UNIVERSITI PUTRA MALAYSIA

METHOD FOR DETERMINATION OF GLUFOSINATE AMMONIUM RESIDUE IN PALM OIL AND WATER SAMPLES USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH FLOURESCENCE DETECTOR

MUHAMMAD DANIAL BIN AHMAD FAUDZI

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By

MUHAMMAD DANIAL BIN AHMAD FAUDZI

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METHOD FOR DETERMINATION OF GLUFOSINATE AMMONIUM RESIDUE IN PALM OIL AND WATER SAMPLES USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH FLOURESCENCE DETECTOR

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May 2016

Chairman : Professor Dzolkhifli Omar, PhD
Faculty : Agriculture

New method for determination for glufosinate ammonium residues in crude palm oil (CPO), crude palm kernel oil (CPKO) and water samples using high performance chromatography with fluorescence detector (HPLC-FLD) was investigated. The first part of the thesis studied the development of glufosinate ammonium extraction from water sample. In the preliminary study on the extraction technique, several types of SPE were evaluate for the suitability of the sorbent to retain the glufosinate ammonium compound. The SPE SAX/NH_2 was the most suitable and stable to be used for the extraction. The extraction was done using SPE SAX/NH_2 connected to the SPE vacuum manifold to assist the elution of the solvent through the cartridge. The cartridge was first precondition with 3ml of methanol and 5mL of water (pH 7). Then a known amount of standard glufosinate ammonium was injected and 100 mL of ultrapure water (pH 7) was allowed to flow through the SPE cartridge. The cartridge was then eluted with 5 mL of KH_2PO_4 solution (pH 6-7). The elution solution was collected in a vial and derivatized using 9-fluoronylmethylchloroformate (FMOC-Cl).The implement of solid phase extraction (SPE) SAX/NH_2 was able to handle up to 1L volume of water sample in preconcentration process makes this method applicable to be used in real water sample. The percentage recovery for glufosinate ammonium in water sample were in the range 82 to 113% with RSD below 10.The limit of detection was 0.03 μg ml^{-1} and limit of quantification of this method was 0.1 μg ml^{-1}. Glufosinate ammonium extraction from CPO and CPKO samples was conducted by liquid-liquid extraction (LLE). Preliminary study to determine the most suitable solvent for sample spiking was conducted. The mixture of acetone: water with ratio of 70:30 was the most suitable solvent mixture for the sample spiking solution. Comprehensive investigation in order to select the appropriate solvent extraction in LLE was done. The outcome from the test showed that water and dichloromethane was the best solvent to be used in LLE for the extraction of glufosinate ammonium compound from CPO and CPKO samples. This method gave a good extraction and high recovery ranging from 86-112% for CPO sample and 80-81% for CPKO sample. The RSD also showed good accuracy and repeatability with all the

values obtained was below 10. The optimized method also went through the validation test. Both developed methods gave good linearity, accuracy, precision, LOD, LOQ and ruggedness. The method linearity correlation coefficient was 0.9994 and 0.9997 for oil and water sample respectively at concentrations ranging from 0.05 to 1.0 μg ml^{-1}. The limit of detection and limit of quantification of this method were found to be 0.03 and 0.1 μg ml^{-1}, respectively. The research findings suggest that this method could be considered as reliable for the determination of glufosinate ammonium in palm oil for food safety evaluation and water sample.

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

PEMBANGUNAN KAEDAH BAGI PENENTUAN SISA GLUFOSINATE AMMONIUM DI DALAM MINYAK KELAPA SAWIT DAN AIR DENGAN MENGGUNAKAN KROMATOGRAFI CECAIR BERPRESTASI TINGGI

Oleh

MUHAMMAD DANIAL BIN AHMAD FAUDZI

Mei 2016

Pengerusi : Profesor Dzolkhifli Omar, PhD
Fakulti : Pertanian

Dalam kajian ini, kaedah baru telah dibangunkan bagi menentukan sisa baki racun glufosinate ammonia di dalam minyak sawit mentah (CPO), minyak isirung sawit mentah (CPKO) dan sampel air menggunakan kromatografi cecair berprestasi tinggi dengan pengesan pendarfluor (HPLC-FLD). Bahagian pertama tesis ini mengkaji pembangunan pengekstrakan racun glufosinate ammonium dari sampel air. Kajian awal mengenai teknik pengekstrakan menggunakan beberapa jenis pengekstrakan fasa pepejal (SPE) telah diuji untuk menilai kesesuaian sorbent untuk memerangkap kompaund glufosinate ammonium daripada sampel air. Daripada kajian ini, didapati bahawa jenis SPE SAX/NH2 adalah yang paling sesuai dan stabil bagi menjalankan pengekstrakan. Proses ekstraksi dijalankan menggunakan SAX/NH2 dengan bantuan manifold SPE vakum bagi memmbantu elusi pelarut melalui katrij. Katrij telah dikondisikan dengan 3 mL methanol dan 5 mL air (pH 7). Kemudian, racun glufosinate yang telah diketahui kandunganya telah dimasukkan ke dalam 100 mL air ultra asli dan dilalukan melalui katrij SPE. Katrij itu kemudan telah dielusi dengan 5 mL larutan KH2PO4 (pH 6-7). Hasil elusi tersebut telah dikumpulkan untuk diderivatasikan menggunakan 9-flouronylmethylchloroformate (FMOC-Cl). Penggunaan pengekstrakan pepejal SAX/NH2 mampu untuk menampung sampel air sehingga satu liter. Proses pre-kepekatan didalam kaedah ini boleh digunakan bagi sampel air sebenar daripada ladang. Peratus pemulihan bagi glufosinate ammonium di dalam sampel air adalah dari 82 ke 113% dengan nilai RSD dibawah 10. Had pengesanan adalah 0.03 μg ml^{-1} dan had kuantifikasi kaedah ini adalah 0.1 μg ml^{-1}. Separuh kedua tesis ini mengenai pembangunan pengekstrakan glufosinate ammonium daripada sampel CPO dan CPKO. Teknik pengekstrakan cecair-cecair (LLE) telah dipilih sebagai teknik pengekstrakan bagi kedua-dua sampel. Kajian awal adalah untuk menentukan pelarut yang paling sesuai bagi melarutkan racun didalam sampel telah dijalankan. Telah didapati bahawa campuran acetone: air dengan nisbah 70:30 adalah yang paling sesuai untuk digunakan bagi melarutkan racun didalam sampel. Kajian yang mendalam bagi memilih pelarut yang sesuai di dalam LLE telah dijalankan. Hasil dari ujikaji menunjukan air dan

diklorometana adalah pelarut yang terbaik digunakan dalam LLE untuk pengekstrakan sebatian glufosinate ammonium daripada minyak sawit mentah dan minyak isirung sawit mentah. Kaedah ini memberi pemulihan yang tinggi di antara 86 sehingga 112% bagi sampel CPO dan 80 sehingga 81% bagi sampel CPKO. Nilai RSD juga menunjukan ketepatan dan keboleh ulangan yang baik dengan semua nilai yang diperolehi dibawah nilai 10. Kaedah yang dibangunkan telah dijalankan ujian pengesahan. Kedua-dua kaedah yang dibangunkan telah menunjukan kelineran, ketepatan, LOD, LOQ dan keteguhan yang baik. Pekali kolerasi linear bagi sampel minyak adalah 0.9994, manakala bagi sampel air ialah 0.9997 bagi kepekatan diantara 0.05 sehingga 1.0 µg ml^{-1}. Had pengesanan dan had kuantifikasi kaedah ini didapati 0.03 dan 0.1 µg ml-1. Dapatan kajian menunjukan kaedah ini boleh dipercayai bagi penentuan racun glufosinate ammonium untuk penilaian keselamatan makanan dan sampel air.

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May Allah showers all of you with His bless and guidance.

Thank You.

I certify that a Thesis Examination Committee has met on 9 May 2016 to conduct the final examination of Muhammad Danial bin Ahmad Faudzi on his thesis entitled "Method for Determination of Glufosinate Ammonium Residue in Palm Oil and Water Samples using High Performance Liquid Chromatography with Flourescence Detector" 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

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Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Samsuri bin Abd. Wahid, PhD
Senior Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Internal Examiner)

Dato' Ismail Sahid, PhD
Professor
National University of Malaysia
Malaysia
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 3 November 2016

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

Dzolkhifli Omar, PhD
Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Norida Mazlan, PhD
Senior Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

Halimah Muhamad, PhD
Head of Unit
Quality Development and Analytical Unit
Malaysian Palm Oil Board
(Member)

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Signature: _____
Name of Member of Supervisory Committee: Dr. Norida Mazlan

Signature: _____
Name of Member of Supervisory Committee: Dr. Halimah Muhamad

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LIST OF ABBREVIATIONS

%	Percent
°C	celcius
µg/mL	microgram per mililiter
µl	microliter
AES	Alkylether sulphate
BSR	Basal stem rot
CPO	Crude palm oil
CPKO	Crude palm kernel oil
DAG	Diacylglycerol
DAD	Diode array detector
DPX	Disposable pipette extraction
EPA	Environmental Protection Agency
ECD	Electron capture detector
FAO	Agriculture organization
ELISA	Enzyme-linked immunosorbent assay
FLD	Fluorescence detector
FID	Flame ionization detector
FFB	Fresh fruit bunches
GC	Gas chromatography
GAP	Good agriculture practice
HPLC	High performance liquid chromatography
LLE	Liquid-liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
MPOB	Malaysian Palm Oil Berhad
MS	Mass spectrometer
MAG	Monoacylglycerol
MPPA	3-methylphosphinicopropionic acid

MPA	2-methylphophinicoacetic acid
MPB	4-methyl-phosphinico-butanoic acid
MSPD	Matrix solid-phase dispersion
NAG	*N*-acetyl-glufosinate
NPD	Nitrogen phosphorus detector
OP	Organophosphorus
PPO	4-methyl-phosphinico-2-oxo-butanoic acid
RSD	Relative standard deviation
SPE	Solid phase extraction
SPME	Solid phase microextraction
SCX	Strong cation exchange
SAX	Strong anion exchnage
SIM	Selected ion monitoring
TAG	Triacylglycerol
UV	Ultraviolet
USR	Upper stem rot

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Malaysia is known for its excellent performance in the oil palm industry. Malaysia is among the leading producers of palm oil and the largest exporter of crude palm oil (CPO) worldwide. Oil palm is a major commodity in Malaysia and among the largest contributor to Malaysian`s economy (Che Johari Mamat, 2009). In 2006, the price of CPO increased from RM1410/ tonnes to RM4200/ tonnes in March 2008. The price pattern for CPO has shown an increment by almost 200% each year (The Edge Malaysia 2008). In Malaysia, the palm oil industry is governed by government agencies such as the Malaysian Palm Oil Board (MPOB) and Malaysia Palm Oil Council (MPOC). MPOB is responsible to expand this sector by managing the research and development activities while MPOC focused on the promotional and marketing activities in the global market (The Edge Malaysia 2008).

Indeed, it is essential to produce high quality palm oil to maintain Malaysia`s status as the world`s largest exporter as well to ensure that the demand for palm oil is met. Therefore, palm oil trees need to be protected from diseases, pests and weed. The attack from these pests are inevitable which can cause yield lost and lowering the quality of palm oil. Thus, a few methods were introduced to treat the pests, including the use of pesticide in the oil palm plantation. There are various types of pesticide applied in the oil palm plantation. Usually, pesticides are classified based on the target organism. According to Carabias-Martinez et al., (2004), about 50% of pesticide applications in the plantation are herbicide. This is due to thehigh existence of various species of weeds in the plantation. Among the commonly used herbicides are glyphosate, glufosinate ammonium, paraquat, fluroxypyr, dicamba, triclopyr, and diuron (Chung et al., 2000).

The use of pesticides may lead to adverse effects on the environment. The continuous use of pesticide in plantation not only kills the microorganism, but also contaminates the environment. When apesticideis sprayed on the oil palm trees, the pesticide residue tends to stay on the soil surface. Pesticide residue on the soil surface is transported by rainwater and flows into rivers and lakes through movements on the surface or underground. Eventually, river or water located around the spray area will be contaminated. For example, laboratory and field studies have shown that glufosinate ammonium compound`s half-life was 3-11 days in the soil (Smith and Belyk., 1989; Behrendt et al., 1990). In another study stated that the toxicity for atrazine and lambda-cyhalothrin were measured in water from unvegetated microcosms after 28 days (Bouldin et al., 2005).

Besides environmental pollutions in the plantation ecosystem, persistency of some pesticide residue to remain in the fruits and leaves can lead to food contamination. Some ofthe herbicides such as glyphosate and glufosinate ammonium are systemic herbicide. Systemic herbicides are absorbed either by roots or foliar parts of a plant and translocated within the plant system to tissues that may be remote from the point of application.

(Stalikas 2001). In one study, residues of glufosinate were found in spinach, radishes, wheat and carrots planted 120 days after glufosinate had been applied (Glufosinate ammonium fact sheet 1998). In oil palm plantation, there is possibility of contaminated oil palm fruits to be processed to produce CPO and other oil fractions. Consequently, there would be residue of pesticide in the oil. Pesticide residues in palm oil are important considerations in the safety of edible oil. Exposure of pesticide in a long period of time causes health problems to humans such as cancer, neurological and reproductive effects.

It is important to develop a method for determining pesticide residue in environmental and palm oil. However, determination of pesticide residue is a challenging task. Analysis pesticide in a real water sample from the environment is difficult due to the compound that exists in a very low concentration. Determination of pesticide in soil samples is hard because of high organic content in the soil will interrupt the extraction process and analysis of the pesticide (Carolina et al., 2008). As for palm oil samples which consist of triacylglycerol (TAG), diacylglycerol (DAG), monoacylglycerol (MAG), free fatty acids, phospholipid and carotene, the complexity of the oil sample can prevent detection and quantification of the target analytes (Halimah et al., 2012). Prior extraction process, palm oil sample needs to undergo the clean-up process to eliminate large fatty molecules in the oil. Elimination of fatty components is important for preventing damage to the instrument. Besides that, the overlap of the peak in the chromatogram may happen due to the fatty components.

Usually, determination of pesticide residue in environmental samples, food and oil were conducted either by gas chromatography (GC) or high-performance liquid chromatography (HPLC) (Lucio et al., 2004). Both of these instruments were chosen because of their flexibility in term of detection. Gas chromatography can be equipped with nitrogen-phosphorus detector (NPD) and flame ionization detector (FID). For HPLC, it can be equipped with fluorescence detector (FLD), ultraviolet detector (UV), and diode array detector (DAD). In addition, both of these instruments can now be equipped with mass spectrometry (MS) which can give more sensitivity in the analysis.

1.2 Research Objective

The researchobjectivesof this study are as follows:

i. To develop a method for determination of glufosinate ammonium residue in palm oil and water samples.
ii. To validate the method developed for the determination of glufosinate ammonium in palm oils and water samples.

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