UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF ELECTROSPUN-CELLULOSE FIBRE/GRAPHENE OXIDE FOR ORGANOPHOSPHORUS PESTICIDES ADSORPTION STUDY USING MICROEXTRACTION APPROACH

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By

NOR IZZATI FIKRAH BINTI ARIS

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SYNTHESIS AND CHARACTERIZATION OF ELECTROSPUN-CELLULOSE FIBRE/GRAPHENE OXIDE FOR ORGANOPHOSPHORUS PESTICIDES ADSORPTION STUDY USING MICROEXTRACTION APPROACH

By

NOR IZZATI FIKRAH BINTI ARIS

October 2019

Chair : Sazlinda binti Kamaruzaman, PhD
Faculty : Science

Electrospun cellulose nanofiber/graphene oxide (CNF/GO) was synthesized, characterized and successfully utilized in solid phase membrane tip adsorption (SPMTA) as an adsorbent towards a simultaneous analysis of polar organophosphorus pesticides (OPPs) in several food and water samples prior to ultra performance liquid chromatography coupled with ultraviolet (UPLC-UV) analysis. The electrospun CNF/GO was characterized using Fourier transform-infrared spectroscopy (FTIR), BET surface area and field emission scanning electron microscopy (FESEM). Four OPPs as model analytes were selected, namely methyl parathion, ethoprophos, sulfotepp and chlorpyrifos. Several important parameters, such as sample pH, adsorption time, adsorbent dosage and initial concentration were optimized. The electrospun CNF/GO-SPMTA method showed a good linearity in between 0.05 and 10 mg/L under the optimum adsorption conditions (sample pH 12; 5 mg of adsorbent dosage; 15 min of adsorption time) with excellent correlation coefficients (R^2 = 0.994 to 0.999). Acceptable RSDs for intra day (0.06 to 5.44%, n = 3) and inter day (0.17 to 7.76%, n = 3), low limits of detection (0.01 to 0.05 mg/L) and satisfactory consistency in adsorption (71.14 to 99.95%) were obtained. The adsorption data was well followed the second order kinetic model and fits the Freundlich adsorption model. A possible mechanism is by exchanging or sharing of electrons between the OPPs molecules and the vacant active sites of the electrospun CNF/GO. Therefore, the developed method showed a good acceptance to the samples and the newly synthesized electrospun CNF/GO showed a great adsorbent potential for OPPs analysis and can be used as an alternative adsorbent to be utilized in environmental applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN ELEKTROSPUN-SERAT SELULOSA/GRAFIN OKSIDA UNTUK KAJIAN PENJERAPAN RACUN PEROSAK ORGANOFOSPOR MENGGUNAKAN PENDEKATAN EKSTRAKSI MIKRO

Oleh

NOR IZZATI FIKRAH BINTI ARIS

Oktober 2019

Pengerusi : Sazlinda binti Kamaruzaman, PhD
Fakulti : Sains

Serat selulosa nano/grafin oksida (CNF/GO) elektrospun telah disintesis, dicirikan dan berjaya digunakan dalam kajian penjerapan tip membran fasa pepejal (SPMTA) sebagai penyerap terhadap analisis racun perosak organofospor (OPPs) dalam beberapa sampel makanan dan air menggunakan analisis kromatografi cecair berprestasi ultra dengan pengesan ultraungu (UPLC-UV). Elektospun CNF/GO dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR), kawasan permukaan (BET) dan mikroskop pengimbasan elektron pelepasan medan (FESEM). Empat OPPs sebagai model analit dipilih, iaitu metil paration, etopropos, sulfotep dan khlorpirifos. Beberapa parameter penting seperti pH sampel, masa penjerapan, dos penjerap dan kepekatan awal telah dioptimumkan. Kaedah elektrospun CNF/GO-SPMTA menunjukkan julat lurus yang baik di antara 0.05 dan 10 mg/L di bawah keadaan penjerapan optimum (pH sampel 12; 5 mg dos penjerap; 15 min masa penjerapan) dengan pekali korelasi yang sangat baik (R^2 = 0.994 hingga 0.999). Jumlah RSDs yang diterima untuk sehari (0.06 hingga 5.44%, n = 3) dan antara hari (0.17 hingga 7.76%, n = 3), had pengesanan yang rendah (0.01 hingga 0.05 mg/L) dan konsisten penjerapaan yang memuaskan (71.14 hingga 99.95%). Data penjerapan juga didapati mengikuti model kinetik pesanan kedua dan sesuai dengan model penjerapan Freundlich. Mekanisma yang berlaku mungkin adalah dengan bertukar atau berkongsi elektron antara molekul OPPs dan tapak aktif kosong elektrospun CNF/GO. Oleh itu, kaedah yang dibangunkan menunjukkan penerimaan yang baik terhadap sampel dan elektrospun yang baru disintesis CNF/GO menunjukkan potensi penjerap yang hebat untuk analisis OPPs dan boleh menjadi penjerap alternatif yang akan digunakan dalam aplikasi alam sekitar.

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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 Master of Science. The members of the Supervisory Committee were as follows:

Sazlinda binti Kamaruzaman, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Norizah binti Abdul Rahman, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Noorfatimah binti Yahaya, PhD
Senior Lecturer
Advanced Medical and Dental Institute
Universiti Sains Malaysia
(Member)

____
ZALILAH MOHD SHARIFF, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Name and Matric No.: Nor Izzati Fikrah binti Aris (GS 49969)

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Signature: ____________________
Name of Chairman of Supervisory Committee: Sazlinda binti Kamaruzaman

Signature: ____________________
Name of Member of Supervisory Committee: Norizah binti Abdul Rahman

Signature: ____________________
Name of Member of Supervisory Committee: Noorfatimah binti Yahaya

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LIST OF ABBREVIATIONS

OPPs	Organophosphorus Pesticides
CA	Cellulose Acetate
GO	Graphene Oxide
CNF/GO	Cellulose Nanofiber/Graphene Oxide
SPMTA	Solid Phase Membrane Tip Adsorption
UPLC-UV	Ultra Performance Liquid Chromatography-Ultraviolet Detector
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
BET	Brunauer–Emmett–Teller
LOD	Limit of Detection
LOQ	Limit of Quantification
RSD	Relative Standard Deviation
SPE	Solid Phase Extraction
SPMTE	Solid Phase Membrane Tip Extraction
DLLME	Dispersive Liquid-Liquid Microextraction
v/v	Volume/Volume
wt%	Percentage of The Mass Fraction of The Species
q_e	Adsorption Capacity
q_m	Maximum Adsorption Capacity
C_e	Equilibrium Concentration
K_L	Langmuir Constant
n	Freundlich Adsorption Favorability

K_F	Freundlich Constants
q_t	Adsorption Capacity at Time t
q_e	Adsorption Capacity at Equilibrium
k_1	Pseudo First Order Rate Constant
k_2	Pseudo Second Order Rate Constant
C_f	Final Concentration
C_i	Initial Concentration
C_{des}	Desorbed Concentration
C_{ad}	Adsorbed Concentration
R^2	Correlation Coefficients
o	Standard Deviation
S	Slope of The Calibration Curve

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Organophosphorus pesticides (OPPs) are among the most broadly used pesticides with high toxicity in the world since the 1970s (Wanjeri *et al.*, 2018). Their popularity is largely contributed by their favourable characteristics such as short persistence and biodegradable (Sapahin *et al.*, 2014). Methyl parathion (O,O-Dimethyl-O-p-nitrophenylphosphorothioate), ethoprophos (1-(ethoxy-propylsulfanylphosphoryl)sulfanylpropane), chlorpyrifos (O,O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate) and sulfotepp (diethoxyphosphinothioyloxy-diethoxy-sulfanylidene-λ5-phosphane) are examples from the most used classes of OPPs. Frequent exposure for a long period of time to even low (ppb) levels of OPPs from air, water and food can lead to OPPs accumulation in the body due to their ability to inhibit acetylcholinesterase activity and reported to exhibit teratogenicity, immunotoxicity, cytotoxicity and genotoxicity (Suo *et al.*, 2018). Thus result in dysfunction of many behavioural and autonomic systems, eventually leading to muscles and respiratory weakness or paralysis as well as death (Liu *et al.*, 2018; Wanjeri *et al.*, 2018).

According to the European Union, a maximum level for each pesticides and total pesticides in water that intended for human consumption is 0.1 µg/L and 0.5 µg/L respectively (Funari, 2012). Whereas the maximum residue limits set by the European Unions for pesticide residues in vegetables and fruits is 0.01 mg/kg (European Economic Community (EEC), 1976; European Communities, 2005).

Since the OPPs concentration in the real samples are in trace amounts, some techniques are necessary to determine these compounds. The most conventional technique for the OPPs analysis in food and water samples is adsorption. It is due to its availability of different adsorbents, simple and low cost. Previously, the universally method used for OPPs analysis in food and water is solid phase adsorption (Picó *et al.*, 2007). However, this method have several drawbacks, such as it requires a larger quantities of organic solvents and adsorbents in which limit the extensive deployment of solid phase adsorption (Yan *et al.*, 2014).

Pipette-tip solid phase adsorption is an attractive alternatives to normal solid phase adsorption in terms of the set up. This miniaturized method offers the superior and unique combination of shorter operation period, lower analysis costs, lower consumptions of organic solvent and adsorbent dosage and economic methods of targeting multiple analytes (Hasegawa *et al.*, 2011; Gao *et al.*, 2012). This method involve the utilization of tiny adsorbent held in a holder as an adsorption medium and it relies on the fact that most of the analytes are adsorb in the adsorption region of the adsorbent through some interaction by stirring the solution. This adsorption corresponds specifically to the bonds present in the analytes and the sorbent. In general, the efficiency of pipette-tip solid phase adsorption relies on the adsorbents performance. Thus, an adsorbents exploration with great adsorption capacity is essential (Martín-Esteban, 2013).

From the previous study, OPPs adsorption from aqueous solution has been investigated using amino-substituted p-tert-butylcalix[4]arene-based magnetic sporopollenin, Calix-EPPTMS-MS (Kamboh *et al.*, 2016). The study was conducted using various different pH values, adsorbent dosage and contact times.

The scope of this study is to investigate the adsorption of OPPs namely methyl parathion, sulfotepp, chlorpyrifos and ethoprophos using electrospun cellulose nanofiber/graphene oxide (CNF/GO) as an adsorbent in solid phase membrane tip adsorption (SPMTA) technique. These four pesticides was chosen as a target analytes in the SPMTA as to indicate which structure are the most compatible and work best with the electrospun CNF/GO as an adsorbent during the adsorption process. SPMTA technique offers the superior combination of fast operation period. Electrospun CNF/GO is consists of high density of –OH and –COOH groups that will enhance the adsorption of the OPPs. The influence of sample pH, adsorption time, initial concentration and adsorbent dosage were investigated to optimize the conditions for maximum OPPs adsorption from environmental water and food samples specifically from Sungai Pahang, Tasik Cheras, cabbages and rice. The experimental data obtained were calculated and fitted using adsorption isotherm and adsorption kinetic studies. The analysis of the OPPs from selected environmental water and food samples was done prior to ultra performance liquid chromatography coupled with ultraviolet detector (UPLC-UV).

1.2 Problem Statement

Over so many years, pesticides been used by growers and farmers for food production in order to increase the quality and the production of crops. In a consequence, consumers are expose to pesticides even though the exposure are usually in a small number of quantities (Sanagi *et al.*, 2013). Due to sparing of plants or crops, only some pesticides remain in crops in a significant amounts and others leach out in water and disperse into environment through wind, rain and fog (Abdelhameed *et al.*, 2018). Contamination of agricultural products and environmental water has become a major concern, as OPPs are one of the most common classes of pesticides involved in poisoning. Thus, analysis and monitoring of trace levels of OPPs in environmental water and food contamination are very crucial as for environmental control and human health protection (Sanagi *et al.*, 2013). However, OPPs determination constitutes a real analytical challenge for very low concentration levels in environmental water and food samples.

These OPPs have the possibility to be analyzed by liquid chromatography (LC) as they exhibit a wide range of physico chemical properties. UPLC is a chromatographic technique that has overcome conventional HPLC limitations such as speed of analysis and lower separation capacity (Romera *et al.*, 2018).

Consequently, effective adsorption of OPPs from water and food samples has become a global issue. Several techniques have been developed for pollutant determination, such as photocatalysis, oxidation (Kamboh *et al.*, 2016), membrane separation, ion-exchange (Saini and Kumar, 2016) and adsorption (Liu *et al.*, 2018). Among all methods mentioned above, adsorption process has recently considered as a promising technique for OPPs adsorption due to its availability of different adsorbents, simple, economical, possible low cost and environment friendly. Unfortunately, obtaining adsorbents for effective and rapid adsorption of OPPs from water and food samples remains a great challenge.

Adsorbents that have been reported for fast adsorption of pesticides are organic porous polymers (Saini and Kumar, 2016), cellulose acetate (CA) (Du and Pan, 2014), silica particles (Liu *et al.*, 2018), graphene oxide (GO) (Rashidi Nodeh *et al.*, 2017) and multi-walled carbon nanotubes (Zhao *et al.*, 2012). CA have been widely investigated as a type of hybrid adsorbent and exhibit potential applications for pesticides adsorption. CA is highly hydrophilic in nature and has high strength, large specific surface area and might be molded easily into different forms, such as spheres, fibers and membranes making them a suitable candidate as a mechanical support and an adsorbent (Bhongsuwan and Bhongsuwan, 2008; Kafy *et al.*, 2016).

CA has strong inter and intra molecular hydrogen bondings that are responsible for the hydrophilic nature of the polymer. However, CA have some limitations in terms of high moisture absorption, associated dimensional instability as well as ultraviolet (UV) stability. CA also can be easily attacked by concentrated alkalies and acids. Therefore CA could be tailored and modify with graphene oxide (GO) in order to overcome the limitation and enhancing the adsorption capacity of analytes (Kafy *et al.*, 2016). Recently, GO which is a class of two-dimensional material is broadly used in many research fields as for their high specific surface area and high adsorption capacity. Moreover GO has a high mechanical strength and a range of oxygen functional groups for instance ketone, carbonyls, epoxides, carboxylic and hydroxyl group on both edges and basal planes (Tabani *et al.*, 2013; Yang *et al.*, 2017) thus making GO a hydrophilic material. These oxygen functionalities provide the affinity toward a great number of compounds over different interactions, such as π–π stacking dispersion forces, hydrogen bonding and electrostatic interaction (Wanjeri *et al.*, 2018) which are ideal characteristics for an adsorbent as it extend the application and enhance the material properties towards polar analytes (Zhang *et al.*, 2018).

Combining CA and GO could be a feasible way to overcome the limitations for the adsorption of polar OPPs from food and water samples. As the hydrophilicity properties will be increased through these combinations, a narrow pore-size distribution and improve adsorption capacity will be acquired. In enhancing the capabilities and advantages of this adsorbent, a special method, electrospinning is introduced. Electrospun process has the ability to form a fibrous membrane with diameters ranging from micrometers to several nanometers with excellent pores interconnection, high porosity and expanded functional groups as high density of functional groups (–COOH and –OH) are grafted on the fiber (Ao *et al.*, 2017; Pordel *et al.*, 2019). The combination of CA and GO is considered to enhance the efficiency, strengthen the structure and reinforce the fiber as the addition of inorganic or organic materials to electrospun solution leads to the production of nanofibers with additional properties.

1.3 Objectives

The objectives of the study are as follows:

1) To synthesize and characterize the electrospun-cellulose nanofiber/graphene oxide (CNF/GO).

2) To optimize the adsorption parameters by using electrospun CNF/GO as an adsorbent by solid phase membrane tip adsorption (SPMTA) technique.

3) To determine the performance of the proposed method by determining the linearity, consistency in adsorption, repeatability, limit of detection (LOD) and limit of quantification (LOQ) of the method.

4) To apply the proposed method to analyze various water and food samples.

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BIODATA OF STUDENT

Nor Izzati Fikrah binti Aris is from Pahang, Malaysia and was born in the year of 1994. She completed her primary school study and graduated from SK Kerdau in the year 2006. She then pursued her secondary school education at SMK Clifford and graduated in the year of 2011. She completed her foundation study at UiTM Puncak Alam in the year of 2013, and subsequently enrolled in Universiti Putra Malaysia to pursue a Bachelor's Science Degree in Industrial Chemistry. Upon graduation in the year of 2017, she continued her study at the same university and pursued the degree of Master of Science which is currently ongoing.

LIST OF PUBLICATIONS

Nor Izzati Fikrah Aris, Norizah Abdul Rahman, Noorfatimah Yahaya, Aemi Syazwani Abdul Keyon, Mohd Haniff Wahid, Sazlinda Kamaruzaman. Superhydrophilic Graphene Oxide/Electrospun Cellulose Nanofiber for Efficient Adsorption of Organophosphorus Pesticides from Environmental Samples. Accepted for publication in Journal of Royal Society Open Science, on 11 February 2020.

Nor Izzati Fikrah Aris, Sazlinda Kamaruzaman, Norizah Abdul Rahman, Noorfatimah Yahaya. Synthesis and Characterization of Electrospun-Cellulose Nanofiber/Graphene Oxide for Organophosphorus Pesticides (OPPs) Removal from Water Samples. Poster presentation in Fundamental Science Congress 2018.

Nor Izzati Fikrah Aris, Sazlinda Kamaruzaman, Norizah Abdul Rahman, Noorfatimah Yahaya, Mohd Hanif Wahid. Pest-µ-Tip Kit. Project exhibition in The 8th International Invention, Innovation & Design (INDES) 2019.

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