

## Fabrication of copper incorporated graphene oxide nanocomposites used for electrochemical determination of methyl parathion contaminants

V. Deepa<sup>1,2</sup>, B. Kavitha<sup>\*3</sup>, S. Aeji<sup>3</sup>, H. Aswathaman<sup>4</sup>, S.Thanikaikarasan<sup>5</sup>and N. Senthil Kumar<sup>\*6</sup>

<sup>1</sup>Research Scholar, PG & Research Department of Chemistry, Arignar Anna Government Arts College, Cheyyar – 604 407, Tiruvannamalai, Affiliated to Thiruvalluvar University, Tamilnadu, India.

<sup>2</sup>PG& Research Department of Chemistry, Shanmuga Industries Arts and Science College, Tiruvannamalai, 606603, Tamilnadu, India.

<sup>3</sup>Department of Chemistry, Sri Ranganathar Institute of Engineering and Technology Athipalayam, Coimbatore, 641110, Tamilnadu, India.

<sup>4</sup>Department of Science, Christ College of Science and Management, Sonnur, 563 160, Karnataka, India.

<sup>5</sup>Department of Physical Sciences, SIMATS School of Engineering, SIMATS, Chennai-602105, Tamil Nadu, India.

<sup>6</sup>PG & Research Department of Chemistry, Arignar Anna Government Arts College, Cheyyar – 604 407, Tiruvannamalai, Tamilnadu, India.

\*Corresponding Author Email:[nsk.nagai@gmail.com](mailto:nsk.nagai@gmail.com), [ootykavi@gmail.com](mailto:ootykavi@gmail.com), Mobile- 9943260525

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### ABSTRACT

Electrochemical studies of methyl parathion on novel nanocomposites electrode surface systems reached distinction in recent years because of their application in trace determination. Cyclic voltammetric behaviours of methyl parathion on nanocomposites modified glassy carbon electrodes at different pH in aqueous ethanol media were carried out. Influence of pH led to the selection of pH 1.0 as the best pH for the electroanalysis of methyl parathion. Voltammogram of pesticide exhibits two cathodic and one anodic peak responding at all pH media with the novel modified electrode system. The modified electrode shows one redox couple around the potential range from 0.1 to 0.3 V and one reduction peak around at - 0.75 V with higher peak current responding to the modified electrode. The reduction peaks were selected for stripping analysis owing to their maximum current response. The experimental parameters were optimized using the differential pulse stripping mode. A calibration plot was made. The determination limit and standard deviations were arrived. The applicability of the method was also verified in a sample soil analysis.

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### Keywords:

Methylparathion, Voltammetry, GrapheneOxide, Nanocomposites, Copper, Pesticide

### 1. INTRODUCTION

Electrochemical analysis based on chemically modified electrodes has proved a sensitive and selective method for the determination of organo phosphorus pesticides [1-3]. The electrochemical detection can be accomplished rapidly without tedious separation and might be suitable for continuous monitoring. Direct electrochemical methods for the detection of electro active electro-active organo phosphorus pesticides compounds or applied electrochemical and gravimetric techniques in conjunction with enzymes have also been reported [4–6]. The determination of parathion and its substituted derivatives has, therefore, become increasingly important in environmental monitoring [7].

Most pesticides can be successfully analyzed by chromatographic techniques, but because of the high price and immobility of the apparatus, the complexity of the method and the necessary special preparation of the samples [8]. There are many methods for detecting methyl parathion. Among them, traditional methods for detecting methyl parathion residues include gas chromatography [9], high performance liquid chromatography [10], mass spectrometry [11] and electrophoresis [12]. Although these analytical techniques have high sensitivity and reproducibility, there are still many disadvantages, such as complex and expensive experimental instruments,

complicated sample preparation and purification steps, and so on. In addition, one of the major disadvantages of these methods is the limitation of field and real-time detection, which makes it impossible to be used in emergencies. Therefore, people have made many efforts to seek a rapid, sensitive, selective, accurate, and easy-to-detect pesticide technology to replace these traditional technologies. Electrochemical sensors are the best alternative to traditional detection methods, because of their low cost, small size, good portability, high sensitivity, and trace detection [13-17].

With remarkable achievements in nanotechnology and nanoscience, nanomaterial-based electrochemical signal amplifications have great potential of improving both sensitivity and selectivity for electrochemical sensors and biosensors [18]. Great progress has been made in using highly active catalytic nanomaterials as substitutes for natural enzymes. Due to the large surface area and many other unique characteristics of nanomaterials, they have various functions such as catalytic electrochemical reaction, enhanced electron transfer, labeling, and reactants in electrochemical sensing systems [19]. The growing concerns about environmental health emphasize the necessity of continuous monitoring of pollutants [20].

Graphene is a novel two-dimensional carbon nanomaterial composed of a single layer of carbon atoms. It

has large specific surface area, high thermal conductivity, excellent mechanical properties, and high charge mobility and thus exhibits broad application prospects in the field of electrochemical sensing [21, 22]. The structure of graphene oxide is very similar to that of graphene, but it has a large amount of oxygen-containing functional groups (common forms include carboxyl groups, hydroxyl groups, carbonyl groups, and epoxy groups, etc.) on the two-dimensional base. These oxygen-containing groups are connected to graphite oxide sheets by covalent bonds, which make graphene oxide have excellent intercalation properties and give it good hydrophilic properties. Therefore, graphene oxide is widely used as a precursor of graphene. In previous literatures, the reduction methods of graphene oxide mainly include thermal reduction [23], optical reduction [24, 25], chemical reduction [26, 27], and electrochemical reduction [28-30]. While in recent years, the method of electrochemically reducing graphene oxide has been applied increasingly widely. In this experiment, electrochemistry is a method of electrochemical removal of oxygen-containing functional groups of graphene oxide to produce graphene without special chemical reagents and has fewer by-products. Among the carbon-based materials are carbon nanotubes and graphenic carbon nanomaterials. For instance, graphene-derived nanomaterials are recognized owing to environmentally friendly synthesis methods; for example, during EC synthesis of graphene, nontoxic solvents are used; comparatively high yield is obtained and minimum residual defects are formed [31].

As the main limitation for the use of this method is the electrochemical inactivity of many pesticides, this paper gives the essence of all electroanalytical methods for pesticide quantification applied in the last period, with an overview of the electrode materials and modifiers applied with a purpose to enhance the analytical quantification application.

## 2. EXPERIMENTAL

### 2.1. Materials and Methods

Methyl parathion (CAS No 298-00-0), Graphene oxide (CAS no 7782-42-5) were purchased from Sigma-Aldrich and all other reagents of supporting electrolyte chemicals including solvents were purchased from Merck. The reagents are used without further purification.

The electrochemical measurements were carried out by CHI 650C electrochemical work station (CH Instruments, Inc., U.S.A). Electrochemical studies were carried out in a conventional undivided three-electrode cell using a modified glassy carbon electrode (GCE) as a working electrode (area 0.0341 cm<sup>2</sup>), Ag|AgCl as a reference electrode and Pt wire as a counter electrode. Prior to each electrochemical experiment, the electrolyte solutions were deoxygenated with pre-purified nitrogen for 10 min unless otherwise specified. Were prepared and used with different pH solutions as supporting electrolyte for throughout the electrochemical studies. The experiments are carried out three times and the average value is used to plot the figures and calibration plots.

### 2.2. Synthesis and fabrication of Cu incorporated GO nanocomposites

Graphite oxide (GO) was prepared from graphite by Hummers' method and exfoliated with grapheneoxide in water viaultrasonic agitation for 2 hrs. This method provides a simple, low-cost, efficient, and reproducible method for the production of GO using top-down methodologies. The chemical composition of the resulting GO was dependent on both the oxidation and exfoliation of the bulk graphite. The structure of GO is stochastic because of the different nature and distribution patterns of oxygen containing functional groups. Theoretically, hydroxyl and epoxy functional groups are located in the basal plane of GO [32, 33], while the carbonyl and carboxyl groups are available at the edges of the GO. Furthermore, the functional groups of GO have served as adsorptive sites for doping CuNPs. GCE surface was polished with 0.05  $\mu\text{m}$  alumina slurry using a Buehler polishing kit, then washed with distilled water and dried. 5  $\mu\text{l}$  dispersion of Cu/graphene oxide NC was dropped on the precleaned GCE and dried at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of pH

Cyclic voltammetry provides a fruitful insight into both half reactions occurring at the working electrode surface and the chemical or physical properties coupled to the target electrochemical reaction. In cyclic voltammetry, initiating from a potential ( $E_i$ ), a staircase or linear potential sweep is applied to the working electrode. When reaching a switching potential is  $E_f$ , the potential sweep is reversed and returns to its initial point. The data output of the voltammogram is a current-potential curve, where the main features are the peak potentials and currents at anode and cathode. The effect of pH range was investigated from 1.0 to 13.0. The results obtained are presented in Figures 1 and 2, the variation in the pH has shown a distinguished effect on the reduction peak current.

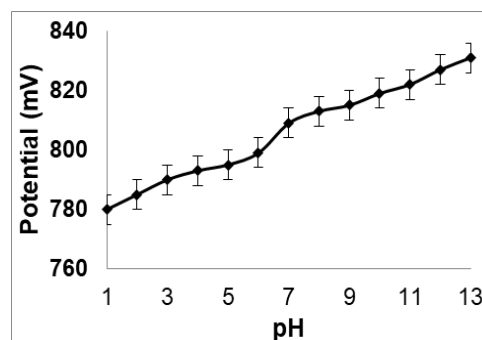


Figure 1. Curve of peak potential against pH

The observed effect is a displacement of the peak potential with more reduction. This effect on the potential was expected with respect to the electrochemical reactions that involve the consumption of protons to achieve the reduction reactions. Under these conditions, proton-rich media are expected to favor electron transfer at the electrode surface. In the particular case of the reduction of the nitroso group, the plot of the peak potential as a function of the pH of the electrolytic solution is a curve line. There is also a pH effect on the measured cathodic peak current. For the nitroso

group, the general trend is a slight increase in the reduction current with an increase of pH. For the nitro group, the current intensities are higher in acidic media and drop sharply when pH becomes basic. The best compromise for the pH of the electrolytic solution corresponds to the value pH 1.0.

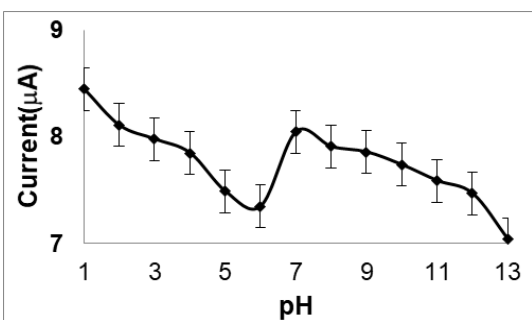


Figure 2. Curve of reduction peak current Vs pH

### 3.2. Voltammetric studies

The voltammogram of 50 µM concentration of methyl parathion was studied at various sweep rates from 50 to 250 mV/s using nanocomposites modified GCE. Figure 3 represents the typical cyclic voltammogram of methyl parathion exhibiting three peaks [34–39]. In the first cycle, one main cathodic peak around 0.130 V and one anodic peak in the range 0.600 V are observed. In the second cycle, a new small cathodic peak around 0.400 V is observed. As the sweep rate increases, the peak current increases.

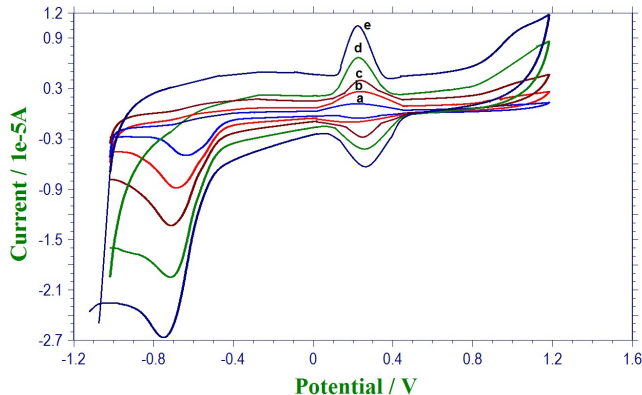


Figure 3. Voltammetric behaviour of 100 µM of methyl parathion on Cu/GO modified GCE at different scan rate a) 50 b) 100 c) 150 d) 200 and e) 250 mV/s.

The second cathodic peak was considered as the scan rate variation because it shows higher peak current value. As the scan rate increases, the peak current also increases linearly and presents Figure 4. A nonlinear correlation between the peak current and the square root of the sweep rate was observed and given Figure 5. These facts suggest an adsorption-controlled reaction of MP on nanocomposites modified electrode surface.

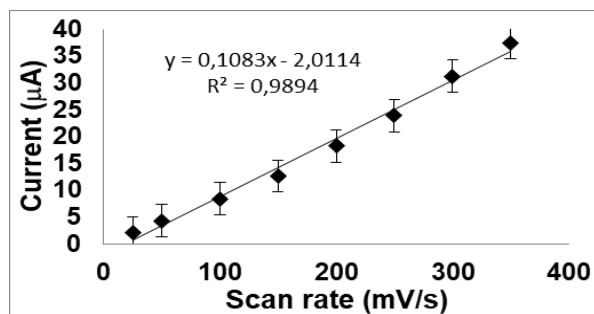


Figure 4. plot of reduction peak current Vs scan rate

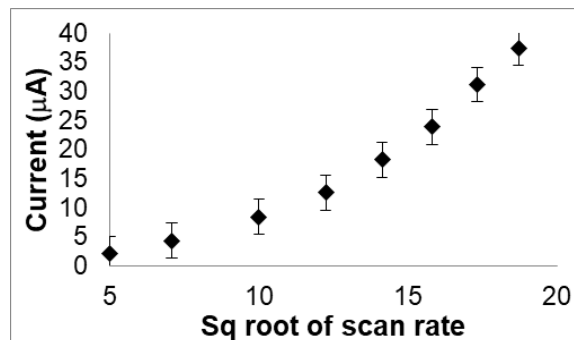


Figure 5. Curve of reduction peak current Vs square root of scan rate

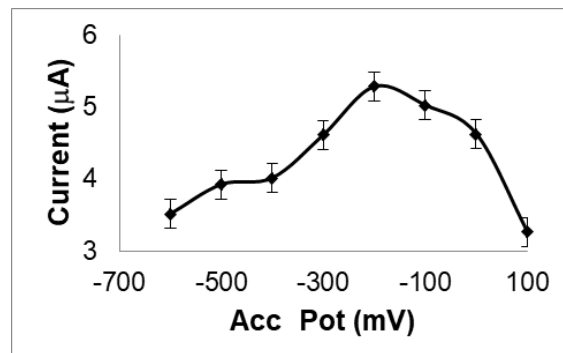


Figure 6. Curve of reduction peak current Vs accumulation potential

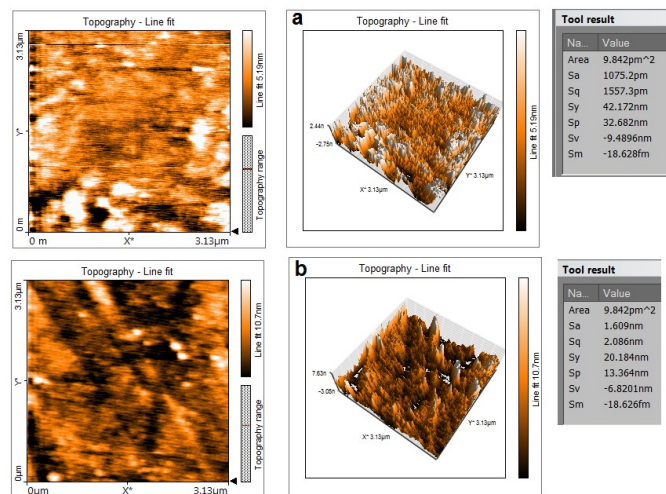
### 3.3. Differential Pulse Stripping Voltammetry (DPSV)

To carry out differential pulse stripping voltammetry on copper incorporated graphene oxide nanocomposites modified glassy carbon electrode, a preliminary confirmation experiment was tried. The 100 nM MP test solution was purged with nitrogen gas for 20 minutes and a suitable accumulation potential was applied to the electrode. The solution was stirred throughout of 120 seconds of accumulation period. After a 10 second rest period, a differential pulse sweep under default conditions was run. A systematic study of various instrumental parameters that affect the stripping response has been carried out to establish the optimum conditions.

#### 3.3.1. Effect of Accumulation Potential and Time

The optimization of the accumulation potential was done as the first part of this study. The potential was varied from

100 to -600 mV (Figure 6) at an accumulation time of 60 s. Maximum peak current was observed at -200 mV and it was fixed as the optimum accumulation potential. This shows the maximum adsorption of the substrate at this potential. Pesticide deposited on the electrode surface was characterized by atomic force microscopy. The nanoparticles composites coated surface exhibits a uniform granular and fiber-mixed-like structure. After the accumulation of pesticide of MP on nanocomposites, the surface observed small size needle-like morphologies are presented in Figure-7.



**Figure 7.** AFM photographs of a) Nanocomposites b) MP adsorption on modified GCE

By varying the deposition time from 30 to 150 s, the effect of deposition time was studied after fixing the deposition potential at -200 mV. The maximum current response is observed at 120 s deposition time. Hence, this accumulation time is taken as the optimum value for further study.

### 3.3.2. Effect of Initial Scanning Potential

The initial scanning potential is another important parameter as it confirms the non-faradaic nature of the preconcentration step. It also controls both the peak potential and peak current in the stripping voltammogram. The influence of the initial potential on the peak current was studied by varying the initial scan potential from 900 to 200 mV. Maximum peak current with better resolution was observed at 600 mV. Hence, 600 mV was fixed as the initial scanning potential and the reproducibility of the method was confirmed by making successive measurements.

### 3.3.3. Effect of Pulse Height and Width

Effect of pulse height was studied by varying from 25 to 150 mV. The optimum pulse height observed was at 50 mV. Similar to pulse height, the pulse width was also studied by varying between 25 and 150 ms. The sharp peak nature with higher current was observed at the pulse width of 75ms. Hence, the pulse width of 75ms was chosen as the optimum value.

### 3.3.4. Effect of Scan Increment and Scan Rate

The scan increment was varied between 2 to 18 mV and the maximum peak current response was obtained at 6 mV scan increment.

After fixing the above parameters, the effect of scan rate was also studied using MP solution of 100 nM concentration. Scan rate was varied from 10 to 75 mV/s. Highly resolved stripping response with maximum peak current was obtained at the scan rate of 50 mV/s. The experimental parameters are optimized as discussed above. The range of study and the optimum values are given in Table 1.

**Table 1.** Optimum parameters condition of DPSV of MP on modified glassy carbon electrode at pH 1.0

Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )		Recovery (%)		R.S.D	
	water	soil	water	soil	water	soil
50	46	48	92.00	96.00	3.2	2.3
100	92	94	92.00	94.00	2.7	3.1
150	143	145	95.33	96.66	2.9	2.7
200	195	196	97.50	98.00	2.1	2.2
250	239	243	95.60	97.20	2.5	1.9

The spiked water sample was prepared by adding known amounts of pesticide stock solution and pesticide-free water and then allowing them to stand 24 hrs. The extract was evaporated to dryness by gentle heating on a water bath. The residue was transferred into a 250 ml calibrated flask, dissolved in ethanol and made up to the mark. The MP was determined by differential pulse stripping voltammetric method. The percentage of recovery and relative standard deviation of pesticides were determined and the results are presented in Table 2.

**Table 2.** Recovery of methyl parathion percentage from soil and water samples

Parameters	Range	Optimum
Accumulation potential (mV)	100 to -600	-200
Deposit time (sec)	30 to 150	120
Initial scan potential (mV)	900 to 200	600
Pulse height (mV)	25 to 150	50
Pulse width (msec)	25 to 150	75
Scan rate (mV/sec)	10 to 75	50
Scan increment (mV)	2 to 18	6

### 3.3.5. Analytical Characteristic

The optimum and experimental conditions arrived were used to study the effect of concentration. As the concentration of MP increased, the current increased. A typical DPSV response obtained under the optimum experimental conditions 100 nM concentration of MP is given in Figure 8. A calibration plot was made and shown in Figure 9. This showed the linear dependency of the peak current on the concentration of substrate. The range of concentration limits is 50 to 350 nM. The lower limit of detection is 20nM. The precision of the method was ascertained by measuring the peak current of the MP responses in six standard samples. Ten replicates were

analyzed and standard deviations were calculated for a concentration 100 nM. The low value of standard deviation, 3.2 % indicates the good reproducibility and feasibility of this method for the determination of MP.

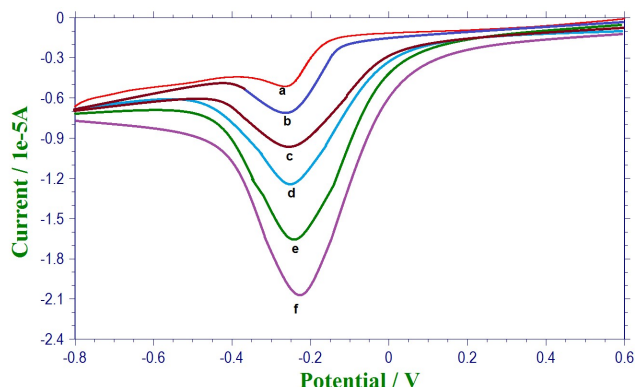


Figure 8. Difference pulse voltammetric behavior of various concentration methyl parathion

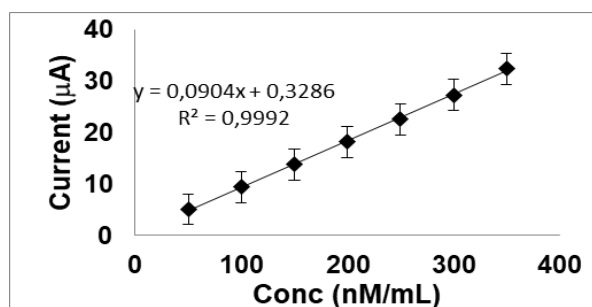


Figure 9. Calibration plot of different concentration MP

### 3.3.6. Soil and Water sample analysis

The soil sample analyzed was collected from a field and was washed repeatedly with water and exposed to the atmosphere. Approximately 50 grams of the sieved soil was spiked with 25 ml of 50  $\mu\text{M}$  pesticide solution by shaking in a closed bottle for about 30 minutes. The extract was filtered and evaporated to dryness by gentle heating on a water bath. The residue was transferred into a 250 ml calibrated flask, dissolved in ethanol and made up to the mark. A 10 ml portion of this solution was transferred into a 50 ml calibrated flask and 0.1 mM  $\text{H}_2\text{SO}_4$  containing aqueous ethanol was used to dilute the contents of the flask to the required volume. The standard addition method was used. 0.05 ml aliquot of the 50  $\mu\text{M}$  standard stock solution was added to the solution prepared as described above. Differential pulse stripping voltammetric studies under the maximum current signal experimental conditions were carried out. A relative standard deviation of 1.9% was obtained for 50  $\mu\text{M}$ .

## 4. CONCLUSION

Electrochemical detection of pesticide pollutants utilizing electrodes modified with nanocomposites materials. Graphene with metal nanocomposites synthesis and electrode modification exhibits enhanced sensor configurations in the development of portable sensor devices. The other advantage of the sensor is low detection limit, fast response time, good selectivity, excellent repeatability and

reproducibility, appreciable storage stability. Besides, the sensor has shown good recovery in the determination of spiked methyl parathion in water and soil samples, indicating the potential application of this method for real-time applications.

## REFERENCES

- [1] Xingyuan, Liu. (2011). Electrochemical Sensor for Determination of Parathion Based on Electropolymerization Poly(Safranin) Film Electrode. Article ID 986494, <https://doi.org/10.4061/2011/986494>
- [2] Zen, J. M., Jou, J. J., Senthil, Kumar, A. (1999). A sensitive voltammetric method for the determination of parathion insecticide, *Analytica Chimica Acta*, 396: 39–44
- [3] Xu, C., Wu, K., Hu, S., Cui, D. (2002). Electrochemical detection of parathion at a glassy-carbon electrode modified with hexadecane, *Analytical and Bioanalytical Chemistry*, 373: 284–288.
- [4] Sacks, V., Eshkenazi, I., Neufeld, T., Dosoretz, C., Rishpon, J. (2000). Immobilized parathion hydrolase: an amperometric sensor for parathion, *Analytical Chemistry*, 72:2055–2058.
- [5] Mulchandani, A., Mulchandani, P., Chen, W., Wang, J. (1999). Amperometric thick-film strip electrodes for monitoring organophosphate nerve agents based on immobilized organophosphorus hydrolase, *Analytical Chemistry*, 71:2246–2249.
- [6] Chough, S. H., Mulchandani, A., Mulchandani, P., Chen, W., Wang, J., Rogers, K.R. (2002). Organophosphorus hydrolase-based amperometric sensor: modulation of sensitivity and substrate selectivity, *Electroanalysis*, 14: 273–276.
- [7] Barceló, D. (1991). Occurrence, handling and chromatographic determination of pesticides in the aquatic environment, *The Analyst*, 116: 681–689.
- [8] Sonja, Jevtić., Dalibor, Stanković., Anja, Jokić., Branka, Petković. (2019). A mini-review of electroanalytical methods for pesticides quantification, *University Thought Publication in Natural Sciences*, 9:19-32 doi:10.5937/univtho9-20130
- [9] Bird, S. B., Sutherland, T. D., Gresham, C., Oakeshott, J., Scott, C., Eddleston, M. (2008). OpdA, a bacterial organophosphorus hydrolase, prevents lethality in rats after poisoning with highly toxic organophosphorus pesticides, *Toxicol.*, 247: 88–92.
- [10] Harshit, D., Charmy, K., Nrupesh, P. (2017). Organophosphorus pesticides determination by novel HPLC and spectrophotometric method, *Food Chem.*, 230:448–453.
- [11] Yang, G., Xu, X., Shen, M., Wang, W., Xu, L., Chen, G., Fu, F. (2009). Speciation analysis of arsenic in *Mya arenaria* Linnaeus and Shrimp with capillary electrophoresis-inductively coupled plasma mass spectrometry, *Electrophoresis*, 30:1718–1723.
- [12] Tang, T., Deng, J., Zhang, M., Shi, G., Zhou, T. (2016). Quantum dot-DNA aptamer conjugates coupled with capillary electrophoresis: A universal strategy for ratiometric detection of organophosphorus pesticides, *Talanta*, 55–61.
- [13] Rahman, M. M., Ahmed, J. (2018). Cd-doped  $\text{Sb}_2\text{O}_4$  nanostructures modified glassy carbon electrode

- for efficient detection of melamine by electrochemical approach, *Biosens Bioelectron.*, 102:631–636.
- [14] Manisankar, P., Selvanathan, G., Vedhi, C. (2005). Utilization of sodium montmorillonite clay-modified electrode for the determination of isoproturon and carbendazim in soil and water samples, *Applied Clay Science*, 29: 249–257.
- [15] Manisankar, P., Selvanathan, G., Vedhi, C. (2006). Determination of pesticides using hetero polyacid montmorillonite clay modified electrode with surfactant, *Talanta*, 68:686-692.
- [16] Manisankar, P., Selvanathan, G., Vedhi, C. (2005). Utilization of polypyrrole modified electrode for the determination of pesticides, *International Journal of Environmental and Analytical Chemistry*, 85: 409–422.
- [17] Manisankar, P., Vedhi, C., Selvanathan, G. (2002). Electrochemical Studies of Isoproturon, *Trans SAEST*, 37: 135-140.
- [18] Manisankar, P., Vedhi, C., Selvanathan, G. (2003). Electrochemical Determination of Methyl Parathion Using Modified Electrode, *Toxicological and Environmental Chemistry*, 85:233-241.
- [19] Manisankar, P., Vedhi, C., Selvanathan, G. (2004). Electrochemical Studies of Carbendazim, *Bulletin of Electrochemistry*, 20:81-86.
- [20] Manisankar, P., Vedhi, C., Viswanathan, S., Prabu, H.G. (2004). Investigation on the usage of clay modified electrode for the electrochemical determination of some pollutants, *Journal of Environmental Science and Health -Part B*, B39: 89-100.
- [21] Chengzhou, Zhu., Guohai, Yang., He, Li., Dan, Du., Yuehe, Lin. (2015). Electrochemical Sensors and Biosensors Based on Nanomaterials and Nanostructures, *Anal. Chem.* 87:230–249.
- [22] Braininal, Kh., Stozhko, N., Bukharinova, M., Vikulova, E. (2018). Nanomaterials: Electrochemical Properties and Application in Sensors, *Physical Sciences Reviews*. 2018; 20188050
- [23] Ademar Wong, Tiago A. Silva, Fábio R. Caetano, Márcio F. Bergamini, Luiz, H. Marcolino-Junior, Orlando Fatibello-Filho, Bruno C. Janegitz. (2017) An Overview of Pesticide Monitoring at Environmental Samples Using Carbon Nanotubes-Based Electrochemical Sensors, *C- J Carbon Research*, 3: 8, doi:10.3390/c3010008
- [24] Sun, J., Guo, F., Shi, Q., Wu, H., Sun, Y., Chen, M., Diao, G. (2019). Electrochemical detection of paraquat based on silver nanoparticles/water-soluble pillar[5]arene functionalized graphene oxide modified glassy carbon electrode, *J Electroanal Chem.*, 847, Art. ID 113221.
- [25] Qian, J., Yang, X., Yang, Z., Zhu, G., Mao, H., Wang, K. (2015). Multiwalled carbon nanotube@reduced graphene oxide nanoribbon heterostructure: synthesis, intrinsic peroxidase-like catalytic activity, and its application in colorimetric biosensing, *J Mater Chem B*, 3:1624–1632.
- [26] Li, S.J., Qian, C., Wang, K., Hua, B.Y., Wang, F.B., Sheng, Z.H., Xia, X.H. (2012). Application of thermally reduced graphene oxide modified electrode in simultaneous determination of dihydroxybenzene isomers, *Sens Actuators B Chem.*, 174:441–448.
- [27] Akhavan, O., Ghaderi, E. (2009). Photocatalytic Reduction of Graphene Oxide Nanosheets on TiO<sub>2</sub> Thin Film for Photoinactivation of Bacteria in Solar Light Irradiation, *J Phys Chem C.*, 113: 20214–20220.
- [28] Choobtashani, M., Akhavan, O. (2013). Visible light-induced photocatalytic reduction of graphene oxide by tungsten oxide thin films, *Appl Surf Sci.*, 276:628–634.
- [29] Mani, V., Periasamy, A.P., Chen, S.M. (2012). Highly selective amperometric nitrite sensor based on chemically reduced graphene oxide modified electrode, *Electrochem. Commun.*, 17:75–78.
- [30] Yang, S., Li, G., Wang, G., Zhao, J., Qiao, Z., Qu, L. (2015). Decoration of chemically reduced graphene oxide modified carbon paste electrode with yttrium hexacyano ferrate nanoparticles for nanomolar detection of rutin, *Sens. Actuators B Chem.*, 206:126–132.
- [31] Ramesha, G.K., Sampath, S. (2009). Electrochemical Reduction of Oriented Graphene Oxide Films: An in Situ Raman Spectroelectrochemical Study, *J. Phys. Chem. C*, 113:7985–7989.
- [32] Shao, Y., Wang, J., Wu, H., Liu, J., Aksay, I.A., Lin, Y. (2010). Graphene Based Electrochemical Sensors and Biosensors: A Review, *Electroanalysis*, 22:1027–1036.
- [33] Peng, X.Y., Liu, X.X., Diamond, D., Lau, K.T. (2010). Synthesis of electrochemically-reduced graphene oxide film with controllable size and thickness and its use in supercapacitor, *Carbon*, 49:3488–3496.
- [34] Coster, Kumunda., Abolanle, S, Adekunle., Bhekie, B, Mamba., Ntuthuko, W. Hlongwa., Thabo, T. I. Nkambule. (2021). Electrochemical Detection of Environmental Pollutants Based on Graphene Derivatives: A Review, *Front. Mater.* 7:616787. doi: 10.3389/fmats.2020.616787
- [35] Piumie, Rajapaksha., Samuel, Cheeseman., Stuart, Hombsch., Billy, James, Murdoch., Sheeana, Gangadoo., Ewan, W. Blanch., Yen Truong., Daniel Cozzolino., Chris, F. McConville., Russell, J, Crawford., Vi, Khanh, Truong., Aaron, Elbourne., James Chapman. (2019). Antibacterial Properties of Graphene Oxide–Copper Oxide Nanoparticle Nanocomposites, *ACS Appl Bio Mater.* 2:5687–5696.
- [36] Mani, Govindasamy., Shen-Ming, Chen., Veerappan, Mani., Muthumariappan, Akilarasan., Sakthivel, Kogularasu., Boopathi, Subramani. (2017). Nanocomposites composed of layered molybdenum disulfide and graphene for highly sensitive amperometric determination of methyl parathion, *Microchim Acta*, 184: 725-733.
- [37] Shyamala, S., Kalaiarasi, S., Karpagavinayagam, P., Vedhi, C., Muthuchudarkodi, R. R., Saminathan, K., Lakshmi, A. (2021). Synthesis of metal oxide nanoparticles doped poly 3 anisidine nanocomposites with enhanced electrocatalytic activity for methanol oxidation, *Materials Today Proceedings*, Inpress..
- [38] Peter, Joseph., Karpagavinayagam, Petchimuthu., Vedhi, Chinnapiyan. (2016). Enhanced Band Gap Energy and Electrochromic Behaviour of Selenium Incorporated Copper Thin Film, *Journal of Physical Science*, 27: 41-54.
- [39] Kalaiarasi, S., Kavitha, M., Karpagavinayagam, P., Vedhi, C., Muthuchudarkodi, R. R. (2021). Tungsten oxide decorated graphene oxide nanocomposite: Chemical synthesis, characterization and application in super capacitors, *Materials Today Proceedings*, Inpress.