The Effectiveness of Rice Husk Biochar Application to Metsulfuron Methyl Persistence

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Keywords: Herbicide, Metsulfuron Methyl, Persistence, Leaching, Rice Husk Biochar.

Abstract: Metsulfuron methyl is an herbicide which has low toxicity and rapidly degraded in the soil, however DuPont stated that it is very poisonous to aquatic organism. Rice husk biochar is commonly used as ameliorants, moreoverit has ability to absorb and degradeharmful chemicals. This study aimed at investigating the effectiveness of rice husk biochar application towards the persistence of metsulfuronmethyl in soil and seepage water. This study applied completely randomized design factorial with two levels of herbicide dose (0 and 300 gr/ha) and four levels of percentage of rice husk biochar(0%, 5%, 10% and 15% of total soil). The results of this research revealed that there was no metsulfuron methyl residue in soil of all treatments after 28 days of herbicide treatment. The residue was found in seepageas much as 7.7 μg/L in treatment of 0% husk biochar and 6.8 μg/L in treatment of 5%husk biochar. The seepage reduced by the increasing of the percentage of rice husk biochar application. Thus, it can be concluded that giving the rice husk biochar is effective for absorbing metsulfuron methyl and preventing it from leaching. However, itcould not hold the presence of metsulfuron methyl longer in soil.

1 INTRODUCTION

Metsulfuron methyl is an herbicide active substance which has low toxicity (LD50 in mice > 5000 mg/ kg), a low recommended dosage, and is also rapidly degraded in the soil. Devlin et al. (1992) reported thatmetsulfuron methyl, known as *Ally*, contains DT50 for 2-4 weeks. However, in the DuPont Safety Data Sheet, it is explained that *Ally 20 WG*(20% metsulfuron methyl) is very poisonous to aquatic organisms; it can cause long-term adverse effects in the aquatic environment.

Persistence is the ability of the herbicide to remain on the ground in an active state. The longer the persistence of herbicides in the soil, the more beneficial it will be, in terms of efficacy. However, from an ecological perspective which is related to environmental quality, the too-long persistence of herbicides is certainly undesirable and should be avoided because it will pollute the surrounding environment. The persistence of herbicides in the soil is influenced by several factors including: volatilization, photodecomposition, adsorption, leaching, microbial decomposition, chemical decomposition, and uptake by plants (Rao, 2000). Meanwhile, Jansar and Sahid (2016) stated that the level of metsulfuronmethyl residue in the river near oil palm plantations significantly increased during the rainy season because of leaching.

Rice husk biochar is commonly used as ameliorants in agricultural cultivation to improve soil quality by improving the physical, chemical and biological properties of the soil. In addition, rice husk biochar is also known to have the ability to absorb agricultural chemicals and it is decomposed in physically, chemically and biologically into compounds that are not harmful for the environment. Jing et al. (2018) assert that giving rice husk biochar could reduce the loss of ethyl phenoxaprop herbicides in the soil, and decreased the toxic effects to earthworms. Moreover, Sudirja et al. (2015) stated that the adsorption of paraquat herbicides by soil increases in line with the increasing doses of zeolite, straw, and activated charcoal in the soil.

This research was conducted to investigate the effectiveness of giving rice husk biochar ameliorant towards the persistence of metsulfuron methyl in soil and seepage water.

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2 MATERIAL AND METHODS

2.1 Materials

The The materials applied in this research include: Ally 20 WG herbicide, top soil, rice husk biochar, 98% purified metsulfuron methyl solution (brand: Sigma Aldrich), methanol gred HPLC, acetonitrile, acetic acid, KH_2PO_4, $NaHCO_3$, HCl, and distilled water.

The tools include: plastic pots, Krisbow-semiautomatic handsprayers, scales, Agilent 1220 Infinity LC HPLC-VWD, OpenlabChemstation Software, Gyrozen centrifugation machines, hot plate stirrers Thermolyne, orbital shaker Protech, Sartorius analytic scales, Sartorius pH meters, ultrasonic machines, Biotage ISL Isolate Env+ Solid Phase Extraction (SPE) cartridge, manifold vacuum, vacuum pump, syringe, 0.2 micron syringe filter, analysis vial bottle, beaker glass, volumetric flask, centrifuge tube, flask, measuring tube, glass bottle 20 ml, and micropipette.

2.2 Research Site and Methodology

This research was conducted in the green house of the experimental garden at the Faculty of Agriculture, Universitas Islam Riau. The extraction and residual analysis of the active substance of metsulfuron methyl herbicide was executed in the pesticide analysis laboratory of the Faculty of Science and Technology, UniversitiKebangsaan Malaysia. The research was conducted from April to June 2018. This research applied a completely randomized design (CRD) factorial pattern with two levels of herbicide dose (0 and 300 gr/ha) and four levels of percentage of rice husk biochar ameliorant (0%, 5%, 10% and 15% of total soil). The total amount of soil and rice husk biochar in the pot is 2 kg, which was mixed evenly (Figure 1). The treatment was repeated 3 times, so that there were 24 units of the total experimental treatments.

Herbicide was sprayed onto the ground with a concentration of herbicide application 0.67 gr/L of water and a spray volume of 450 l/ha. Each pot was watered with 200 ml of water after 17 days of herbicide application daily. The water that seeped out under the pot was collected to be analyzed.

2.3 Sampling

The soil with the same treatment was composited, stirred evenly, aerated for 2 hours then taken as much as 500 grams per treatment. Meanwhile, seeped out water from pots that have been collected each day was taken as the sample for as much as $\pm$ 250 ml per treatment and it was put in a glass bottle.

Figure 1: Mixture of soil and rice husk biochar.

2.4 Metsulfuron Methyl Extraction

For the extraction of metsulfuron methyl in the soil, 5 grams of soil sample were prepared, then mixed with 0.1 M $NaHCO_3$. The samples were shaken with orbital shaker (200 rpm, 2 hours). After that, they were centrifuged for 20 minutes at 4000 rpm. The SPE cartridge was rinsed with 3 ml of acetonitrile and 3 ml of distilled water. The supernatant resulted was flowed about 2-3 ml per minute through the SPE cartridge (Figure 2). Then, metsulfuron methyl absorbed in the SPE cartridge was separated with methanol and stored in a 20 ml glass bottle. The extraction results were dried to a range of 1 ml. After that, it was sucked with a syringe equipped with a 0.2 micron filter, then transferred to a 1.5 ml analysis vial bottle.

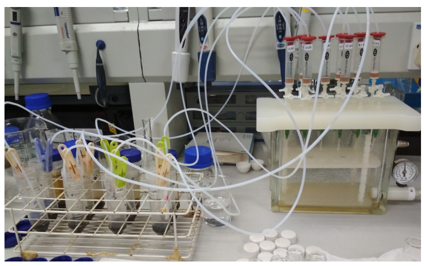

Figure 2: Soil supernatant was flowed through SPE cartridge for absorbingmetsulfuron methyl.

For the extraction of metsulfuron methyl in seepage, 250 ml of seepage water samples were prepared in a glass bottle. The pH of the water sample was adjusted between 5-6 with potassium hydroxide and or hydrochloric acid. The cartridge was rinsed with 3 ml of acetonitrile and 3 ml of distilled water. Then, the water sample was flowed about 2-3 ml per minute through the SPE cartridge. Next, the metsulfuron methyl that was absorbed in the SPE cartridge was separated with methanol and stored in a 20 ml glass bottle. The extraction results were dried to a range of 1 ml. After that, it was sucked with a syringe equipped with a 0.2 micron filter, then transferred to a 1.5 ml analysis vial bottle.

2.5 Metsulfuron Methyl Analysis

To provide a standard metsulfuron methyl primary solution, 1.02 mg metsulfuron methyl (98% purity) was weighed and dissolved with 50 ml of methanol gred HPLC to produce a solution with a concentration of 20 mg/L. Then, it was diluted so that the concentration became 10 mg/L.

Next, to produce a standard metsulfuron methyl curve, 5 series of secondary solutions were formulated with concentrations of 50 μg/L, 100 μg/L, 200 μg/L, 300 μg/L and 500 μg/L respectively. A secondary solution was formulated by dissolving the primary solution as much as 0.05 ml, 0.1 ml, 0.2 ml, 0.3 ml, and 0.5 ml with methanol gred HPLC until the solution volume became 10 ml in a volumetric flask. All the solutions made were placed in an ultrasonic device for 20 minutes and then injected into a 1.5 ml vial analysis bottle by filtering it using 0.2 micron filters to be analyzed using HPLC.

Furthermore, the standard solution of metsulfuron methyl, methanol, soil samples and water samples stored in 1.5 ml vial bottle was inserted into the Agilent 1220 Infinity LC HPLC. Samples of each vial bottle were automatically analyzed for 18 minutes and the results of the analysis were displayed through the OpenlabChemstation interface on a computer screen.

3 RESULTS AND DISCUSSION

3.1 Calibration Curve

The highest correlation was obtained from a combination of 3 series of metsulfuronmethyl standard solutions, namely 100 g/L, 200 μg/L, and 300 μg/L, which had a correlation coefficient of 0.995. This implies that the concentration of standard solutions gives an effect of 99% on the response of the instrument, while the rest is influenced by other variables.The above curve also shows that metsulfuron methyl can be detected in the range of RT (retention time) 5,391 minutes (Figure 3).

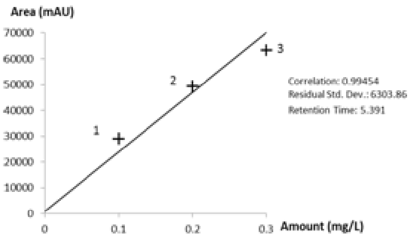

Figure 3: Linear regression curve of standard metsulfuron methyl solution.

3.2 The Persistence of Metsulfuron Methyl in Soil

Table 1 demonstrates that the metsulfuron methyl residue was not found on the soil during HPLC analysis. The ameliorant treatment of rice husk biocharrevealed the same effect as the one without the treatment of husk biochar after 28 days of herbicide application. In other words, this research found that rice husk biochar could not maintain the persistence of metsulfuron methyl longer in the soil.

Table 1: Level of metsulfuron methyl residues in soiln

Treatment	Metsulfuron Methyl		
	Ret Time (minute)	Area (mAU*s)	Residual Level (μg/L)
0% husk biochar	5.391	0	0
5% husk biochar	5.391	0	0
10% husk biochar	5.391	0	0
15% husk biochar	5.391	0	0

One of the important processes that control the behavior of herbicides in the soil is the adsorption carried out by the soil components. Herbicides can be found in soil in the form of dissolved molecules of the liquid phase and/or molecules that are bound to soil phases such as minerals, organic matter, plant residues, etc. (Zanini et al., 2008). In addition, more than 36.3% to 55.7% of the applied metsulfuron methyl turns into a residual form that binds to the soil (Pons and Baniuso, 1998; Xu et al., 2002; Wang et al., 2002). However, how the mechanism of colloidal soil holds metsulfuron methyl and its metabolites is still not clearly confirmed. Possible bonds between herbicides and colloidal soils include: (1) ionic bonds,

(2) hydrogen bonds, (3) van der waals forces, (4) ligand exchanges, (5) charge transfer complexes, (6) hydrophobic partitioning, (7) covalent bonds and (8) sequestration (Gevao et al., 2000).

Based on the results of this research, the degradation of metsulfuron methyl herbicide in the soil is resulted from through several degradation processes, namely: hydrolysis, photolysis and microbial decomposition. However, the authors assume that the degradation of metsulfuron methyl was more influenced by chemical degradation (hydrolysis) than by biochemistry (microorganisms) or physics (photolysis). This is in accordance with Devlin et. al. (1992) who reported that the degradation of sulfonylurea herbicides, such as Ally Classic and Glean, is mostly caused by hydrolysis. It is supported by a research conducted by Manna (2015), which reported that the main mechanism of chemical degradation of sulfonylurea herbicides is caused by hydrolysis.

3.3 The Levels of Methyl Metsulfuron Residue in Seepage

Based on the results of HPLC analysis, it was found that the residual level of metsulfuron methyl in seepage was 7.7 μg/L in the treatment of 0% husk biochar and 6.8 μg/L in the treatment of 5% husk biochar. Whereas, there was no metsulfuron methyl residue was found in seepage at 10% husk biochar and 15% husk biochar(table 2). This shows that the level of residual metsulfuron methyl in seepage water tends to decrease with the increasing amount of rice husk biochar applied.

Table 2: Level of metsulfuron methyl residues in seepage water

Treatment	Metsulfuron Methyl		
	Ret Time (minute)	Area (mAU*s)	Residual Level (μg/L)
0% husk biochar	5.365	1745.06	7.68
5% husk biochar	5.357	1533.71	6.75
10% husk biochar	5.391	0	0
15% husk biochar	5.391	0	0

The authors believe that this tendency occured due to the adsorption by rice husk biochar applied in the soil, preventingmetsulfuron methyl from being leached. Hence, it can be concluded that the addition of rice husk biochar in this research is very effective to prevent metsulfuron methyl from leaching. As a result, it can reduce the negative impacts that arise in the water ecosystem around it.

This research finding is in accordance with that of by Zhelezova et al. (2017) who reported that adding wood charcoal to sandy and clay soils cause the adsorption of diuron herbicides increased. The increasing of diuron adsorption in line with the addition of charcoal, because charcoal has many absorbent surfaces that can bind non-polar herbicides so it can reduce the risk of leaching. Jing et al. (2018) investigated that the addition of rice husk biochar could slow the loss of ethyl phenoxaprop herbicide in the soil.

The prevention of metsulfuron methyl leaching can certainly be used as a solution to prevent the contamination of active substance of herbicides reaching to underground water and other water ecosystems such as rivers and lakes.

A very low residual level of metsulfuron methyl does not mean have no negative impact on the environment. Fairchild (1995) reported that metsulfuron methyl could cause the reduction of 50% of the number of Lemna minor leaves in a period of 14 days with an EC50 0.4 μg/L. If it accumulates continuously over a long period of time, it is not impossible that other aquatic organisms can be affected, including: algae (Selenastrumcapricornutum, EbC_{50} 3.9 mg/L), crustaceans (Daphnia magna, $EC_{50} >$ 150 mg/L), and fish (Bluegill sunfish, $LC_{50} >$ 150 mg/L).

4 CONCLUSIONS

Metsulfuron methyl was completely degraded 28 days after herbicide application regardless the application of rice huskbiochar, which is assumed to be caused by hydrolysis as the main factor.

The residual metsulfuron methyl was found in seepage water in the treatment of 0% husk biocharas much as 7.7 μg/L and in the treatment of 5% husk biochar as much as 6.8 μg/L, while the treatment of 10% and 15% husk biochar was 0 μg/L. This indicates that the addition of rice husk charcoal ameliorant is very effective in absorbing and breaking down metsulfuron methyl in the soil, so that the further contamination of herbicide metsulfuron methyl into the surrounding water environment can be avoided.

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REFERENCES

Devlin, D. L., Peterson, D. E., and Regehr, D. L. *1992*. Residual Herbicides, Degradation and Recropping Interval.

Fairchild, J. F., Ruessier, D. S., Lovely, P. A., Whites, D. A., and Heine, P. R. *1995*. An Aquatic Plant Risk Assessment of Sixteen Herbicides Using Toxicity Tests with Selenastrumcapricornutum and Lemna minor.

Gevao, B., Semple, K. T., and Jones, K. C. 2000. *Bound Pesticide Residue in Soils: A review. Environmental Pollution*, 108:3–14.

Jansar, K. M. and Sahid, I. B. (20). 2016. *Residue Determination and Monitoring of The Levels of Metsulfuron Methyl in Selected Rivers at TasikChini Pahang Malaysia. Malaysian Journal of Analytical Sciences 20*.

Jing, X., Wang, T., Yang, J., Wang, Y., and Xu, H. 2018. *Effect of Biochar on The Fate and Toxicity of Herbicide Fenoxaprop-Ethyl in Soil. R. Soc. Open Sci*, 5:171875.

Pons, N. and Baniuso, E. 1998. *Fate of metsulfuron-methyl in soils in relation to pedo-climatic conditions. Pestic. Sci*, 53:311–323.

PT. (20). *DuPont Agricultural Products Indonesia*. Lembar Data Keselamatan Ally 20 WDG.

Rao, V. S. (2000). *Principle of Weed Science 2nd Eds*. Science Publisher, Inc.

S., M. (2015). *Effect of Biochar Amendments on Fate of Pyrazosulfuron-Ethyl in Soil*.

Sudirja, R., Arifin, M., and Joy, B. 2015. *AdsorpsiParaquatdanSifat Tanah padaTigaSubgrup Tanah AkibatPemberianAmelioran. JurnalAgrikultura*, 26.

Wang, H. Z., Xu, J. M., Xie, Z. M., and Ye, Q. F. 2002. *Dynamics of bound residues of metsulfuron-methyl in soil humus. Acta Sci. Curcum. 22*, 22.

Xu, J. M., Wang, H. Z., Xie, Z. M., and Chen, Z. L. 2002. *Distribution of bound residues of metsulfuron-methyl in soil combined humus. China Environ. Sci. 22*, 22.

Zanini, G. P., Maneiro, C., Waiman, C., Galantini, J. A., and Rosell, R. A. 2009. *Adsorption of Metsulfuron Methyl on Soils under No-Till System in Semiarid Pampean Region, Argentina. Geoderma*, 149:110–115.

Zhelezova, A., Cederlund, H., and Stenstrom, J. 2017. *Effect of Biochar Amendment and Ageing on Adsorption and Degradation of Two Herbicides. Water Air Soil Pollut*, 228:216.