UNIVERSITI PUTRA MALAYSIA

MODIFICATION OF SCREEN PRINTED ELECTRODE USING REDUCED GRAPHENE OXIDE-GOLD NANOPARTICLES FOR VOLTAMMETRIC DETECTION OF DIURON AND FENITROTHION

NAFISEH SHAMS

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By

NAFISEH SHAMS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,In Fulfilment of the Requirements for the Degree of Doctor of Philosophy

November 2016

DEDICATION

I dedicate this thesis to my beloved husband for braving the many ups and downs with me during the trying times, steadily and stoically

You are indeed my pillar of strength

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair: Hong Ngee Lim, PhD
Faculty: Institute of Advanced Technology

In recent years, increasing attention has been given to the distortion of the aquatic ecosystem around the world. The risk of chemical pollution in water bodies is getting worst day by day. One of the possible sources of these pollutants is pesticides. Thus, the development of an on-line selective and sensitive monitoring system needs to be given priority. The use of electrochemical sensor is the most promising monitoring system due to its low instrumentation cost, simple operation, short response time, highly sensitivity and selectivity compared to other conventional monitoring systems. Recently, the use of nanomaterials such as reduced graphene oxide (rGO) and gold nanoparticles (AuNPs) have been given more attention among researchers around the world. They have been extensively used as sensing materials due to their outstanding properties in terms of conductivity, effective surface area, stability and catalytic effect. In this project, two different approaches have been used to fabricate the electrochemical sensor materials based on rGO/AuNPs nanocomposite for detection of diuron and fenitrothion as herbicide and insecticide respectively in natural waters.

In the first work, rGO/AuNPs nanocomposite was synthesized based on electrochemical co-reduction of graphene oxide and chloroauric acid via cyclic voltammetry technique on the surface of screen printed electrode (SPE). The fabricated sensor (rGO-AuNPs/SPE) showed higher sensitivity towards diuron and its cathodic peak current was directly correlated to the diuron concentration. The field emission scanning electron microscopy (FESEM) image shows the uniform distribution of AuNPs on the surface of rGO nanosheets. The presence of rGO nanosheets was further proven by Raman Spectroscopy. Under optimized conditions, the cathodic peak current was proportional to the diuron concentration over a wide range between 0.5 to 30.0 μg mL^{-1} with the detection limit of 0.125 μg mL^{-1} (S/N=3). The proposed diuron electrochemical sensor also exhibited a relative standard deviation of 4.25% for six replicate analysis of 10.0 μg mL^{-1} diuron and the response of the electrode was declined up to 20% after keeping for 30 days in ambient temperature. In addition, the sensor was successfully employed for the determination of diuron in real natural water samples including lake and sea water.

In spite of the fact that rGO-AuNPs/SPE sensor (via electrochemical reduction of GO) is environmentally green technique, nevertheless, the modified substrate is polarized in a short potential range due to incomplete reduction of GO functional groups. Therefore, in the second study, a new synthesis procedure was reported for the preparation of rGO/AuNPs nanocomposite using ethylenediamine (en) as a cross- linker for chemical reduction of GO functional groups in order to fabricate a polarized sensor. The constructed nanocomposite (AuNPs/rGO-en) was homogenized in dimethylformamide (DMF) and drop-casted on a SPE to fabricate an electrochemical sensor (AuNPs/rGO-en/SPE) which was sensitive to fenitrothion. The nanocomposite electrode was characterized with FESEM, X-Ray diffraction (XRD) spectroscopy, Fourier transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), Raman spectroscopy and cyclic voltammetry (CV). The anodic peak current at around 0.06 V was proportional to fenitrothion concentration over a wide range of 0.1 to 6.25 ng mL^{-1} with the limit of detection of 0.036 ng mL^{-1} (S/N=3). Moreover, in order to evaluate the repeatability of the AuNP/en-rGO/SPE, the peak currents of fenitrothion at two different concentrations (0.5 ng mL^{-1} and 4.0 ng mL^{-1}) were determined successively under optimum conditions for six times with the same modified sensor, and the RSD values were found to be 4.1% and 4.3%, respectively, exhibiting good repeatability. The stability study showed that the oxidation peak current of fenitrothion at 4.0 ng mL^{-1} decreased 2.2% after recording 50 successivecyclic voltammograms. In addition, the proposed senor was successfully employed for the determination of fenitrothion residue in the natural water samples including tap and lake water. The validity of the response was checked with gas chromatography as a standard method and the result was in agreement with constructed sensor.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENGUBAHSUAIAN ELEKTROD CETAK SKRIN MENGGUAN-NANOBAHAN EMAS UNTUK PENGESANAN VOLTAMMETRIK DIURON DAN FENITROTHION

Oleh

NAFISEH SHAMS

November 2016

Pengerusi : Hong Ngee Lim, PhD
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Dalam tahun-tahun kebelakangan ini, peningkatan penumpuan terhadap herotan akuatik ekosistem diseluruh dunia telah diberikan. Risiko pencemaran kimia dalam badan-badan air telah menjadi teruk dari hari ke hari. Salah satu sumber utama pencemaran ini ialah racun perosak. Oleh itu, pekembangan secara dalam talian bagi pengawasan system yang memilih dan peka perlu diberikan keutamaan. Penggunaan sensor elektrokimia adalah pengawasan system yang lebih menjanjikan disebabkan oleh peralatan kos rendah, mudah untuk dikendalikan, sambutan masa yang singkat, lebih peka dan pemilihan berbanding pengawasan sistem konvensional yang lain. Baru-baru ini, penggunaan bahan nano seperti grafin (rGO) dan nanopartikel emas (AuNPs) telah diberikan perhatian antara penyelidik diseluruh dunia. Ianya telah digunakan secara meluas sebagai bahan pengesanan disebabkan sifatnya yang cemerlang dan had pengesanan sasaran analit yang rendah telah direkodkan. Dalam projek ini, dua pendekatan yang berbeza telah digunakan untuk membikin bahan sensor elektrokimia berasaskan rGO/AuNPs kompositnano untuk pengesanan diuron dan fenitrothion, masing-masing sebagai racun herba dan rerun serangga dalam air semula jadi.

Dalam kerja yang pertama, rGO/AuNPs kompositnano telah disintesis berasaskan elektrokimia bersama pengurangan grafin oksida (GO) dan acid chloroauric melalui teknik voltammetri berkitar pada skrin elektrod bercetak (SPE). Penghasilan sensor (rGO/AuNPs/SPE) menunjukkan kepekaan yang tinggi cenderung terhadap diuron dan puncak arus katodenya adalah berkolerasi secara terus dengan kepekatan diuron. Imej mikroskop elektron pengimbas pancaran medan (FESEM) menunjukkan kehadiran AuNPs yang sama rata di atas permukaan nano kepingan rGO. Raman spektrometri membuktikan lagi pengurangan GO kepada nano kepingan rGO melalui pengurangan elektrokimia. Di bawah keadaan optimum, puncak arus katode adalah berkadaran dengan kepekatan diuron di atas julat yang luas di antara 0.5 dan 30.0 $\mu g\ mL^{-1}$ dengan

had pengesanan 0.125 µg mL^{-1} (S/N=3). Sensor elektrokimia yang dicadangkan juga mempamirkan relatif sisihan piawai sebanyak 4.25% berdasarkan enam analisis yang direplikakan bagi 10.0 µg mL^{-1} diuron dan sambutan bagi elektrod menurun 20% selepas disimpan selama 30 hari dalam keadaan sekitaran. Tambahan pula, sensor ini telah berjaya bekerja untuk penentuan diuron dalam air semula jadi nyata termasuk tasik dan air laut.

Meskipun secara faktanya sensor rGO-AuNPs/SPE (melalui elektrokimia pengurangan GO) adalah kaedah hijau persekitaran, namun substrat yang diubah suai adalah berkutub dalam julat potensi yang pendek disebabkan oleh pengurangan yang tidak lengkap GO kumpulan berfungsi. Oleh itu, dalam kajian kedua, satu tatacara sintesis baru telah dilaporkan bagi penyediaan rGO-AuNPs kompositnano menggunakan ethylenediamin (en) sebagai pemaut silang untuk pengurangan kumpulan kefungsian GO secara kimia bagi pembikinan sensor berkutub. Penghasilan kompositnano (AuNPs/en-rGO) telah dihomogenkan dalam dimethylformamide (DMF) dan kaedah 'drop-casted' di atas SPE bagi pembikinan sensor elektrokimia yang peka terhadap fenitrothion. Elecktrod kompositnano telah dicirikan dengan FESEM, EDX, Spektroskopi Pembiasan X-Ray (XRD), Spektroskopi inframerah transformasi Fourioer (FTIR), Spektroskopi elektrokimia impedan (EIS), Spektroskopi Raman and voltammetri berkitar (CV). Puncak arus anodal pada kira-kira 0.06V adalah berkadaran pada kepekatan fenitrothion di atas julat yang luas di antara 0.1 to 6.25 ng mL^{-1}, dengan had pengesanan 0.036 ng mL^{-1} (S/N=3). Tambahan pula, untuk menilai kebolehulangan AuNP/en-rGO/SPE, puncak arus fenitrothion pada dua kepekatan yang berbeza (0.5 ng mL^{-1} and 4.0 ng mL^{-1}) telah berjaya ditentukan di bawah keadaan optimum enam kali dengan pengubah suaian sensor yang sama, dan nilai RSD didapati masing-masing 4.1% dan 4.3%, mempamerkan kebolehulangan yang baik. Kajian kestabilan menunjukkan bahawa pengoksidaan puncak arus fenitrothion pada 4.0 ng mL^{-1} menurun 2.2% selepas mencatat 50 kitaran voltammetri berturut-urut. Tambahan pula, sensor ini telah berjaya bekerja untuk penentuan sisa fenitrothion dalam pelbagai sampel air termasuk air paip dan air tasik. Kesahan sambutan telah diperiksakan dengan gas chromatografi sebagai keadah piawaian dan keputusan adalah dalam persetujuan dengan sensor yang dihasilkan.

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I certify that a Thesis Examination Committee has met 2016to conduct the final examination of Nafiseh Shams on her thesis entitled "Modification of Screen Printed Electrode using Reduced Graphene Oxide-Gold Nanoparticles for Voltammetric Detection of Diuron and Fenitrothion" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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I hereby confirm that:

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LIST OF ABBREVIATIONS

AdSV	Adsorptive Stripping Voltammetry
ASV	Anodic stripping voltammetry
C.E	Counter electrode
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
DPV	Differential pulse voltammetry
D	Diffusion coefficient
DMF	Dimethyl formamide
DME	Dropping mercury electrode
EIS	Electrochemical impedance spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
F	Faradic constant
FESEM	Filed emission scanning electron microscopy
FID	Flame ionization detector
FTIR	Fourier Transformed Infrared Spectroscopy
GC	Gas chromatography
GC-MAS	Gas chromatography- mass spectrometry
R	Gas constant
GCE	Glassy carbon electrode

GO	Graphene Oxide
AuNP/en-rGO	Gold nanoparticles/ ethylenediamine-reduced Graphene Oxide
K	Kelvin
LOD	Limit of detection
LOQ	Limit of quantitative
LSV	Linear Sweep Voltammetry
NPs	Nanoparticles
NPV	Normal pulse voltammetry
n	Number of electron transfer
PAMAN	Polyamidoamine
rGO-AuNP	Reduced graphene oxide- gold nanoparticle
rGO	Reduced graphene oxide
SEM	Scanning electron microscopy
HME	Hanging mercury electrode
RE	Reference electrode
RSD	Relative standard deviation
υ	Scan rate
SPE	Screen-printed electrode
SWV	Square wave voltammetry
A	Surface area
α	transition coefficient

UV	Ultraviolet
W.E	Working electrode
XRD	X-ray diffractometry

CHAPTER 1

INTRODUCTION

1.1 Background of study

Undoubtedly, human population around the world is increasing day by day. It is expected that by 2050 the population will reach more than 9 billion and still expected that our population will increase more than 2 billion within the next 40 years (Matlack, 2010). As a result, we will need to double the amount of food we currently produce in order to feed everyone. This has resulted in the maximization of yields of many crops grown under conditions that reduce insect and disease pressure and on soils enriched with inorganic fertilizer. Therefore, the agriculture industry has changed a lot over the past century and too many efforts have been done to improve soil fertility to reach more quantitative and qualitative of agricultural products. One of the major problems in the agricultural sectors is the loss of crop products due to the insect pests, which targeted on the specific hosts and lead serious lesions on fruit and vegetables (Litz & Gray, 1995). Research has shown that since the 1940s, some of the chemicals such as pesticides helps in increasing the crop yield by preventing the destruction of food crops by pests or unpleasant plants and also provides a better plant quality (Grung *et al.*, 2015). Moreover, it was also been reported in the USA, by ceasing the use of pesticides can lead to the reduction of the total output of the crops and livestock about 30% and therefore increase the price of farm products around 50 to 70% (Wolfenburger *et al.*, 2004). As a matter of fact, the pesticides industry has become one of the most important supporting industries in agriculture. For instance, just in Malaysia, the estimation value of herbicides imported in 1995 was 31,708 million Ringgit (Matlack, 2010). Even though pesticides has been considered as the toxic and harmful chemical to the environment, but their contribution in controlling and monitoring the pests, and also deficit alternative, equivalent and effective methods available have made the use of pesticides the best candidate in controlling the pest and thus in overall increasing the crop production.The extensive use of pesticides for agricultural products has resulted in the presence of residues in numerous environmental media. Pesticide contamination on the water surface has been well documented worldwide and constitute a major issue that gives rise to concerns at local, regional, national and global scales (Cerejeira *et al.*, 2003; Huber *et al.*, 2000; Planas *et al.*, 1997). However, since the use of pesticides is necessary for agricultural industries, the environmental contamination of their residue need to be taken into consideration and appropriate measures should be put in place to prevent their environmental pollution (Hikita *et al.*, 1977).

There has been a great deal of concern and argument for decades over pesticides and their toxicology to human and animals. However pesticide consumption is necessary to improve the agricultural products, but there is a large body of evidence claim that pesticides will cause too many side effects in human and animals due to direct and indirectly environmental contamination. Multiple organ cancer is one of the most crucial problems due to misuse of pesticides (Anwar, 1997). The endocrine complication is another problem which is caused by the effects of pesticides (van der Werf, 1996). The potential side effect related to endocrine complication always affected on male hormones such as testosterone which are responsible for healthy male reproductive systems. In addition, infertility and sterility are other reported potential side effects, when an individual is vulnerable to pesticides. Most of these problems commonly affect people who are unprotected against pesticides such as workers in farms or daily consumers of sprayed products. It was reported that most of the gardeners and farmers have higher possibilities of being affected with brain damage, which may result in the lack of ability to talk smoothly, detect words or colours (Edwards, 2013). An even human embryo is also not safe if there is too much exposure to pesticide and this excessive vulnerable could lead to miscarriage and birth defects (van der Werf, 1996). Therefore, exposure to pesticides must be avoided for pregnant mothers. Besides, respiratory disorders such as wheezing, chronic bronchitis and asthma, and skin irritation are the other common diseases occur in humans who are frequently vulnerable to the pesticides in agricultural products (Ündeğer & Başaran, 2005). Aforementioned exposures to pesticides have reported a shocking number of deaths correlated to either chronic kidney sickness or intestinal nephritis in India, and normally victims are persons who worked on farms and exposed to sprayed pesticides. Negative impacts of pesticides not only affecting human health but also affecting on animals, environmental and water as well and this phenomenon was observed to indirectly lead to many forthcoming problems to humans being. Therefore, the environmental monitoring and rapid sensing of these compounds have become important urgency in order to ensure the homeland security and health protection (Arduini *et al.*, 2006; Corley, 2003; Fukata *et al.*, 2005). In conclusion, the necessity to develop simple, selective and sensitive on-site monitoring systems need to be considered and given a major priority.

1.2 Problem statement

Diuron, N'-(3,4-dichlorophenyl)-N, N-dimethylurea (DCMU), is an herbicide derived from urea. It is considered to be highly toxic and persistent when applied in high dosages to the soil, with a half-life of over 300 days (Katsumata et al., 2009). In order to evaluate the impact of diuron on coral reefs, it is important to monitor its concentration in coastal and coral reef waters. Malaysia is the world's second largest palm oil producer (Ong & Goh, 2002). Previous studies have shown that pesticides such as diuron have played an important role in controlling and preventing pests and harmful plants, and indirectly increase palm oil production (Sapozhnikova, Wirth, Schiff, Brown, & Fulton, 2007). As a result, it is often detected in ground water and surface water. However, it is considered to be a priority hazardous substance by the European Commission (Feng et al., 2009). Diuron kills plants by blocking electron transport at photosystem II, thus inhibiting photosynthesis (R. J. Jones & Kerswell, 2003). Ecotoxicological studies show that diuron has significant impacts on the host and/or symbionts of corals and aquatics (R. Jones, 2005).Moreover, Fenitrothion [O,O-dimethyl O-(4-nitro-m-tolyl) phosphor] is a contact organophosphate insecticide that has been used since 1959 in place of dichlorodiphenyltrichloroethane (DDT) for operational control of insects on rice, cereals, fruits, vegetables, stored grains, cotton, and in forests, and for fly, mosquito, and cockroach control in public health programs (Sreedhar *et al*. 2011). Generally, organophosphate compounds disrupt the cholinesterase enzyme that regulates acetylcholine (Cremisini *et al*. 1995; Fennouh *et al.* 1997; Zhang et al. 2001). Although fenitrothion is useful for the treatment of agricultural products, its residue is reported to be very toxic to non-target species such as birds, mammals, and aquatic life (Sreedhar *et al.* 2015; Story *et al*. 2011).

Various quantitative analysis of pesticides have been carried out with different techniques such as high-performance liquid chromatography (HPLC) (Bester *et al.*, 2001; Leandro *et al.*, 2006; Topuz *et al.*, 2005), mass spectrometry *(Dallüge et al., 2002*), molecular imprinting (Pardieu *et al.*, 2009; Sánchez-Barragán *et al.*, 2007), gas chromatography (Berijani *et al.*, 2006; Eisert & Levsen, 1995; Lehotay *et al.*, 2005), enzyme-linked immunosorbent assay (ELISA) (Ferrer *et al.*, 1997; Liang *et al.*, 2007; Wengatz *et al.*, 1998), biosensors (Liu *et al.*, 2014; Sassolas *et al.*, 2012; Zhang *et al.*, 2015) and electrochemical sensors (Bakas *et al.*, 2014; Rapini & Marrazza, 2015). It is clear that chromatography and mass spectrometry equipment are expensive and require tedious sample treatment including extraction, as well as skilled technicians for operations. On the other hand, ELISA systems require long-time analysis, have low stability, disposable and sometimes have low precision due to the use of biological elements for detection. As a result, the development of rapid, inexpensive, sensitive and on-site analytical strategies for detection of pesticides is desirable. On the other hand, rGO-AuNPs nanocomposite films can generate synergy on electrocatalytic activity and improve the sensitivity of the sensors. The introduction of AuNPs can both improve the conductivity of rGO and prevent the agglomeration process.

In this respect, electrochemical sensors are adequate candidates for quantitative analysis of pesticides due to their great benefits including simplicity, portability and low cost. They give attractive sensing characteristics, accurate results and fast response time with little or no complications of pre-treatment steps, thereby opening up the possibilities of direct on-site analysis with intuitive devices. Hence, they are used as alternative analytical methods for pesticide's control (Agüı *et al.*, 2002; Kurzawa & Kowalczyk-Marzec, 2004; Ronkainen *et al.*, 2010). In this sense rGO-AuNPs nanocomposites based electrochemical sensors improve the performance of the electrochemical reactions, due to increasing on surface area, as well as achieving faster kinetics (Downard *et al.*, 2006; Welch & Compton, 2006).

1.3 Hypothesis of study

- The combination of rGO and AuNPs has a synergic effect in terms of surface area and conductivity to enhance the performance of electrochemical detection of pesticides.
- Diuron and fenitrothion as two pesticide compounds can reduce/oxidize on the surface of modified electrodes.

1.4 Research objective

The main objective of this study is to develop simple, rapid, stable, selective and sensitive electrochemical sensors based on reduced graphene oxide/gold nanoparticles for determination of some pesticides in natural water resources. The specific objectives of the research are summarized and listed as follows:

i. To synthesizerGO/AuNPs nanocomposites based on two different reduction methods through electrochemical and chemical methods.

ii. To fabricate electrochemical sensors based on rGO/AuNPs without using any mediator.

iii. To optimize the electrochemical sensors towards diuron and fenitrothion detection.

iv. To evaluate selectivity, stability and precision of the sensors.

v. To evaluate the applicability of the fabricated electrochemical sensors in real natural water samples.

vi. To validate accuracy of the electrochemical sensors with a standard test method.

1.5 Scope and limitation

Electroanalytical sensors can play an important role in monitoring the environmental pollution and thus indirectly protect our green nature to become contaminate and extinct for the next century. The electroanalytical sensor devices have been satisfied many of the requirements for on-site monitoring of priority pollutants. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and cheap. These advantages provide them to be used as ultra-microelectrodes, highly sensitive chemicals, computerized instrumentations and flow detectors. On the other hand, electrochemical sensors have shown some limitations such as short-term stability, troublesome electron-transfer pathways and electrochemically active interferences in the sample. These kinds of problems become more serious in real sample analysis due to the unknown matrix and in this case, even standard addition method cannot be useful. So the improvement of these drawbacks must be given priority.

1.6 Thesis outline

This thesis contains five chapters including an introduction, literature review, methodology, result and discussion and finally conclusion and recommendation. A brief idea of each chapter is given as bellow.

Chapter One is divided into six sections. This chapter is started with the background of study and then, the toxicology of pesticide to human and environment is being introduced as the problem statement. In the third section, the hypotheses of the proposed research study are mentioned and the objectives of this research are described in the fourth section. Finally, scope and limitation and thesis outline are being explained in the fifth and sixth section of this chapter, respectively.

Chapter Two highlights the basic principles of this work and detailed literature review of previous techniques based on electrochemical sensors. Diuron and fenitrothion are introduced and after an overview on the determination of diuron and fenitrothion in water through different methods, the classification of sensors is discussed. After that voltammetric techniques are explained as the most sensitive electrochemical techniques. This chapter is followed by an introduction on GO and AuNPs, its unique properties and synthesis methods. Finally, the voltammetric sensors have been reviewed separately for the determination of diuron and fenitrothion.

Chapter Three describes the materials and methods of the diuron sensor. Synthesis of GO, rGO and rGO-AuNPs were illustrated.All instruments used for characterization of nanocomposites such asfield emission scanning electron microscopy (FESEM), and Raman spectrometry are introduced in this chapter. Moreover, electrochemical devices for quantitative analysis of diuron also described in this chapter. Finally, results and discussion were demonstrated and the details of the results are interpreted and discussed.

Chapter Four describes the materials and methods of the fenitrothion sensor. Synthesis of GO, rGO-en and AuNPs/en-rGO were illustrated. All instruments used for characterization of nanocomposites such asfield emission scanning electron microscopy (FESEM), Fourier transform infrared microscopy (FTIR), X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS) and Raman spectrometry are introduced in this chapter. Moreover, electrochemical devices for quantitative analysis of fenitrothion also described in this chapter. Finally, results and discussion were demonstrated and the details of the results are interpreted and discussed.

The conclusion of the research study is demonstrated in Chapter Five by summarizing the results of the study and given some suggestions for further research efforts.

Some additional subjects are covered in Chapter Six as Appendices.

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