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Analytical Methods

A novel, biocompatible and electrocatalytic stearic acid/nanosilver modified glassy carbon electrode for the sensing of paraoxon pesticide in food samples and commercial formulations

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ABSTRACT

A simple, biocompatible and an enzyme-free sensing platform was developed for detection of paraoxon. The surface of a glassy carbon electrode was modified with an electrodeposition of stearic acid/nanosilver composite at −0.7 V for 40 s. The paraoxon undergoes electro-reduction at −550 mV on the modified electrode, and the limits of detection (LOD) was calculated as 0.1 nM (S/N = 3) using differential pulse voltammetry which is lower than that of the existing materials reported. The high stability observed with the modified electrode for prolonging period indicated that the sensitivity of the electrode remains active for several runs of the analysis. The developed analytical strategy was implemented for onion and paddy grain samples and good recovery rates were observed. Also, it was applied for analyzing the purity of the commercial paraoxon sample. The reliability of the developed strategy was confirmed by comparing the results of electrochemical approach with that of HPLC technique.

1. Introduction

Pesticides are substances that are used to control pests, including weeds. Excessive usages of these pesticides result in the existence of pesticide residues in the environmental samples including food and water. It creates a severe health problems to humans due to their high toxicity to acetylcholinesterase (AChE), a most important enzyme for central nervous system's function (Yin, Ai, Xu, Shi, & Zhu, 2009). Many people lost their lives due to pesticides poisoning (Eddleston, Dawson, & Buckley, 2008; Hu et al., 2017; Slavica, Dubravko, & Milan, 2018).

Paraoxon is one of the organophosphate pesticides which irreversibly inhibits AChE degradation in the human body that results in an uncontrollable muscle stimulation which leads to end the live quickly (De La Peña Mattozzi, Tehara, Hong, & Keasling, 2006). This synthetic pesticide compound does not undergo natural degradation and persists for long time in the environment. Whereas the other organophosphate pesticides such as parathion and methyl parathion have less reactive P═S group which must be converted into P═O in order to inhibit the AChE (Özkütük, Diltemiz, Özalp, Say, & Ersöz, 2013). Paraoxon itself contains P═O group that exhibits more inhibition power (Prins, Chao, Jacobson, Thompson, & George, 2014). Pesticides are highly insoluble in water. In order to minimize its toxic effects in the environment and educate the people about its toxicity, rapid detection of this toxic compound becomes a need of the hour (Kumaravel & Chandrasekaran, 2010). Organophosphate pesticides, including paraoxon is routinely analyzed by using gas chromatography (Yang et al., 2012), liquid chromatography and mass spectrometry (Mol, Van Dam, & Steijger, 2003), gas chromatography and mass spectrometry (GCMS) (Stan, 2000), high-performance liquid chromatography (Carabias-Martínez, Rodríguez-Gonzalo, Paniagua-Marcos, & Hernández-Méndez, 2000; Rossi et al., 2001). Due to limited availability of these sophisticated instruments, analysis of the samples cannot be carried out in short span of time. Hence, economically viable, easy and fast analytical methods are needed to assess the toxicity level of the pesticides in the environment. An excellent alternative for the sophisticated instruments is electroanalytical sensors. It has various advantages in terms of its (i) portability, (ii) short analysis time, (iii) low cost, (iv) sensitivity and selectivity and (v) quick response time (Lawal, 2018; Rhouati, Majdinasab, & Hayat, 2018; Samsidar, Siddiquee, & Shaarani, 2018). However, the sensitivity and accuracy of the results taken from the electroanalytical sensors are depending on the surface of the working electrode. The reduced/oxidized products formed at the electrode

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surface, must move away then only a diffusion of the pesticide molecules to the electrode surface from the bulk, could be possible. Since pesticide molecules are bulky and get adsorbed on the electrode surface upon oxidation/reduction step, the inhibition of diffusion of the analytes into the surface is inevitable thereby a fouling (Kumaravel & Chandrasekaran, 2011). Many researchers attempted to reduce the electrode fouling by applying the catalytic materials as well as enzymes on the surface of electrodes (Khairy, Ayoub, & Banks, 2018). Amperometric biosensor based on acetylcholinesterase/gold nanoparticles modified platinum electrode for the detection of methylparaoxon, carbofuran and phoxim was reported (Yin et al., 2009). In this work, the authors adopted an indirect method to detect the organophosphate pesticides. Since, it is an indirect method, requires longer analysis time. The other enzymatic methods for the detection of paraoxon based on AChE followed by fluorescence quenching (Wang, Wang, Jiang, & Hu, 2011), conducting polymer and silver nanowire (Turan et al., 2016) were reported. Also, a report based on colorimetric detection using the AChE and choline oxidase (ChO) is available (Guo et al., 2017). Enzymes are highly sensitive to the environmental conditions, which cannot widely be used for practical applications (Goud et al., 2018). The enzymeless detection of paraoxon based on ordered mesoporous carbons was reported with the linear range of 0.01 to 20 μM. A simple drop dry method was used for the modification of the electrode surface. The film may not be adherent for multiple analysis of the pesticide in field trials (Zhang et al., 2014). A graphitic film electrode with immobilized bismuth was employed for paraoxon detection. The obtained reduction potential was about −0.700 V vs. SCE in cyclic voltammetry (Stoytcheva, Zlatev, Montero, Velkova, & Gochev, 2017). PEDOT-based electrochemical sensor for the detection of nitrophenols and organophosphates was reported and the obtained reduction potential was about −0.600 V (Hryniewicz, Orth, & Vidotti, 2018). The sensor probes with higher reduction/oxidation potentials are not desirable because other electro-active species may interfere while detecting the target analyte species (Kumaravel & Chandrasekaran, 2011). Graphene oxide encapsulated 3D porous chalcopyrite electrocatalyst for methyl paraoxon detection with a detection limit of 4.5 nM was reported (Rajaji et al., 2019). Electrochemical transducer based sensing methods using molecularly imprinted polymer was also reported (Alizadeh, 2010). In the literatures, no reports for electrochemical detection of paraoxon using stearic acid/ nanosilver modified electrode, was available. Most of the works of paraoxon detection were focused on developing biosensor-based device. The LOD obtained so far is high which cannot be suitable for an analytical application of trace quantity. Stearic acid is a good biocompatible material which has been used as the electrode modifier for the detection of parathion and methyl parathion (Nancy Nirmala, Kumaravel, & Chandrasekaran, 2010). Silver nanoparticles, known for its good antibacterial and electrocatalytic properties, which are advantageous for the detection of pesticides (Kumaravel & Chandrasekaran, 2012). For the first time, the work on stearic acid/ nanosilver modified electrode is reported herein. A very low detection limit and lower reduction potential for paraoxon were accomplished compared to the earlier works. The developed sensor was used to analyze the various real samples. The reliability of the results was confirmed by comparing the results of electrochemical approach with that of HPLC instrumental technique. The electrochemical techniques such as cyclic voltammetry, differential pulse voltammetry and amperometry were used in this work. The morphology of the electrode surface was analyzed using SEM, AFM and XRD.

2. Experimental

2.1. Apparatus

Scanning electron microscopic (SEM) analysis was performed using a Hitachi Model S-3000H with 10 kV (acceleration voltage). PANalytical diffractometer Model PW3040/60 X'pert PRO operating with Cu Kα radiation (k = 0.15406 nm) generated at 40 Kv, was used to obtain the XRD patterns. Scanning was done at 3° min^{-1} for 2θ values between 10° and 80°. High pressure liquid chromatographic (HPLC) analysis was carried out using Shimpack CLC ODS-18 column with an LC-10AT pump and SPD-10A detector (Shimadzu, Japan) at 254 nm. The quantity of the silver ions formed on the electrode surface was analyzed using Varian Spectraa 220 atomic absorption spectrometer. All the electrochemical experiments were carried out using BioLogic Science Instruments, France, model SP150 Potentiostat/ Galvanostat. A three-electrode configuration was used which consists of stearic acid/nanosilver coated GCE (Alfa Aesar 3 mm diameter), platinum foil and saturated calomel electrode (SCE) as working, counter and reference electrodes, respectively. A glass cell having 10 ml capacity was used to perform the electrochemical experiments. All electrochemical studies were performed at room temperature (30 ± 1 °C). The dissolved oxygen from the solution was removed by purging with pure argon for 15 min.

2.2. Reagents and chemicals

Paraoxon was purchased from AccuStandard, USA and a stock solution of paraoxon (2140 μM) was prepared using methanol. The stock solution was diluted using phosphate buffer having pH 7 and was used as analyte solution. The phosphate buffer solution of pH 7 was prepared by adding sodium phosphate dibasic heptahydrate and sodium phosphate monobasic monohydrate. The desired pH was obtained by adding HCl or NaOH. Stearic acid and a commercial grade paraoxon were purchased from Merck India Ltd. and Hindustan Insecticides Ltd, India, respectively. All other reagents used were of analytical reagent grade.

2.3. Preparation of stearic acid/nanosilver modified GCE

Stearic acid was first converted into a sodium stearate by treating it with sodium hydroxide. Then, the silver stearate was prepared using silver nitrate. The procedure for the preparation of the silver stearate is as follows: In a typical experiment, 1 g of the pulverized sodium stearate was dissolved in 100 ml of water and stirred for one hour to get a homogeneous solution. In this solution, a 50 ml of 1 mM silver nitrate was added under a constant stirring and the stirring continued for one hour till obtaining the white precipitate of silver stearate. The resultant product was filtered and the precipitate was washed with lavish water, so that the excess silver nitrate can be removed. The washed precipitate was dried under ambient temperature for eight hours in dark. The GCE was hand polished using alumina slurry and the polished GCE was thoroughly washed with water and degreased using trichloroethylene. Stearic acid/nanosilver composite was electrodeposited on GCE for 40 s at −0.7 V vs. Ag, employing the silver wire as counter electrode in the solution of 10 ml DMF containing 0.1 g of silver stearate. 0.1 M tetrabutyl ammonium perchlorate was used as the supporting electrolyte. Stearic acid/nanosilver modified electrode was washed with water and dried in air. The modified GCE was employed in the present electrochemical studies.

3. Results and discussion

3.1. Surface morphology of the modified electrode

Fig. 1A & B. show the SEM image of stearic acid/nanosilver modified glassy carbon electrode. From the SEM image, it is worthy to note that stearic acid plays an important role in controlling the size of the silver particles formed on the electrode surface. The silver particles get aggregated during its deposition from silver nitrate solution. Also, the electrode is not stable due to peeling off the silver film in the course of the electrochemical detection of paraoxon. From the AFM image (Fig. 1C) it is vividly seen that the stearic acid/nanosilver modified electrode has uniform surface topography. To determine the

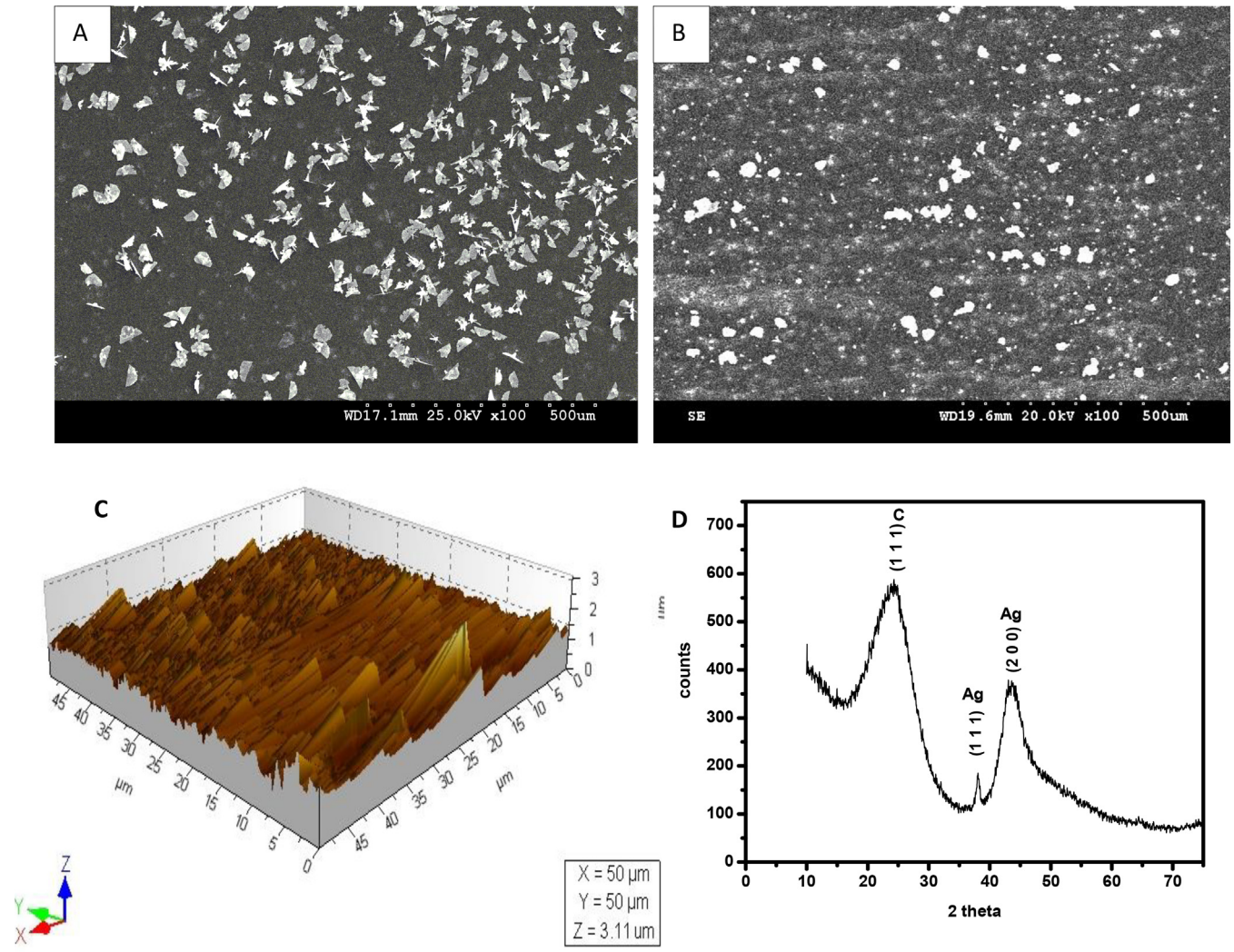

Fig. 1. SEM images of silver modified GCE (A) and stearic acid/nanosilver modified GCE (B), AFM image of the stearic acid/nanosilver modified GCE (C), XRD pattern of stearic acid/nanosilver modified GCE (D).

approximate crystallite size of the silver particles formed on the electrode surface, XRD patterns of the stearic acid/nanosilver composite were obtained which is shown in Fig. 1D. XRD peaks were indexed using the ICDD file (Swanson, McMurdie, Morris, Evans, Paretzkin, DeGroot, & Carmel, 1971). The two major peaks, one peak at 38.11° and another peak at 44.31° were observed. It can be assigned to the diffraction from the (1 1 1) and the (2 0 0) planes, respectively, of the face-centered cubic lattice of Ag (0). The average crystallite size of the silver was calculated by using Scherrer equation (Kumaravel & Chandrasekaran, 2010). The crystallite size was found to be less than 50 nm.

3.2. Optimization of experimental parameters

The experimental parameters were optimized using cyclic voltammetric technique and the paraoxon concentration used for the optimization studies is 50 µM. Voltammograms were recorded for the reduction of paraoxon at different pHs. The pH plays an important role on the reduction of paraoxon. The peak current increases with the electrolyte pH up to 7, beyond which a decreasing trend in the peak current was observed (Fig. S1A). Since higher reduction current was observed at pH 7, the same has been considered for further study. The reduction behavior of paraoxon at high pH (> 10) was also studied. But no peak was observed. The discharge of the background electrolyte was observed at around −1.2 V. Duration of the deposition plays a vital role for the catalytic activity of the silver nanoparticles on GCE. An optimization of the silver deposition duration was accomplished. The peak current was maximum at 40 s of deposition duration, for the reduction of 50 µM paraoxon in cyclic voltammetry. It is shown in Fig. S1B. As the duration of silver deposition increased, there was a reduction in the peak current value which may be due to the formation of a bulk deposit of silver on the electrode surface which hinders the diffusion of the pesticide molecules into the surface of GCE. The quantity of the silver particles formed on the electrode surface was estimated using atomic absorption spectroscopy. At 40 s duration of deposition time, the quantity of the silver formed on the electrode surface was 0.31 ppm.

3.3. Detection of paraoxon using electrochemical methods

In the case of developing electrochemical sensors, it is most important to study their electrochemical properties and their sensing abilities. The preliminary electrochemical characterization and the electrochemical behaviors of the sensors were studied by using cyclic voltammetric experiments. Fig. 2A shows the cyclic voltammetric response of paraoxon at bare and modified electrodes. The reduction of paraoxon at stearic acid/nanosilver modified glassy carbon electrode was observed at around −550 mV vs. SCE. Paraoxon gets reduced at −700 mV and −600 mV for bare GCE and silver modified electrode,

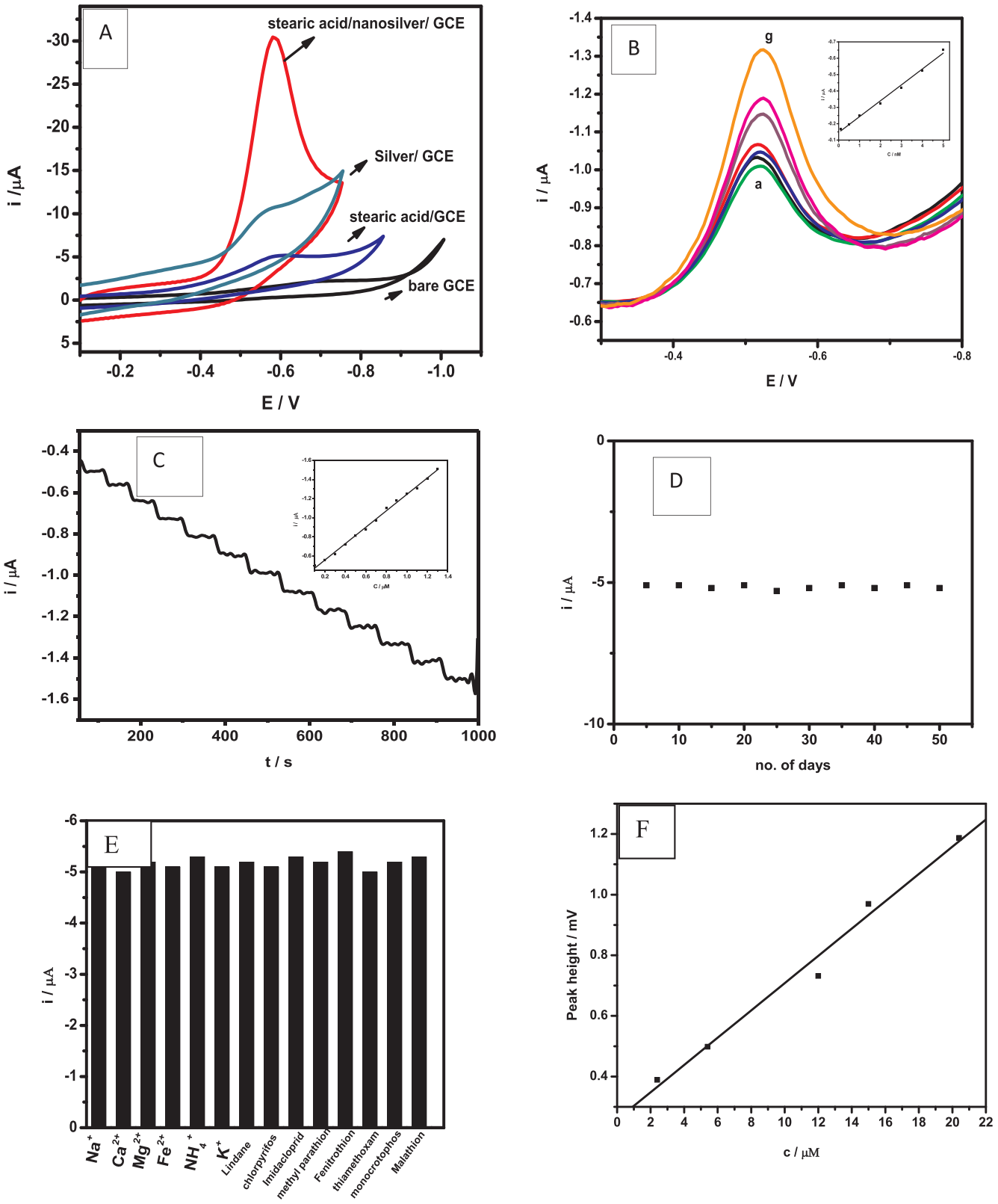

Fig. 2. Cyclic voltammetric response of 50 µM paraoxon at bare and modified glassy carbon electrodes (A), Differential pulse voltammetric response of different concentrations of paraoxon (a) 0.1, (b) 0.5, (c) 1, (d) 2, (e) 3, (f) 4, and (g) 5 nM in pH 7 phosphate buffer solution under optimized instrumental settings (B), Amperometric response of paraoxon on stearic acid/nanosilver modified GCE for the constant addition of 0.1 µM in pH 7 phosphate buffer solution. Set potential: −550 mV (C). Plot of peak current vs. number of days for 50 µM paraoxon in 7 pH phosphate buffer (D), Interference study of inorganic species and nitroaromatic pesticides on the reduction signal of 50 µM paraoxon at 100 mV s^{-1} in 7 pH phosphate buffer solution at stearic acid/nanosilver modified GCE (E). HPLC calibration graph (F).

respectively. The reduction of paraoxon was observed at less over-potential on stearic acid/nanosilver modified electrode with higher sensing current. To check the role of silver nanoparticles in this work, silver modified electrode was employed as well. The shift in potential with lower sensing current was observed at the silver modified electrode. But both potential shift and higher sensing current was observed at stearic acid/nanosilver modified electrode. Paraoxon undergoes an irreversible reduction on stearic acid/nanosilver, stearic acid, and the silver modified glassy carbon electrodes since no reverse peaks were obtained on all the electrodes. This reduction peak is due to the reduction of nitro group of the paraoxon into the corresponding hydroxylamine group through 4 e^- (Xu, Wu, Hu, & Cui, 2002). While increasing the scan rate, the peak current gets increased. This gives a linear relationship between the square root of the scan rate and peak current. It indicates that the reduction process is diffusion controlled. A well-defined reduction peak with higher sensing current and lower reduction potential was observed on stearic acid/nanosilver modified GCE. This may be due to the electrocatalytic effect of silver nanoparticles and stearic acid film. When silver is co-deposited along with stearic acid, stearic acid plays a vital role in the formation of silver nanoparticles on the electrode surface. The glassy carbon electrode is highly hydrophobic in nature which interacts hydrophobic tail end stearic acid through hydrophobic-hydrophobic interaction (Downard & Roddick, 1995; Hu, Wu, Yi, & Cui, 2002; Periasamy, Chang, & Chen, 2011; Wang, Zhang, Zhou, & Dong, 2001). The stearic acid may control the size of silver in the course of potentiostatic deposition. During the formation of silver nanoparticles on the electrode surface, the stearic acid molecules would cover the surface of the nanoparticles thereby reducing the formation of aggregation. When silver is deposited from silver nitrate solution, particles are agglomerated and the film is not intact on the electrode surface which is vividly seen in the SEM image (Fig. 1A). The increase in reduction current on stearic acid/nanosilver modified GCE is due to the synergic effect of stearic acid film which attracts the hydrophobic pesticide molecules through hydrophobic-hydrophobic interaction and electrocatalytic effect of silver nanoparticles formed on the electrode surface (Kumaravel & Chandrasekaran, 2012). In this work, lower reduction potential and high sensing current for the reduction of paraoxon is achieved. Differential pulse voltammetry (DPV) experiments were carried out under optimized instrumental settings: modulation amplitude 40 mV, modulation frequency 30 Hz and modulation step 4 mV. Typical DPV response of various concentrations of paraoxon is shown in Fig. 2B. The peak current was noticed to linearly increase as the concentration of paraoxon increases ranging from 0.1 to 5 nM with a correlation coefficient of 0.99 which was calculated from the linear fit data obtained using origin software (in-set graph in Fig. 2B). The increase of current was not proportional to the concentration of higher range cause electrode fouling. One of the major problems associated with the sensing of pesticides is the electrode fouling. Pesticides are bulky molecules which get adsorbed on the electrode surface upon oxidation/reduction step. It reduces the sensitivity of the sensor. In this work, minimum electrode fouling was observed compared to the earlier reports (Rajaji et al., 2019; Stoytcheva et al., 2017; Turan et al., 2016). The LOD was found to be 0.1 nM (S/N = 3). The detection limit attained in the present work is very low compared to the existing works (Table 1). Since the designing of portable ampermetric sensor is easier among the electrochemical methods, the amperometric response of paraoxon was recorded. Fig. 2C shows the amperometric response of paraoxon at stearic acid/nanosilver modified glassy carbon electrode. The reduction current increased for each addition of paraoxon.

3.4. Reproducibility and stability of the stearic acid/nanosilver modified electrode

The reproducibility of the results was checked by repeating the experimental run for seven times, at a fixed concentration (50-μM) of paraoxon. The peak currents were reproducible with the relative standard deviation of 2.7%. Intra electrode reproducibility was also studied. The electrode stability was investigated by using same modified electrode for paraoxon analysis over a period of 50 days (Fig. 2D). The same peak currents were observed with the relative standard deviations of 2.3%. After that, there was a sharp decline in the peak current. It might be due to the instability of the film.

3.5. Electrochemical analysis of interfering ions and pesticides

The interference of metal ions and pesticides were checked with respect to the reduction signal of paraoxon. It was carried out by taking 1:1 ratio of metal ions to paraoxon (2E). The inorganic cations analyzed in this work did not interfere the sensing signal of paraoxon. The pesticides viz. methyl parathion and imidacloprid did not interfere with the reduction signal of paraoxon. However, parathion interferes in the paraoxon reduction signal. The possible interference of organochlorine pesticides was also analyzed. These pesticides did not interfere in the sensing of paraoxon.

3.6. Extraction and determination of paraoxon in food samples

The analytical application of the above methods was checked with onion samples. The onions were purchased from the local market and 100 μM standard paraoxon was spiked into the 100 g of onion sample. After one day, the sample was extracted using dichloromethane. The residue obtained upon evaporation, was dissolved in pH 7 phosphate buffer solution. This solution was used for the electrochemical measurements. The recovery rates obtained in the electroanalytical techniques are summarized in Table 2. Similarly, the commercial paraoxon was purchased from a local vendor and a concentration of 100 μM was prepared. It was then spiked into the 100 g of onion sample and 100 g of paddy grains which were collected in the farm field at Gobichettipalayam of Erode District, Tamilnadu, India. The results of recovery rates are given in Table 2, and compared with a HPLC technique. In HPLC technique, the calibration graph was constructed between known concentrations of paraoxon and peak heights which is shown in Fig. 2F and the same was used to find the recovery rates of paraoxon in real samples. The results obtained in the electroanalytical techniques have a good agreement with the HPLC approach. Analytical applicability of the proposed technique was extended to verify the purity of the commercial paraoxon.

The assay mentioned in the commercial paraoxon was 30% and based on which, the amount of sample to be taken for a concentration of 10 μM paraoxon was calculated and the same was prepared. The as prepared sample was then used for the analyses of both DPV and HPLC techniques. The observed concentration against DPV and HPLC were 9.8 and 9.7 μM, respectively. It is an evident that the DPV method is an absolute alternate for the high cost HPLC technique.

4. Conclusions

A novel stearic acid/nanosilver modified electrode was fabricated for the analysis of paraoxon. This electrode gives better electrocatalytic activity towards the reduction of paraoxon which is evident from the lower reduction potential and higher sensing current. The lower detection limit was achieved on this modified electrode compared to earlier reports. Since the potentiostatic mode was adopted for the preparation of the modified electrode, the film was intact with the surface which can be used for prolonging period which was confirmed by its electrochemical response towards sensing the paraoxon for several runs with a retained sensitivity of the electrode surface. The deployment of the sensor for field analysis is easier. The recovery rate of standard and commercial food samples was analysed. The results show a good agreement with the HPLC method. Purity of commercial paraoxon sample was verified by using the developed method and the

Table 1
Comparative electrochemical studies on detection limits and linear range of paraoxon with respect to different types of electrodes adopted.

Electrochemical method	Electrode	Linear range	LOD	References
Amperometry	Poly(5,6-bis(octyloxy)-4,7-di(thieno[3][3,2-b]thiophen-2-yl)benzo[c][1,2,5] oxoadiazole) modified graphite electrode	0.5–8 μM and 10–120 μM	0.212 μM	(Turan et al., 2016)
DPV	Ordered mesoporous carbons (OMCs) modified glassy carbon electrode (OMCs/GCE)	0.01–1 μM and 1–20 μM	1.9 nM	(Zhang et al., 2014)
DPV	Graphene oxide encapsulated 3D porous chalcopyrite Modified SPCE	0.07–801 μM	4.5 nM	(Rajaji et al., 2019)
DPV	Bismuth film/GCE	5 to 40 nM	2 nM	(Stoytcheva et al.,2017)
CV	PEDOT:PSS	0–85 μM	4.95 μM	(Hryniewicz et al., 2018)
DPV	Stearic acid/nanosilver/GCE	0.1–5 nM	0.1 nM	This work

Table 2
Comparison of DPV method with HPLC technique with respect to the recovery rate of paraoxon from onion and paddy grain samples.

Samples	Method	Amount added	Amount recovered ± SD[a]	Recovery rate (%)
Standard paraoxon spiked onion samples	DPV	0.2 nM	0.2 nM ± 0.07	100.00
		0.5 nM	0.5 nM ± 0.09	100.00
	HPLC	10 μM	9.8 μM ± 0.09	98.00
Commercial paraoxon spiked onion samples	DPV	0.2 nM	0.2 nM ± 0.09	100.00
		0.4 nM	0.4 nM ± 0.08	100.00
	HPLC	10 μM	9.9 μM ± 0.21	99.00
Analysis of paraoxon in paddy grains	DPV	0.2 nM	0.2 nM ± 0.19	100.00
	HPLC	10 μM	10.3 μM ± 0.11	103.00

[a] n [a] number of sample assayed is 5.

results were in good agreement with that obtained by HPLC approach. The developed sensor is thus opened a new opportunities for detecting the paraoxon in the environmental samples.

CRediT authorship contribution statement

A. Kumaravel: Conceptualization, Methodology, Validation, Writing - original draft, Writing - review & editing. **M. Murugananthan:** Writing - review & editing. **R. Mangalam:** Writing - review & editing. **S. Jayakumar:** Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2020.126814.

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