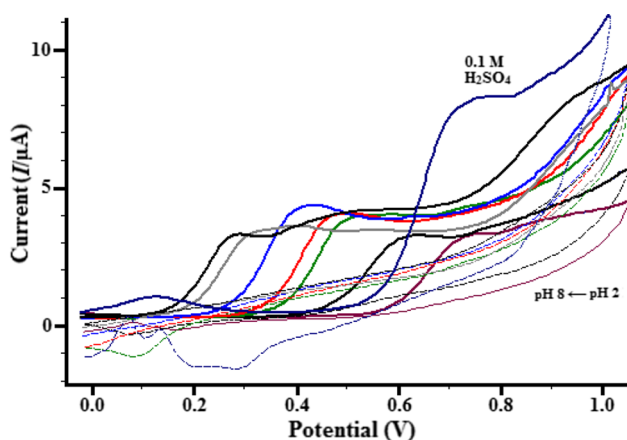


Fig. 2 Cyclic voltammetry of the electropolymerization of 0.1 mM Purpald[®] on the pencil graphite electrode in the presence of different supporting media. Each plot comprises 10 cycles between (0.0 V) and (+1.0 V) vs. Ag/AgCl at the scan rate of 25 mV s⁻¹

in many reactions, and electrolyte redox images the existence of oxidizing/reducing substances. These conditions affect the morphology of the electrode materials and their redox mechanisms. It is of utmost importance to study the changing behaviors of materials to variable factors to optimize experimental conditions and obtain accurate results. The pH value is an important variable in buffer systems, which can be easily manipulated to optimize experimental conditions, as compared to other factors. The electrode surface has to be relatively stable to such changes and not affect the voltammetric signals. In addition, the presence of H⁺ in the electrosynthesis media promotes the growth of Purpald[®] either when using CV. In the same vein, the amount of charge passed in each situation indicates that low pH values promote the formation of more conducting films than those acquired from neutral pH. In this regard, buffer

solutions and H₂SO₄ were used in this paper. When Fig. 2 is scrutinized, the magnitude of the faradaic current composed by the magnification of with 0.1 M H₂SO₄ is higher. As a result, on the surface of the disposable pencil graphite electrode, it will have a higher amount of Purpald[®] deposited.

When cyclic voltammetry is used in electrochemical polymerization for the modification of voltammetric electrodes, it is well known that the thickness of resultant polymer film is somehow related to cycle number. Therefore, it may not be wrong to assume that the number of the cycles not only has a significant effect on the polymer film thickness and morphology but also on its resistivity and charge transfer characteristics. For this reason, the scan rate is one of the important factors affecting the limit of detection of analytes at a given concentration and pH value.

Therefore, 1 × 10⁻⁴ M Purpald[®] was inserted in 0.1 M H₂SO₄ electrolyte solution to deposit Purpald[®] on the PGE surface with different number of cycle. Then, the prepared electrodes were measured by differential pulse voltammetry (DPV) with containing 1 × 10⁻⁴ M fenitrothion (FNT) in pH 2 BR buffer solution. The obtained voltammogram and histogram are shown in Fig. 3.

As seen in Fig. 3, it is seen that the peak current value obtained by FNT analysis with Purpald[®]-coated PG electrode is increased as the number of cycle is increased until the number of cycle 10. After 10 cycles of electropolymerization, the FNT peak currents have approached approximately to the almost steady-state value.

During electropolymerization, the mass transfer mechanism is effective in the formation and growth of the film on the electrode surface of the monomer. To provide this diffusion-controlled condition, it is also necessary to determine the scan rate in the electropolymerization process. To find the optimal value of the scan rate to be used in this electropolymerization process:

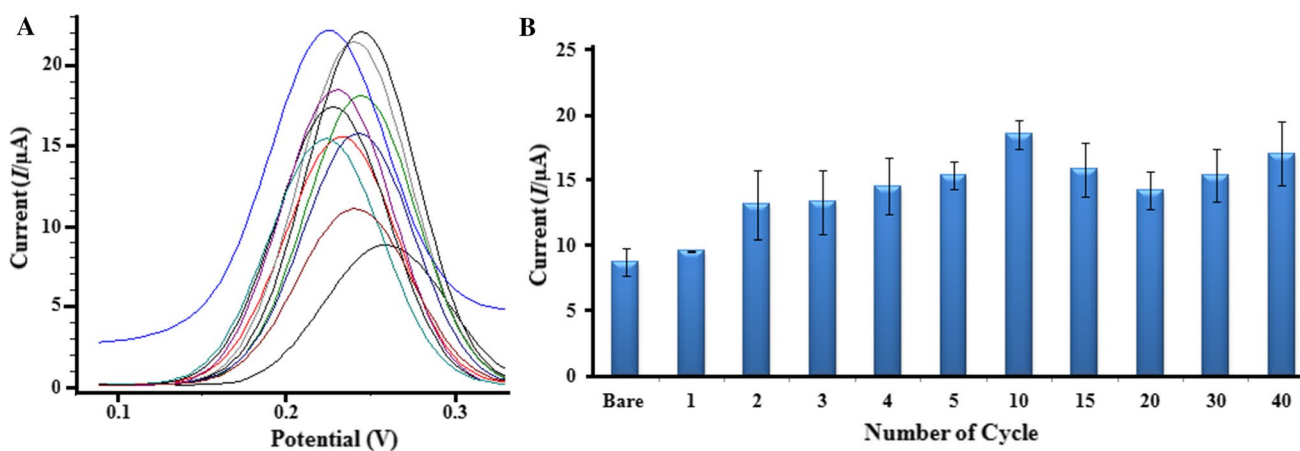


Fig. 3 FNT oxidation peak current values obtained using 1 × 10⁻⁴ M FNT solution of Purpald[®]-PG electrodes coated with various CV cycle numbers. **a** Baseline corrected voltammogram, **b** histogram

Six various scan rates (10, 20, 25, 50, 75 and 100 mV s^{-1}) have been tried by depositing Purpald[®] polymer film on the surface of the PGE using 1×10^{-4} M Purpald[®] solution in 0.1 M H_2SO_4 . The obtained voltammograms and histogram drawn with these DPV data are shown in Fig. 4. As seen in Fig. 4, electrodes formed at six different scan rates show quite close values in the FNT test. Although there are close results, there are minor differences between them. Taking these into consideration, it has been decided to use a scan rate of 25 mV s^{-1} at the next film growth of the polymer film.

Electrochemical behavior of fenitrothion and determination of optimal electrochemical conditions for fenitrothion

The electrochemical response of fenitrothion begins with the formation of an irreversible reduction peak. The mechanism of this peak is explained by the conversion of the nitro group in the fenitrothion molecule to the hydroxylamine in the presence of four hydrogen and four electrons as described in the literature (Bolat et al. 2018; Ensafi et al. 2017a, b; Salehzadeh et al. 2016; Khan et al. 2017; Wang et al. 2016).

The impression of solution pH on the electrochemical behavior of 1×10^{-4} M FNT at the surface of Purpald[®]-modified PGE was examined in the pH range of 1.3–10 utilization on 0.1 M BR with a scan rate of 50 mV s^{-1} . According to the results gained, it is observed that the solution media in the electrochemical cell in which Purpald[®]-modified PGE is used as an increase in the current signal amplitude from FNT up to pH 5.0, almost stabilizing between pH 5.0 and 8.0 and decreasing after pH 8.0. For this reason, it was decided to use pH 8.0 for all subsequent measurements. The oxidation peak current of fenitrothion

was a considerable extent affected by the pH of the media. As the pH of the electrolytic solution raised, the position of oxidation peak obtained from FNT proceeded to negative zone. The pH effect on the oxidation peak current of FNT was examined in the range of pH 1.3–10.0 BR solution. The maximum peak current response was beheld at pH 8.0 BR (as shown in Fig. 5). Hence, pH 8.0 BR was chosen as the optimal electrolyte pH for subsequent measurements.

The following results are achieved when Fig. 5 is interpreted.

1. At the pH values below pH 5, it is observed that the chemical structure of fenitrothion insecticide is demethylation to structure of demethylated fenitrothion as stated in the literature (Lal 1984), thus decreasing the peak current value obtained from FNT.
2. It can be concluded that the pH value should be between 5 and 8 to show the maximum capacity of fenitrothion.
3. The media of pH values above 8, as stated in the literature (Lal 1984), as a result of the hydrolysis of fenitrothion transformed to the structure of 3-methyl-4-nitrophenol due to the peak current values obtained from FNT are seen to be decreasing.

The influence of potential scan rate on the peak current of FNT was tested with DPV in pH 8.0 BR at FNT-PGE in the range 10–200 mV s^{-1} at pulse amplitude of 25 mV with pulse time of 25 ms, and E step of 25 mV. Figure 6 indicates the differential pulse voltammograms of FNT saved at various scan rates. Cathodic peak currents increased linearly between 10 and 50 mV s^{-1} . The resulting FNT values of DPV measurements at scan rates above 50 mV s^{-1} are close to each other. For this reason, in the subsequent steps, a scan rate of 50 mV s^{-1} was used.

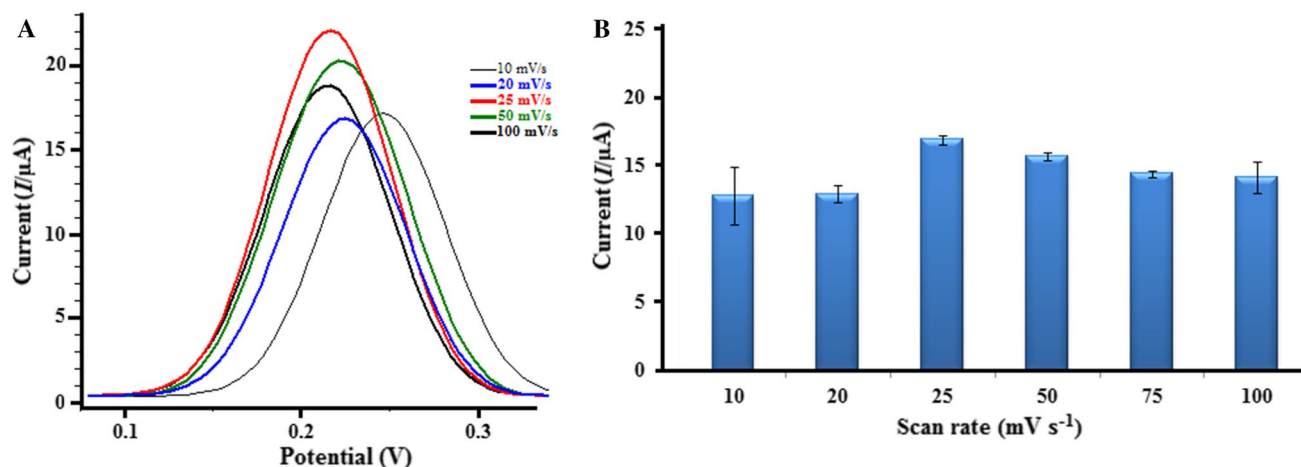


Fig. 4 Differential pulse voltammograms of 1×10^{-4} M FNT at the Purpald[®]-modified PGE at various scan rates from 10 to 100 mV s^{-1} . **a** Baseline corrected DPV, **b** Histogram

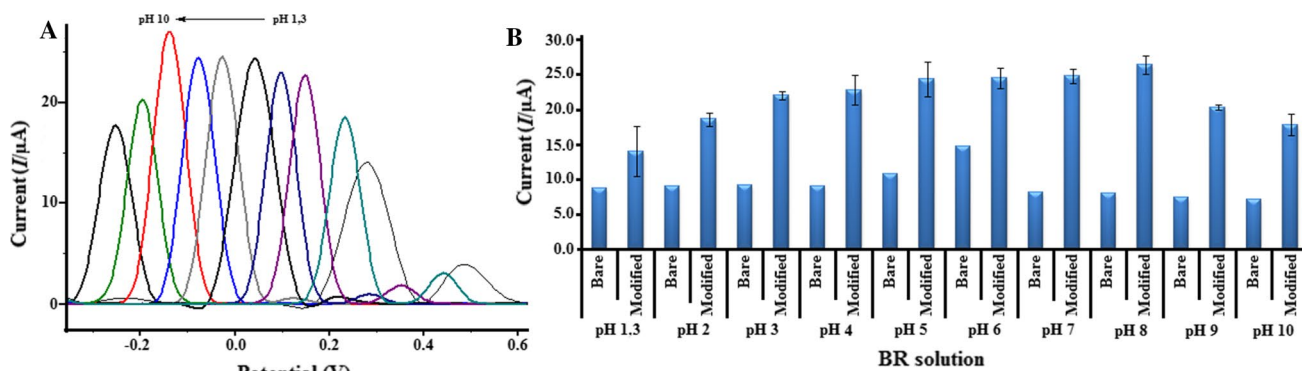


Fig. 5 Differential pulse voltammograms of 1×10^{-4} M FNT at the Purpald[®]-modified PGE at various pH from 1.3 to 10 BR. **a** Baseline corrected DPV, **b** histogram

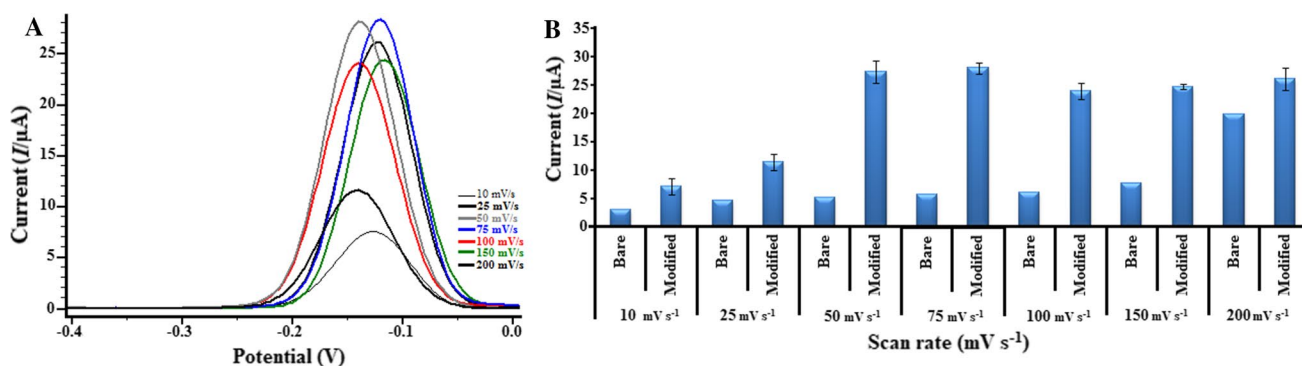


Fig. 6 Relationship between peak current signal magnitudes and determination of FNT scan rate from 10 to 200 mV s^{-1} . **a** Baseline corrected DPV, **b** histogram

The DPV characteristics of FNT on the Purpald[®]-modified PGE availed as an efficacious electrochemical quantitative method to detect FNT. Implementation of Purpald[®]-modified PGE for the determination of FNT has been prospected using differential pulse voltammetry (DPV). DPV used as an analytical tool offers some of the advantages when compared to other electrochemical techniques. DPV is very sensitive, mostly using directly the determination of the innumerable electroactive molecules. As seen in Fig. 7, the typical differential pulse voltammetric responses of FNT in pH 8.0 BR buffer showed a sharp and well-defined peak (-0.14 V (vs. Ag/AgCl) at the potential range from (-0.7) to ($+1.3$) V. Five sets of modified that optimized in terms of film growth were prepared. Each set contained five electrodes. Each one of five sets was intended to study the effect of concentration (25, 50, 75, 100, and $200 \mu\text{M}$) of the FNT. As revealed in Fig. 7, a linear relationship was observed in the concentration range of $25\text{--}200 \mu\text{M}$ with linear equation of $I (\mu\text{A}) = 0.152 \times C (\mu\text{M}) + 9.131$ with a regression coefficient of 0.993 ($n:5$) for the optimized modified electrodes. The LOD and LOQ were obtained as $17.39 \mu\text{M}$ and $52.17 \mu\text{M}$, respectively. Five replicate measurements of peak

current of $25 \mu\text{M}$ FNT showed a relative standard deviation (RSD) of 2.6%. As seen in Fig. 7, bare PGE showed lower sensitivity when compared with that Purpald[®]-modified PGE.

To examine the feasibility of the sensor, interferences study was performed. Imidacloprid (neonicotinoid insecticide), Na^+ , Ca^{2+} , Mg^{2+} , PO_4^{3-} , K^+ , SO_4^{2-} , NH_4^+ , NO_3^- , CO_3^{2-} and Cl^- (common inorganic acid) were selected for the interference studies of sensor. Even in the presence of these interferences, there was no influence the peak current values obtained from fenitrothion. The reproducibility of Purpald[®]-modified PG electrode was achieved by five times repeated $25 \mu\text{M}$ FNT measurements using the modified electrode. The RSD was calculated as 4.7%. The stability of Purpald[®]-modified PG electrode was good because the electrochemical activity of the electrode was 95% after dark storage for 7 days.

To further prove the usability of the recommended electrochemical modified electrode, fenitrothion was studied in real samples. Apple juice and tap water were selected as the real samples. Analysis of these sample solutions with the recommended electrochemical modified electrode founded

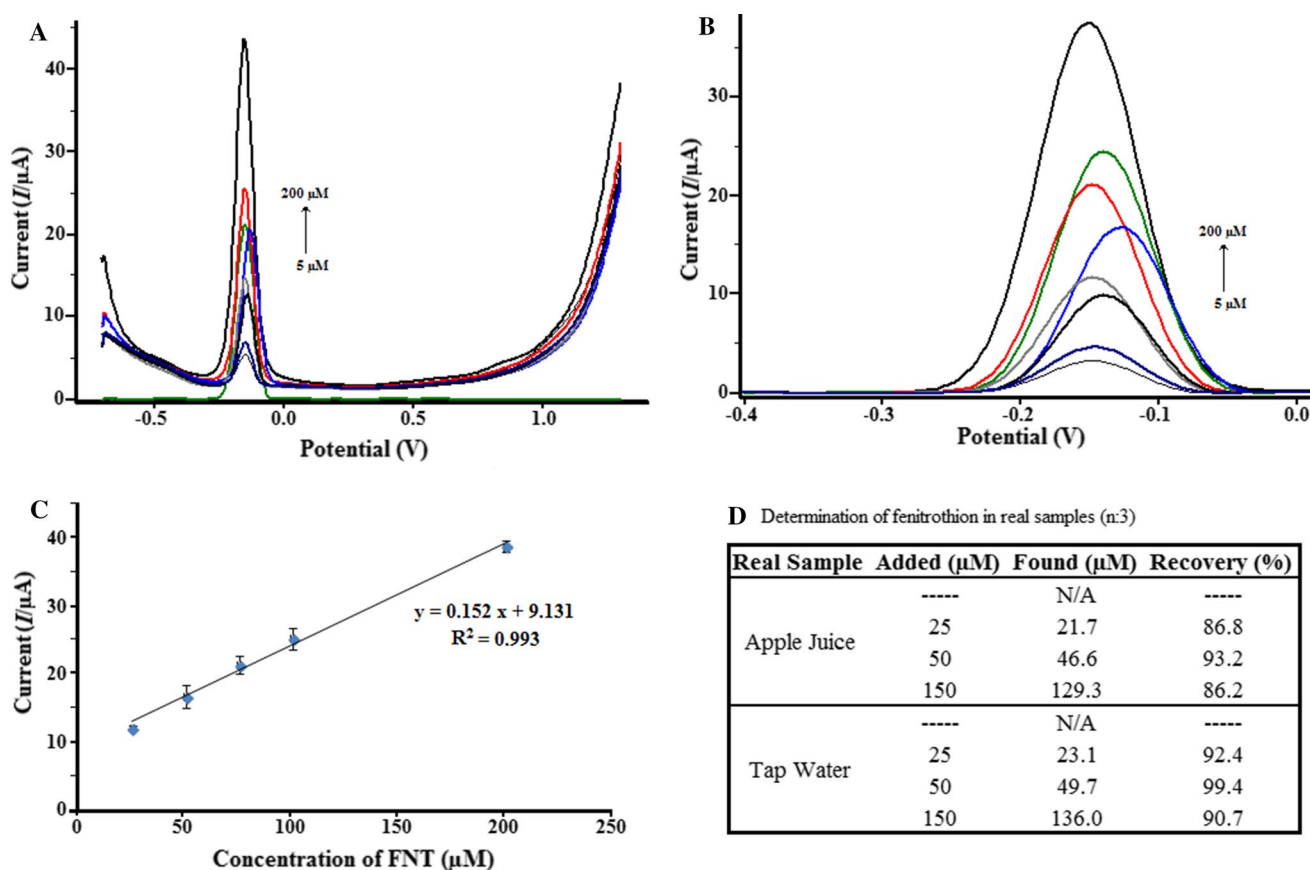


Fig. 7 Relationship between peak current signal magnitudes and concentration of FNT in the range 25–200 μM ($n:5$). **a** Voltammogram, **b** baseline correction of voltammograms, **c** Calibration curve, **d** determination of real samples

that none of the samples involved FNT. Therefore, the known quantity concentration of FNT was added into the samples and recoveries of the added values were determined. These analytical results can be seen in Fig. 7d. The results were admissible showing that the proposed modified electrode could be successfully used for the detection of FNT in real samples.

The published studies shown in Table 1 include electrode modifications developed for the determination of fenitrothion. The obtained LOD values of the studies shown in Table 1 are seen to be lower than the LOD calculated by the FNT determination using the electrode modification proposed. This result shows that the limitation of our study is the LOD value obtained. It can easily be said that the modifiers used in the studies given in the table should have specific, expensive, and complicated processes and the surface areas are quite large. The proposed modifier is a chemical that can be smoothly attached to the electrode surface using a simple electrochemical technique as well as being cheap. In addition, the proposed modifier can be easily combined

with other modifiers, and the LOD value to be obtained with the electrode/sensor is undoubtedly lower.

Conclusions

For the first time in this work, Purpald[®] polymer film on the surfaces of pencil graphite electrodes was successfully electrosynthesized. The optimized conditions of electropolymerization of Purpald[®] film were also investigated.

The electrochemical behavior of the Purpald[®]-modified disposable pencil graphite electrode under several pH conditions was studied. Differential pulse voltammetric technique has displayed fenitrothion oxidation in the linear range of 25–200 μM with a detection limit 17.39 μM .

According to the results obtained, the recommended Purpald[®]-modified electrode can be used for real samples. A successful recovery was obtained from real samples.

Table 1 Comparison of parameters with previously published electrochemical techniques for the determination of fenitrothion

References	Electrode	Modifier	Linear range (μM)	Limit of detection (μM)
Ensafi et al. (2017a)	GCE	CeO ₂ /rGO nanocomposite	0.02–2.00	0.003
Salehzadeh et al. (2016)	GCE	MWCNTs	0.2–60.0	0.08
Canevari et al. (2016)	GCE	SiO ₂ /MWCNTs/RuPc	3.0–66.0	1.6
Zhao et al. (2014)	GCE	AuNPs@GMIP	0.01–5.00	0.008
Geremedhin et al. (2013)	GCE	–	0.4–50.0	0.08
Kumaravel and Chandradekaran (2011)	GCE	Nano TiO ₂ /Nafion composite	0.20–4.00	0.09
Li et al. (2004)	GCE	Nano TiO ₂ polymer	0.02–10.00	0.01
Diaz et al. (2008)	DME	–	0.04–0.20	0.006
Pellicer et al. (2010)	SPE	SPCE-MIP	3.00–100.0	0.80
Sreedhar et al. (2011)	GCE	PANI	0.01–100.0	0.0072
Surucu et al. (2016)	PGE	rGO/DPA	0.10–1.91	0.00348
Wang et al. (2016)	GCE	Graphene oxide	0.0036–14.4	0.00036
Sgobbi and Machado (2018)	SPE	PHA/mPEG	1.0–10.0	0.61
Ensafi et al. (2017b)	GCE	Poly(zincon)	0.005–8.6	0.0015
Bolat et al. (2018)	PGE	Peptide nanotubes	0.114–1.712	0.0196

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