Jurnal Teknologi

Full Paper

OPTIMIZATION OF EXTRACTION AND DETECTION METHOD FOR IMAZAPYR AND IMAZAPIC RESIDUES IN WATER, SOIL AND FISH TISSUE SAMPLES USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Article history
Received
23 June 2015
Received in revised form
27 September 2015
Accepted
11 December 2015

*Corresponding author
hazilia@puncakalam.uitm.edu.my

Siti Norashikin Mohamad Shaifuddin[a*], Hazilia Hussain[a], Hamzah Fansuri Hassan[b]

[a]Department of Environmental Health, Faculty of Health Sciences, Universiti Teknologi MARA (UiTM), Puncak Alam, Selangor, Malaysia
[b]Department of Basic Science, Faculty of Health Sciences, Universiti Teknologi MARA (UiTM), Puncak Alam, Selangor, Malaysia

Abstract

The combination of imazapyr and imazapic herbicides was first introduced to increase the crop yields in agricultural areas around the world by killing unwanted plants. Unfortunately, previous literatures have proved that imazapyr is persistent in environmental media (soil and groundwater). In some studies, these herbicides have also been claimed to pose a potential risk to non-target organisms as well as causing possible health threats to humans. Therefore, developing a suitable extraction and detection method of these residues at low level in biological and environmental samples is highly necessary to ensure food safety and to protect the environment. Imazapyr and imazapic were extracted from water and fish tissues using solid phase extraction, whereas solid-liquid extraction was used for soil samples. The extracts were analyzed using High Performance Liquid Chromatography. Results showed that recoveries were found to range from 80% to 130%. These were the methods used to determine the residues from the actual samples collected in Sawah Sempadan. Analysis showed that a total of 86% of the samples revealed presence of imazapyr and imazapic. Therefore, these methods are proven to be sufficient in analyzing the environmental presence of these herbicides.

Keywords: Imazapyr, imazapic, waters, soils, fish tissues

1.0 INTRODUCTION

Rice is the staple food in Malaysia [1]. A lot of areas have been allocated for the cultivation of rice [2]. The yield of rice in Malaysia is considerably high [2], contributing almost 60 percent of the country's annual rice consumption [3]. However, competition between paddy and wild weeds has imposed a problem that clearly affects the annual rice yield in Malaysia [4, 5]. Therefore, imidazolinone-tolerant rice variety (IMI-TR) was developed by MARDI in collaboration with BASF (Malaysia) where a single application of imazapyr and imazapic herbicides was used to control the weedy rice [6, 7]. Imazapyr and imazapic are two herbicides that belong in the imidazolinone group [8]. They are the most preferred herbicides and are widely used by farmers around the world to control the weed in their crops [8]. These herbicides kill the subject weeds by interfering with their growth and also by inhibiting the action of plant enzyme acetohydroxyacid synthase (AHAS) [8, 9].

Because of the low application rate and low toxicity effects on mammals, imidazolinone herbicides are assumed to be environmentally safe [10]. However, there are several environmental issues that arise due to the application of these herbicides.

The persistency of imazapyr in soil has resulted in the banning of this herbicide in Norway [11] and France [12]. Imazapyr residues were also detected in groundwater in Sweden after 8 years of its application to the related crops [13]. This indicates that this herbicide is also relatively persistent in water. Since the herbicide is able to remain in the environmental media for a considerable length of time, it could pose potential risks to non-target organisms such as fish [14]. The death of fishes, ducks, hens and birds were reported in Sungai Burung and Sawah Sempadan in 2012 [4]. This was caused by ingestion of food contaminated with pesticide [4]. The application of imazapyr and imazapic herbicides could possibly contribute to this problem. Therefore, it is very crucial to monitor the movement, dispersion and transformation of these herbicides in Malaysia as they pose a threat to the environment as well as food safety.

Previous literatures showed that most researchers prefer using liquid chromatography as the method of choice to study the imidazolinone herbicides in soil and water [10, 15, 16, 17, 18, 19] compared to gas chromatography [20]. This technique is the best option to analyze herbicides with low volatilization and high water solubility [17, 18, 21] which is similar to these compounds [8]. However, there is a lack of information on simultaneous determination of imazapyr and imazapic herbicides in water and soil especially under Malaysian climate [22] as well as biological samples such as fish. This paper focuses on developing method for imazapyr and imazapic extraction from water, soil and fish tissue. The proposed procedures were tested by analyzing the actual samples collected from Sawah Sempadan, Tanjung Karang (Malaysia).

2.0 EXPERIMENTAL

The HPLC-UV was initially optimized before developing the extraction method using spiked samples. The extraction method with the highest recovery for imazapyr and imazapic herbicides was selected to analyze the residues level in actual samples collected from paddy field area.

2.1 Chemicals, Reagents and Apparatus

Standards for imazapyr and imazapic were purchased from Sigma-Aldrich with 99.5% and 99.9& of purity, respectively. Acetic acid, magnesium sulphate ($MgSO_4$), potassium chloride (KCl), sodium hydroxide (NaOH) ammonium acetate, acetonitrile (ACN) and methanol with HPLC grade were supplied from Merck (Malaysia). Ultrapure deionized water (Milli-Q water, Milipore) was used to prepare all the solutions in this experiment.

Experiments utilized 6 mL reservoir cartridges with 500 mg of packing material such as HyperSep Retain PEP (Thermo SCIENTIFIC) (Cat:60107-206), Bond Elut-C18 (Agilent Technologies) (Cat:12102052) as well as Bond Elut-PPL (Agilent Technologies) (Cat:12255001). Both 0.45µm glass filter and Falcon Tube (50 mL) were bought from Whatman™ and BD Biosciences.

The complete set for filtration was provided by FAVORIT (Malaysia) to filter water samples and aqueous solutions in this experiment. For centrifuge and mix process, Centurion Scientific K3 Series Centrifuge (UK) (model K241R) and VORTEX-1 GENIE touch mixer (Scientific Industries) (USA) were used. An Agilent 1200 High Performance Liquid Chromatography (HPLC) equipped with UV detector was utilized to quantify the level of herbicides residues in the samples.

2.2 Preparation of Stock Solutions

The standard stock solutions (100 µg mL^{-1}) for imazapyr and imazapic were prepared individually in ACN. The stock solutions were then mixed and were later diluted into several concentrations (50, 25, 10, 5 and 1 µg mL^{-1}). All stock and working solutions were stored below 4°C in the dark [10].

2.3 Optimization of Reverse Phase HPLC Analysis

The separation of chromatographic was performed using an Agilent Zorbax SB-C18 (4.6 x 250mm x 5µm) column assisted by ACN and acidified water (pH 2.8) as mobile phase. Acidified water was prepared using acetic acid. The wavelength, mobile phase, injection volume and flow rate were adjusted to acquire the best separation of the herbicides [23].

2.4 Preparation of Spiked Samples

Spiked water samples were prepared in three different concentrations (2, 1 and 0.5 µg mL^{-1}) using demineralized water [10]. The soil samples were also spiked with herbicides mixture and left to dry for three days at room temperature [24]. The fish tissues were spiked in the same way before leaving it for 30 minutes in the dark [24]. Triplicate of non-spiked samples were also prepared as the control.

2.5 Extraction Procedure for Spiked Samples

Table 1 summarized the extraction procedures tested for water, soil and fish tissues samples. The extracts were transferred into 2mL amber vials before analyzed using HPLC-UV.

2.6 Environmental Sampling and Analysis

Water and soil were sampled after 24 hours sprayed with imazapyr and imazapic herbicides in Sawah Sempadan. An amount of 1 liter water samples were collected with 5cm depth from the water surface at 12 different points in paddy plot and drainage canals. The samples were then filtered using Whatman glass filter before moving on to procedure P4 for extraction (see Table 1). Soil samples were

collected at 14 points and were kept in sterile zip lock bags. The samples were then air-dried and grounded before sieving (2 mm). The isolation of imazapyr and imazapic in soil media were conducted using procedure P6.

Fish (*Anabas testudineus*/ perch) were caught from the paddy field drainage canals during harvest season. The muscle tissues were finely sliced and a total of 5 grams sample was weighed into a Falcon tube (50 mL). Protocol P9 was applied to extract the herbicides from the fish tissue. All matrices were analyzed using HPLC-UV.

3.0 RESULTS AND DISCUSSION

3.1 Optimization of HPLC-UV

The optimized condition for HPLC-UV analysis was obtained when ACN: acidified water (pH 2.8) (35:65, v/v) was used as mobile phase with 1.0 mL/ min flow rate, 251nm detection wavelength and 17µL for injection volume [23, 25].

3.2 Evaluation of the Extraction Procedure

Solid phase and liquid-liquid extraction process were tested to isolate imazapyr and imazapic herbicides residues from the water samples. For solid phase extraction, three different sorbents were tested; Bond Elut-PPL (500 mg/ 6 mL), Bond Elut-C18 (500 mg/ 6 mL) and HyperSep Retain PEP (500 mg/ 6 mL). The results showed that HyperSep Retain PEP cartridge was the best cartridge for extracting the residues (recoveries 124.06% and 118.01% for imazapyr and imazapic, respectively). This might be due to the non-polar characteristic of these herbicides and the capability of polystyrene DVB material modified with urea functional groups sorbent to provide balanced retention of polar and non-polar analytes that allows these compounds to retain [26]. The maximum retention for imidazolinone herbicides was below pK_a (3.6) as reported by Ramezani [10] using the PPL sorbent. Therefore, all the water samples were acidified with acetic acid [16] before passing through HyperSep Retain PEP cartridge.

For water samples with small volume, the proposed procedure (P5) could be used to isolate imazapyr and imazapic residues. This method requires only 10mL samples mixed with 10mL ammonium acetate before directly injected to the HPLC without passing any clean-up process. Ammonium acetate was added to increase the ionic strength of analytes for extraction, where the capacity of the isolation depends on the partition coefficient of each pesticide between organic solvent and the sample itself [27, 28]. This method is simple, fast and cost effective compared to other methods with the recoveries for both herbicides being more than 100%. This result was confirmed with the findings reported by Steven Moser [29] in his experiment.

The extraction of imazapyr and imazapic in soil samples were adjusted using liquid-liquid extraction (LLE). Similar protocol steps modified from D' Ascenzo [30] were applied in both procedures (P6 and P7). Method P6 used 0.1M KCl for the extraction and was able to recover 119.69% and 35.42% of imazapyr and imazapic, respectively. However, the recoveries for both herbicides were highest when using 0.5M NaOH (P7). A similar finding was reported by Ramezani [10] where 0.1 M KCl solutions produced lower recoveries compared to 0.5M NaOH. This indicated that a strong base solution is required to efficiently extract imidazolinone herbicides from soil samples. The use of alkaline aqueous solution for isolation of acidic herbicide proves to be advantageous in terms of its simple preparation as well as the minimum use of harmful solvents [10].

The extraction method (P9) for fish tissue has the highest recovery compared to procedure P8. The tested hydrophobic, bonded silica C18 sorbents showed that this cartridge was able to clean-up and retained imazapyr and imazapic compounds from fish tissue samples. Originally, centrifugation process (P8) was proposed by Steven Moser [29] for the analysis of imidazolinone in water, soil and vegetation. By modifying length of time during centrifuge process, this method (P8) was tested to extract herbicides from fish tissue. Steven Moser's [29] experiment showed that this procedure managed to extract 81.0% to 103.5% of imidazolinone herbicides from tested samples. However, only 40% of imazapyr and imazapic herbicides were isolated from fish tissue in this paper. This might be due to the degradation of analytes exposed to the heat produced during grinding step or insufficient separation phase [31].

Table 1 Extraction procedure for isolation of imazapyr and imazapic residues in water, soil and fish tissue samples

WATER SAMPLES

EXTRACTION PROCEDURE	CARTRIDGE	CONDITIONING PHASE	SAMPLE LOADING STEP	EXTRACTION STEP	RECOVERY (%)
P1	Bond Elut-PPL (500 mg/6 mL)	• 3 mL DCM (2X) • 3 mL MeOH (2X) • 2 mL mili-Q water (pH2)	1000 mL	Condition → load sample → dry the cartridge under vacuum → elute with 3 mL DCM → leave to dry → add 4 mL propanol → evaporate to dryness (1 mL)	Imazapyr: 61.70 Imazapic: 127.81
P2	Bond Elut-C18 (500 mg/6 mL)	• 5 mL MeOH	1000 mL	Condition → load sample → elute with 3 mL MeOH	Imazapyr: 63.48 Imazapic: 126.05
P3	HyperSep Retain PEP (500 mg/6 mL)	• 5 mL MeOH (4X) • 5 mL 1% acetic acid (4X)	1000 mL (pH 2)	Condition → load sample → dry the cartridge under vacuum → elute with 10 mL MeOH	Imazapyr: 124.06 Imazapic: 118.01
P4	Bond Elut-PPL (500 mg/6 mL)	• 5 mL MeOH • 5 mL MeOH:ACN,1:1 • 2 mL ultrapure H_2O (pH2)	1000 mL (pH 2)	Condition → load sample → elute with 3 mL MeOH:ACN (1:1, v/v)	Imazapyr: 75.00 Imazapic: 87.58
P5	Not available	Not available	10 mL	Add 10 mL samples into 50 mL Falcon tube → add 10 mL ammonium acetate solution → vortex (30s) → centrifuge (4000rpm, 20min)	Imazapyr: 101.80 Imazapic:101.29

SOIL SAMPLES

EXTRACTION PROCEDURE	AQUEOUS SOLUTION	EXTRACTION PROCEDURE	RECOVERY (%)
P6	0.1M KCl	5 g soil sample placed into 50 mL Falcon tube → added 20 mL 0.1M KCl → shaked (10 min) → centrifuged (2000 rpm, 10 min) → withdrawn supernatants > added 20 mL 0.1M KCl → shaked (10 min) → centrifuged (2000 rpm, 10 min) → withdrawn supernatants → sonicated (15 min)	Imazapyr: 119.69 Imazapic: 35.42
P7	0.5M NaOH	5 g soil sample placed into 50 mL Falcon tube → added 20 mL 0.5M NaOH → shaked (10 min) → centrifuged (2000 rpm, 10 min) → withdrawn supernatants > added 20 mL 0.5M NaOH → shaked (10 min) → centrifuged (2000 rpm, 10 min) → withdrawn supernatants → sonicated (15 min)	Imazapyr: 104.20 Imazapic: 97.20

FISH SAMPLES

EXTRACTION PROCEDURE	EXTRACTION PROCEDURE	CLEAN-UP PROCEDURE	RECOVERY (%)
P8	5 g samples added into 50 mL Falcon tube → added 10 mL ammonium acetate solution → vortex (30s) → centrifuged (4000 rpm, 20 min)	Not available	Imazapyr: 45.99 Imazapic: 44.83
P9	5 g samples added into 50 mL Falcon tube → added 15 mL ACN → homogenized for 1 min → added 5 g $MgSO_4$ (shaked for 30s) → centrifuge (4000 rpm, 10 min)	The supernatant passed through C18 (condition: 5 mL MeOH, elute: 3 mL MeOH)	Imazapyr: 83.74 Imazapic: 121.31

3.3 Analysis of Environmental Samples

Sawah Sempadan, Tanjung Karang (Malaysia) was selected as the study location because Tanjung Karang and Sabak Bernam are known to produce high yields of rice in the state of Selangor [32]. The samples were collected during rice cultivation period in 2014 and 2015. Analysis of surface water revealed the presence of imidazolinone herbicides residues in the samples (imazapyr: 0.0029 µg mL^{-1} to 0.0439 µg $mL^{-1;}$ imazapic: 0.0037 µg mL^{-1} to 0.2097 µg mL^{-1}). Examination of soil samples found 0.7490 µg g^{-1} to 3.4447 µg g^{-1} of imazapyr and imazapic (0.0658 µg g^{-1} to 2.2043 µg g^{-1}) residues. Imazapyr and imazapic residues were detected in fish tissue at a concentration of 0.0802 µg g^{-1} and 0.135 µg g^{-1}, respectively. Through the analysis of actual samples, it shows that the proposed methods are suitable for investigation of environmental samples. Moreover, there is an inadequacy of other proposed extraction methods for imidazolinone herbicide in fish tissue based on previous literature.

4.0 CONCLUSIONS

This study tested various extraction methods to isolate imazapyr and imazapic residues from environmental matrices. The applications of HyperSep Retain PEP and Bond Elut C18 sorbents to clean-up and retain the herbicides residues from water and fish tissue samples were successful. The best recovery for the herbicides from soil was obtained with 0.5M NaOH. Imazapyr and imazapic residues were detected in 86% of the actual samples collected from Sawah Sempadan. Therefore, this method is suitable for routine monitoring of these herbicides in the environment.

Acknowledgement

The authors would like to thank the fund given by Research Intensive Faculty (854/2012). The authors would also like to express appreciation to the Analytical Unit (Faculty of Pharmacy) and Environmental Analysis Laboratory (Faculty of Health Sciences) for providing the instruments and analysis facility.

References

[1] Ramli, N. N., Shamsudin, M. N., Mohamed, Z. and Radam, A. 2012. The Impact of Fertilizer Subsidy on Malaysia Paddy/ Paddy Industry Using a System Dynamics Approach. *International Journal of Social Science and Huminity*. 2(3): 213-219.

[2] Department of Agriculture Peninsular Malaysia. 2012. *Paddy Statistic of Malaysia 2011*. Retrieved January, 3, 2013 from http://www.doa.gov.my/c/document_library/get_file?uuid=8b3bb7ed-4363-4471-b760-6f528e6273dc&groupId=38371.

[3] Ismail, B. S., Sameni, M., and Halimah, M. 2011. Evaluation of Herbicide Pollution in the Kerian Paddyfield of Perak, Malaysia. *World Applied Sciences Journal.* 15(1): 5-13.

[4] Fuad, M. J. M., Junaidi, A. B., Habibah, A., Hamzah, J., Toriman, M. E., Lyndon, N., Er, A. C., Selvadurai, S., and Azima, A. M. 2012. The Impact of Pesticides on Paddy Farmers and Ecosystem. *Advances in Natural and Applied Sciences.* 6(1): 65-70.

[5] Hidayatul, N., Anuar, S., Mazlan, N., Ahmad, E., Engku, K., Juraimi, A. S., and Yusop, M. R. 2014. A Comparative Study of Vegetation and Reproductive Growth. *Journal of International Society for Southeast Asian Agricultural Sciences.* 20(1): 41-51.

[6] Azmi, M., Azlan, S., Yim, K. M., George, T. V., and Chew, S. E. 2012. Control of Weedy Paddy in Direct-Seeded Paddy Using the Clearfield Production System in Malaysia. *Pakistan Journal of Weed Sciences Research.* 18: 49-53.

[7] Idris, R. 2012. Dua Gen Baru Dihasilkan MARDI Akhiri Belenggu Padi Angin. *Berita Harian*. Retrieved December, 19, 2012 from http://www.bharian.com.my/articles/Duagenbarudihasilkan nMARDIakhiribelenggupadiangin/Article/print_html.

[8] Hess, F. G., Harris, J. E., Pendino, K., and Ponnock, K. 2001. Imidazolinone. In: *Handbook of Pesticide Toxicology*. Academic Press: San Diego.

[9] Colquhoun, J. 2001. *How Herbicides Work: Uptake, Translocation, and Mode of Action*. Retrieved December, 18, 2012 from http://osuext.intermountaintech.org/download/how herbicides work.pdf.

[10] Ramezani, M., Simpson, N., Oliver, D., Kookana, R., Gill, G., and Preston, C. 2009. Improved Extraction and Clean-Up of Imidazolinone Herbicides from Soil Solutions Using Different Sorbents. *Journal of Chromatography A*. 1216: 5092-5100.

[11] Rotterdam Convention. 2001. *Interim Secretariat* for Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade. *PIC CIRCULAR XIV*. December 2001. Retrieved February, 13, 2013 from http://www.pic.int/Portals/5/en/Circular/CIRC14EN.pdf.

[12] Carrier, M., Perol, N., Herrmann, J.-M., Bordes, C., Horikoshi, S., Paisse, J. O., Baudot, R., and Guillard, C. 2006. Kinetics and Reactional Pathway of Imazapyr Photocatalytic Degradation Influence of Ph and Metallic Ions. *Applied Catalysis B: Environmental.* 65: 11-20.

[13] Börjesson, E., Torstensson, L., and Stenström, J. 2004. The Fate Of Imazapyr In A Swedish Railway Embankment. *Pest Management Science*. 60(6): 544-549.

[14] Moraes, B. S., Clasen, B., Loro, V. L., Pretto, A., Toni, C., Antonio de Avila, L., Marchesan, E., Luiz de Oliveira Machado, S., Zanella, R., and Reimche, G. B. 2011. Toxicological Response of *Cyprinus Carpio* after Exposure to a Commercial Herbicide Containing Imazethapyr and Imazapic. *Ecotoxicology and Environmental Safety*. 74: 328-335.

[15] Liu, W., Pusino, A., and Gessa, C. 1992. High-Performance Liquid Chromatographic Determination of the Herbicide Imazapyr Residues in Water and Soil. *The Science of the Total Environment.* 123/124: 39-43.

[16] Laganà, A., Fago, G., and Marino, A. 1998. Simultaneous Determination of Imidazolinone Herbicides from Soil and Natural Waters Using Soil Column Extraction and Off-Line Solid Phase Extraction Followed by Liquid Chromatography With UV Detection or Liquid Chromatography/ Electrospray Mass Spectroscopy. *Analytical Chemistry.* 70(1): 121-130.

[17] Furlong, E. T., Burkhardt, M. R., Gates, P. M., Werner, S. L., and Battaglin, W. A. 2000. Routine Determination of Sulfonylurea, Imidazolinone, and Sulfonamide Herbicides at Nanogram-Per-Liter Concentrations by Solid-Phase Extraction and Liquid Chromatography Mass Spectrometry. *The Science of the Total Environment.* 248: 135-146.

[18] Lao, W., and Gan. J. 2006. High-Performance Liquid Chromatographic Separation of Imidazolinone Herbicide Enantiomers and Their Methyl Derivatives on Polysaccharide-Coated Chiral Stationary Phases. *Journal of Chromatography* A. 1117: 184-193.
[19] Pinna, M. V., and Pusino, A. 2013. Influence of the Isomerism on the Sorption of Imazamethabenz-Methyl by Soil. *Chemosphere*. 91: 265-268.
[20] Anisuzzaman, A. K. M., Amin, M., Ogg, N., Hoq, F., Kanithi, M. R., and Jenkins, E. 2000. Synthesis of Dimethyl Derivatives of Imidazolinone Herbicides: Their Use in Efficient Gas Chromatographic Methods for the Determination of These Herbicides. *Journal of Agricultural and Food Chemistry*. 48: 5893-5902.
[21] Zanella, R., Primel, E. G., Gonçalves, F. F., and Martins, A. F. 2000. Development and Validation of a High-Performance Liquid Chromatographic Method for the Determination of Clomazone Residues in Surface Water. *Journal of Chromatography* A. 904: 257-262.
[22] Ismail, B. S., and Ahmad, A. R. 1994. Attenuation of the Herbicidal Activities of Glufosinate-Ammonium and Imazapyr in Two Soils. *Agriculture, Ecosystems and Environment*. 47: 279-285.
[23] Shaifuddin, S. N. M., Mazlan, A. Z., Hussain, H., Sameni, M., and Ishak, A. R. 2014. Analytical Method Development for Imazapyr and Imazapic Herbicides using High Performance Liquid Chromatography. *International Conference on Chemical, Environment & Biological Sciences (CEBS-2014)*. 5-6.
[24] Wagil, M., Maszkowska, J., Białk-Bielińska, A., Caban, M., Stepnowski, P., and Kumirska, J. 2014. Determination of Metronidazole Residues in Water, Sediment and Fish Tissue Samples. *Chemosphere*. 119: 28-34.
[25] Kuang, H., Wang, L., and Xu, C. 2011. Overview of Analytical Techniques for Herbicides in Foods, Herbicides, Theory and Applications. In Prof. Marcelo Larramendy (Ed.). ISBN: 978-953-307-975-2. InTech. Retrieved October, 7, 2013 from http://www.intechopen.com/books/herbicides-theory-and-applications/overview-of-analyticaltechniques-for-herbicides-in-foods.
[26] Thermo SCIENTIFIC. 2014. *Chromatography Columns and Consumables 2014-2015*. Retrieved December, 29, 2014 from www.thermoscientific.com/chromatography.
[27] Bedendo, G. C., Jardim, I. C. S. F., and Carasek, E. 2012. Multiresidue Determination of Pesticides in Industrial and Fresh Orange Juice by Hollow Fiber Microporous Membrane Liquid-Liquid Extraction and Detection by Liquid-Chromatography-Electrospray-Tandem Mass Spectrometry. *Talanta*. 88: 573-580.
[28] Pérez, J. F. H., Sejerøe-Olsen, B., Alba, A. R. F., Schimmel, H., and Dabrio, M. 2015. Accurate Determination of Selected Pesticides in Soya Beans by Liquid Chromatography Coupled To Isotope Dilution Mass Spectrometry. *Talanta*. 137: 120-129.
[29] Steven Moser. A Fast and Easy Method for Imidazolinone Residue Analysis. Retrieved June, 29, 2014 from http://www.epa.gov/region6/qa/presentations10/c10-moser1-p.pdf.
[30] D' Ascenzo, G., Gentili, A., Marchese, S., Marino, A., and Perret, D. 1998. Rapid and Simple Method for Extraction and Determinantion of Imidazolinone Herbicides in Soil. *Analusis*. 26: 251-255
[31] Lazartigues, A., Fratta, C., Baudot, R., Wiest, L., Feidt, C., Thomas, M., and Cren-Olivé, C. 2011. Multiresidue Method For The Determination Of 13 Pesticides In Three Environmental Matrices: Water, Sediments And Fish Muscle. *Talanta*. 85: 1500-1507.
[32] Rahman, A. A., and Othman, P. F. 2012. The Agricultural Land Tenancy Contract from the Islamic Perspective and Its Practice among Farmers: A Study. *African Journal of Agricultural Research*. 7(10): 1584-1594.