REMEDIATION OF INSECTICIDE RESIDUES IN SOIL USING ACTIVATED CARBON

REMEDIASI RESIDU INSEKTISIDA DALAM TANAH MENGGUNAKAN ARANG AKTIF

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Diterima Agustus 2014, diterima setelah perbaikan Januari 2015
Disetujui untuk diterbitkan Februari 2015

Abstract: *The using of insecticides will have a negative impact on the biodiversity, environment, food quality and human health. One way is a remediation technology by using activated carbon. Research conducted at the Muara experimental station, Bogor-West Java in 2009 (in paddy field) by RCBD with four activated carbons (AC) treatment: coconut shell, corn cobs, rice husk and palm oil empty fruit bunches (POEFB) were tested. Size of AC used was 50 mesh. Quality ofAC should be refers to the SNI06-3730-1995 (Indonesian Standard).Application of AC was in the days before planting. Application AC like as urea fertilizer (by spread). Dose of AC used was 1000 kg/ha or 1.2 kg/plot. Soil sampling was conducted at 1, 40 and 80 days after treatment (DAT). Theinsecticides (lindane and chlorpyrifos) in soil samples were analysed by gas chromatography (GC). In the soil samples was also observed that the presence of insecticide degrading microbes. Based on the field test results showed that AC of coconut shells, corn cobs, rice husk and POEFB have an effect on decrease of chlorpyrifos and lindane residues. AC could be increaseddegrade by microbial populations such as Citrobacter, Enterobacter, and Azotobacter. Activated carbon as a potential bioremediation in soil because its serve as decomposers insecticide residues (chlorpyrifos and lindane).*

Keywords: *remediation, insecticide residue, and activated carbon.*

Abstrak: *Penggunaan insektisida berdampak negatif pada biodiversitas, lingkungan, kualitas pangan, dan kesehatan manusia. Teknologi remdediasi dengan menggunakan arang aktif merupakan salah satu cara penanggulangannya. Penelitian telah dilaksanakan di Kebun Percobaan Muara Bogor, Jawa Barat pada tahun 2009 (padi) dengan rancangan percobaan acak kelompok empat. Perlakuan yang diujikan adalah karbon aktif tempurung kelapa, tongkol jagung, sekam padi, dan tandan kosong kelapa sawit berukuran 50 mesh. Kualitas karbon aktif mengacu SNI06-3730-1995. Aplikasi karbon aktif sehari sebelum tanam sama seperti urea dengan cara ditabur dengan dosis 1000 kg/ha atau 1,2 kg/plot. Pengambilan contoh tanah dilakukan saat 1, 40, dan 80 hari setelah aplikasi (HSA). Residu lindan dan klorpirifos dalam tanah dianalisis menggunakan GC. Selain itu diamati pula keberadaan mikroba yang mendegradasi insektisida. Hasil pengujian lapang menunjukkan bahwa karbon aktif tempurung kelapa, tongkol jagung, sekam padi, dan tandan kosong kelapa sawit berpengaruh menurunkan residu lindan dan klorpirifos. Karbon aktif dapat meningkatkan degradasi insektisida oleh populasi mikroba Citrobacter, Enterobacter, and Azotobacter. Karbon aktif sebagai bioremediasi yang potensial dalam tanah karena membantu decomposer residu insektisida (klorpirifos dan linden).*

Kata kunci: *remediasi, residu insektisida, dan karbon aktif.*

INTRODUCTION

Pesticide has been known and used widely by farmers in Indonesia since the 1950s to protect their crop from pest attacks. Every year, thousands of tonnes of different kinds of pesticides are distributed, bought, and applied by farmers for controlling insect pests, diseases, and weeds. (Untung, 1998). The use of pesticides in Indonesia had been increased very rapidly because of the expansion of area cultivated under food crops and vegetables. However, the major causes concern of its are the undesirable side effects of these chemicals on biodiversity, environment, food quality and human health.

The reduction of insecticide applications to rice to about half their previous level and to about 2/3 their previous levels in highland vegetable crops has significantly reduced the risk of polluting the environment and endangering human health, and has helped to minimize pesticide residue levels in food and the environment (UNIDO, 1984; Untung, 1998).

In fact, until now, the use of pesticides in the field are still uncontrolled (overuse and misuse).Due to the use of pesticides is not control edit will have an impact on the pesticide residues in the environment. Based on research of IAERI (2007), pesticide residues in soil, plant and water the rice fields in Bantul, Yogyakarta are still remain particularly organochlorine residues. Application of pesticides in the field was only 40% of pesticide is absorbed by plants, while 60% of pesticides felt to the soil. Pesticides in soil will partly affect the soil biota, and some will go into the river and finally into the sea. Residual insecticides are not only found in plants, soil and water but also in the blood of farmers.

Remediation is an environmental clean–up technique that is currently being investigated for use on a wide variety of chemicals. It is the use of naturally occurring microorganisms to enhance biodegradation, or normal biological breakdown. It involves establishing the condition in contaminated environment so that appropriate microorganisms flourish and carry out the metabolic activities to detoxify the contaminants (Singh and Walker, 2006) and is also safe, viable remedy for the detoxification of environmentally hazardous chemicals (al-Mihanna *et al*., 1998). There are three primary approaches to bioremediation; Biostimulation, Bioaugmentation {which may include genetically engineered microorganisms (Gem's)} and Phytoremediation. Biodegradation of organic pollutants is a natural process whereby, bacteria and other organisms alter and breakdown organic molecules into substances, eventually producing carbon dioxide and water or methane.

Lindane is an organochlorine insecticide widely used throughout the world and concidered as Persistent Organic Pollutant (POP). Due to the deleterious effect of POP's on environment and human health, the use of many of them has been reduced or even banned in developed countries (Rajendran *et al*., 1999). Lindane is also known as gamma-HCH since it is made up of least 99% of the gamma isomer of hexachlorocyclohexane (HCH). Almost pure γ-HCH i.e lindane, is known as benzene hexachloride (BHC) (Li, 1999). According to previous reports, HCH isomers exhibit long persistence in aerobic soil and water environments. For instance, γ-HCH (lindane persisted for 11 years in temperate upland (non-flooded) soil (Lichtenstein and Polivka, 1959), but only for 3-5 months in a tropical upland soil (IARI, 1978). More recently, degradation of HCH isomers has been demonstrated also in aerobic systems (Bachmann *et al*., 1988a,b; Wada and Senoo, 1989; Sahu *et al*., 1990a). Soil submergence, coupled with organic amendments, can be considered as a viable technology for bioremediation of HCH isomers in the contaminated sites Sethunathan *et al*., (1998). A number of methods have been developed for the removal of lindane from soil and water such as sorption by activated carbon, remediation by nanoparticles, photocatalysis, biocatalytic dechloronation, phytoremediation, biosorption and microbial degradation (Salam and Das, 2012).

Chlorpyrifos (0,0-diethyl-3,5,6-trichloro-2-pyridylphosphorothioate) is a insecticide/acaricide for treatments of crops, lawns, ornamental plants. It is a widely used insecticide and effective against a broad spectrum of insect pests of economically important crops. It is also used for the control of mosquitoes (larvae and adults), flies, various soil pests, many foliar crop pests and household pests. Additionally it is used for ectoparasite control of cattle and sheep. It persists in the soil for 60-120 days, and has very low solubility in water (2 mgl-1), but is readily soluble in most organic solvents.Chlorpyrifos is one of the most widely and commonly used commercial insecticides (Kuperberg *et al*., 2000). The half-life of chlorpyrifos was 34-46 days with negligible effect on microbial characteristics (Singh *et al*., 2002b). It has been observed that chlorpyrifos had insignificant effect on soil microorganism (Singh *et al*., 2002a). In a 2 months study 100% persistent was observed with the survival of Klebsiella sp, (Shahida *et al*., 2004). Chlorpyrifos has been reported previously to be resistant to enhanced degradation due to the accumulation in soil of the antimicrobial degradation product. Its microbial degradation results in higher concentration of 3,5,6, trichloro-2-pyridinol (TCP), a major metabolite (Robertson *et al*., 1998). Sterilization greatly reduced the rate of chlorpyrifos degradation indicating the involvement of microbial activities (Rehman and Motoyama, 2000). Chlorpyrifos incubated for 69 days at 15°C showed that soil pH was strongly co-regionalized with chlorpyrifos residue (Price *et al*., 2003).

Various adsorbents are used for decontamination of soil and water. Among others, activated carbon (AC) is one of the best adsorbents for many organic chemicals because of its hydrophobicity, high specific surface (800-1200 m2/g), and microporous structure. The average pore diameter of AC (1 or 2 nm, 0.35 nm minimum) is closeto the size of monoaromatic molecules (O'Brien, 1992). AC in dense as well as porous solid form is used in a variety of applications such as absorber of pollutants (e.g. pesticide residue). Activated porous carbons are made through pyrolysis and activation of carbonaceous natural as well as synthetic precursors (Manocha, 2003). Soil treated with activated carbon could be attributedto stimulated microbial activity and population after the addition of activated carbon (Ogawa, 1994). The use of activated carbon may help overcome the toxicity of organic pollutants to microbes and plants during soil bioremediation (Vasilyeva *et al*., 2006). AC has also been recomended for reducing the phytotoxicity of many herbicide residues and other chemicals in agricultural soils (Strek *et al*., 1981; Mukhin *et al*., 1995). One of the reasons for the low effectiveness of soil bioremediation is the high toxicity of chemical contaminants to microbes and plants. The research results demonstrate the potential of AC to decrease toxicity and promote biodegradation processes in highly contaminated soils (Vasilyeva *et al*., 2006).

The objective of the research wasto determine the influence of activated carbon (AC) on chlorpyrifos and lindane concentration in paddy field. Chlorpyrifos and lindane are common contaminant of paddy field.

METHODS

Research conducted at the Muara experimental station, Bogor-West Java in 2009 (in paddy field). Four activated carbons (AC) which derived fromcoconut shell, corn cobs, rice husk and palm oil empty fruit bunches (POEFB)were studied.

Preparation of Activated Carbon

The raw materials (coconut shell, corn cobs) obtained from markets around Bogor. Rice husk obtained from agricultural land around Dramaga Bogor. Palm oil empty fruit bunches (POEFB) obtained from palm oil land around Jasinga Bogor. The production process of activated carbons (AC) derived fromcoconut shell, corn cobs, rice husk and POEFB, all consisted of carbonization and chemical activation with phosphoric acid (H_3PO_4).Each dried raw material was cut into small pieces aproximately 1-2 cm^2 and placed into stainless steel box with cover. The carbonization was then condacted in muffle furnace at 300^oC for coconut shell, corn cobs, rice husk and POEFB, respectively. The heating period was 3-4 hours for all materials. After carbonization, the residual char was ground using a laboratory jar mill to pass trough a 50 mesh sieve. The chemical activation was done in the next step by mixing the ground char with concentrated solution of 20% H_3PO_4in the crucible. Sample to H_3PO_4 ratio are 1:2 by weight. The samples were activated at 800-900^oC for 3 hours in a muffle furnace. The obtained activated carbon was washed with hot water to remove phosphoric compound including impurities and dried at 105^oC for 3 hours. The obtained activated carbons were kept in a dessicator and were characterized for iodine number. The standard quality of activated carbons based on Indonesian Standard (SNI 06-3730-1995) are shown in table 2. The iodine number gives an indication of the adsorption capacity of activated carbon in micropores. The physico-chemical properties of activated carbons are shown in table 1.

Table 1. Properties of activated carbons used.

Parameter	Activated carbon			
	Coconut shell	Rice husk	Corn cobs	POEFB[a]
Water content (%)	5.03	6.31	10.76	6.54
Volatile matter (%)	9.42	11.92	13.28	12.60
Ash (%)	1.51	21.80	40.32	38.06
Absorption of I_2 (mgg^{-1})	901.13	330.64	887.13	315.21
Specific gravity (gmL^{-1})	0.34	0.32	0.31	0.30
Mesh	50	50	50	50

[a]POEFB: palm oil empty fruit bunch

Table 2. Standard quality of activated carbons accordance with Indonesian Standard (SNI 06-3730-1995).

No.	Parameter	Required	
		Granular	Powder
1	Water content (%)	Max. 4.5	Max. 15
2	Volatile matter content (%)	Max. 15	Max. 25
3	Ash content (%)	Max. 2.5	Max. 10
4	Non carboneous part (%)	0	0
5	Absorption of I_2 (mgg^{-1})	Min. 750	Min. 750
6	Absorption of C_6H_6 (mgg^{-1})	Min. 25	-
7	Absorption of methylene blue (mgg^{-1})	Min. 60	Min. 120
8	Bulk specific gravity (gmL^{-1}	0.45-0.55	0.3-0.35
9	Escape mesh	-	Min. 90
10	Mesh spacing (%)	90	-
11	Hardness (%)	80	-

Remediation of insecticides by activated carbons

Rice plants, variety Ciherang transplanted at the Muara Experimental Substation of Rice Research Institute in Bogor (oxisol soil type). Physical and chemical soil properties were analyzed according to the official methods of the Indonesian Soil Research Institute (ISRI, 2005).Their physico-chemical properties are shown in table 3. These research was conducted by randomized complete block design (RCBD) with four AC treatment: coconut shell, corn cobs, rice husk and POEFB. The size of each plot was 12 m^2 (4x3 m^2). Lindane and Chlorpyrifos standard (99,5% purity) was obtained from Sigma Corp, Jakarta. Lindane and Chlorpyrifos was applied at the rate 3 ppm per plots (before planting and before application of AC) by hand sprayer (each 600 ml of insecticide solution applied per plots; insecticides applied reference are 500 l/ha). Application of AC was in the days before planting and after application of AC. Each AC was applied like as urea fertilizer (by sow). Dose of AC used was 1000 kg/ha or 1.2 kg/plot (4x3 m^2). Fertilizer are used asurea 250 kg/ha, super phosphat (SP36) 100 kg/ha and KCl 75 kg/ha. Soil sampling was conducted at 1(initial), 40 (primordia) and 80 (harvest) days after treatment (DAT). Each soil was taken from 0-15 dept of plots.Soil samples wereair dried, crushed lightly and then passed through a 2-mm sieve.Residues of insecticides (lindane and chlorpyrifos) in triplicate soil samples from each treatment were further cleaned up and analyzed by gas liquid chromatography (GLC) equiped with electrone capture detector (ECD). The spiked recoveries of lindane and chlorpyrifos in soil using 100 ng of standard were in the range 85-105% and 77-88% respectively. The presence of insecticide-degrading bacteria were further identified. The identification work of bacteria was carried out at Microbiology Laboratory of Padjadjaran University in Bandung.

Table 3. Properties of soil sample used.

Source soil	Texture/type	Clay content (%)	Organic matter (%)	CEC (me/100 g)	pH	
					H_2O	KCl
Muara Exp. St.	Oxisol	55	1.4	20.02	5.5	4.7

DISCUSSION

Soil analysis

The analyzed physico-chemical properties of soil were presented in table 3. The values of soil pH of 5.5 indicating acidic. The content of organic matter and clay on Muara experimental station 1.4% and 55% was observed. The quantity of organic matter and clay attributed a major concern to permit the downward movement of lindan and chlorpyrifos in the lower depth. Soil of Muara experimental station reflected high CEC (20 me/100g) due to rich organic matter content which influenced the adsorption patern of insecticides.

Activated carbon in soil

For the selection of an appropriate raw material for preparation of porous carbon, several factors are taken into consideration. Inexpensive material with high carbon and low inorganic (i.e. low ash) content is perferred as raw material for the production of activated carbon. High absorption of I_2 and low ash content are considerable importance. Raw materials used for preparation of activated carbons vary with their application. Raw materials used in this study are coconut shell,corn cobs, rice husk and palm oil empty fruit bunches (POEFB) with characteristics are given in table 2. Activated carbon from the coconut shell has a higher absorption (above the standard of 750 mg/g) than the corn cobs,rice husk and POEFB. A previous study comprising a complete life cycle assessment of sediment remediation by several amandements as well a natural recovery also indicated that coconut-based AC was the optimal material in a global perspective (Sparrevik *et al*., 2011). Based on the I_2 absorption coconut shell and the corn cobs have more potential absorb than rice husk and POEFB. According Linn cit Verma *et al*., (2014), the relative importance of processes varies with the chemical nature of pesticides and the properties of soil, but two process stand out (degradation and sorption). The introduced AC was shown to maintain a low content of toxicant in soil solution, creating favourable conditions for plant growth, while plants died or were greatly inhibited in unamended soils (Vasilyeva *et al*., 2006).

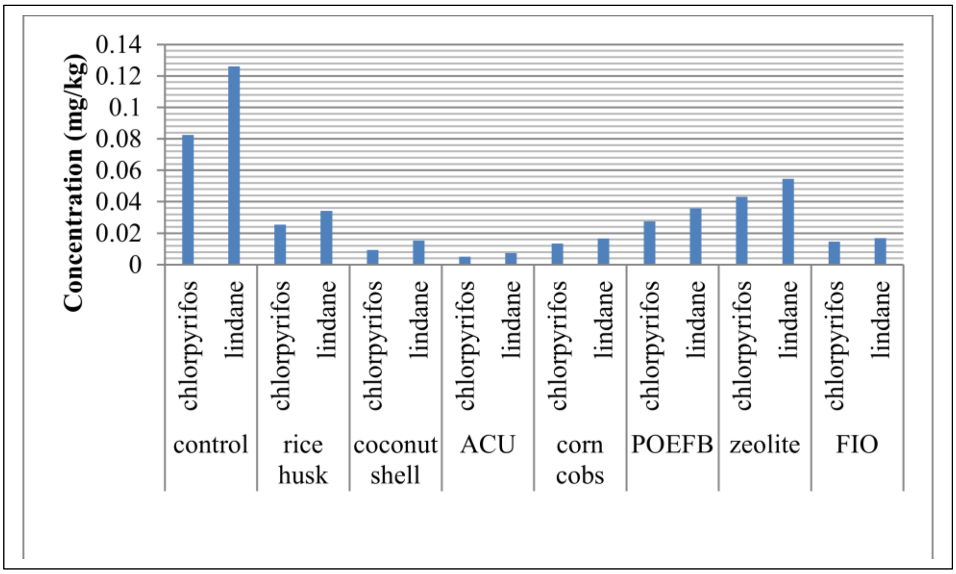

Figure 3. Performance comparison of AC productand zeolite.

Table 4. Concentration insecticide residues in soil (mg/kg) after activated carbon (AC) treatment.

No	AC Treatments	Dose of AC (kg/plot)	Residues concentration (mg/kg)		
			1 DAT	40 DAT	80 DAT
		Chlorpyrifos			
1	Control	-	0.1848	0.1705	0.1345
2	Rice husk	1.2	0.1813	0.1005	0.0654
3	Coconut shell	1.2	0.1727	0.0565	0.0293
4	Corn cobs	1.2	0.1734	0.0595	0.0435
5	POEFB	1.2	0.1822	0.1093	0.0775
		Lindane			
1	Control	-	0.2039	0.1913	0.1661
2	Rice husk	1.2	0.1921	0.1135	0.0842
3	Coconut shell	1.2	0.1926	0.0823	0.0453
4	Corn cobs	1.2	0.1934	0.0957	0.0566
5	POEFB	1.2	0.1941	0.1361	0.0959

POEFB: Palm oil empty fruit bunches' DAT = days after treatment.

Chlorpyrifos in soil

Based on the field test results showed that AC of coconut shells, corn cobs, rice husk and POEFB have an effect on declined of chlorpyrifos residues (table 4). At 1 DAT residues of chlorpyrifos has not seen a significant reduction, but at 40 DAT increasingly apparent decrease in chlorpyrifos residues. At 80 DAT decrease in chlorpyrifos residues reached more than 50% compared to control (figure 1). AC of coconut shells and corn cobs are the best compared to the other. This is inline with the higher absorption capacity of AC of coconut shell and corn cobs compared with other AC. Good decreasing of chlorpyrifos were absorpted by AC of coconut shell, corn cobs,rice husk, and POEFB respectively. Activated carbon from coconut shell has the highest ability to reduce the concentration of chlorpyrifos. Chelsea (1991) reported that chlorpyrifos is moderately persistent in soils with the half-life usually between 60 and 120 days, but can range from 2 weeks to over 1 year, depending on the soil type, climate, and other conditions.Chlorpyrifos showed a major loss (75±90%) of residue during the 24 months incubation period. In the bedding materials, simultaneous accumulation of the primary metabolite of chlorpyrifos, TCP (3,5,6-trichloro-2-pyridinol) was observed. Hydrolysis appeared to have caused the observed rapid loss of chlorpyrifos, especially in the highly alkaline bedding materials (sand-dolomite and quarry sand) (Baskaran *et al*., 1999). The soil retained the residue longer than any component of the rice paddy due to adsorption and bound-residue formation. In addition, the soil is the ultimate sink of pesticide deposition. (Tanah mempertahankan residu lebih lama daripada komponen dari sawah karena adsorpsi dan pembentukan terikat-residu. Selain itu, tanah adalah wastafel utama deposisi pestisida) (Varca and Tejada, 1998). Singh *et al*., (2003) reported a robust bacterial population that utilized chlorpyrifos as a source of carbon in an Australian soil.

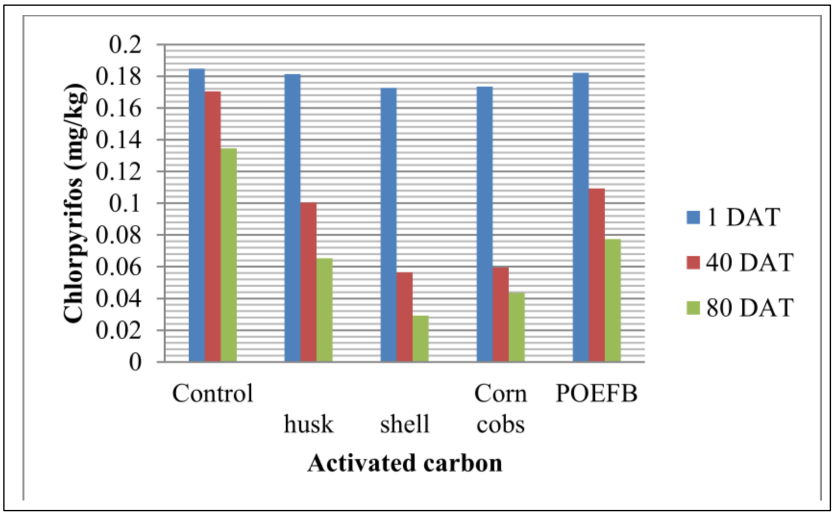

Figure 1. Concentration chlorpyrifos in soil (mg/kg) after activated carbon (AC) treatment.

Lindane in soil

Tsukano (1973) reported that Lindane has favorable properties from standpoint of decontaminating rice field soils, such as rapid release and diffusion from granules, volatility from water surface, relatively low affinity to soil, movability in soil, and high degradability in flooded soil and then microorganism play an important role in the disappearance of lindane in flooded soil. HCH disappeared much faster from the flooded than from the unflooded soils, as also shown by Raghu and Macrae (1966). The soil-bound HCH was maximal at a temperature of 45°C; it was about 16.7% after 28 days, much less than in the flooded soil (ca 4.8%) (Agarwal and Singh, 1998). The most probable mechanism of organochlorine (OC) binding to AC is formation of π-π-bonds with the graphene surface of the adsorbent. These bonds can be especially strong when the planar OC molecules penetrate the nearest nanopores where their molecules may form π-π-bonds with both walls of the slit-like pores of the carbon. Nonplanar molecules of OC having two and more ortho-chlorines should form weaker π-π-bonds with the AC surface, and these bulkier molecules may have less potential to penetrate into the narrow pores (Vasilyeva *et al.*, 2006). The behavior of pesticides in soils is governed by a variety of complex dynamic physical, chemical, and biological processes. The processes include are sorption-desorption, uptake by plants run-off, and leaching that directly control the transport of pesticides within the soil and their transfer from soil to water, air, and food (Arias-Estevez, 2008). However, pesticide degradation process influenced by of temperature and frequent pesticide application in agronomical practice. These activities could accelerate degradation process of pesticide and accelerated degradation mignt be more extensive and costly if pesticide efficacy were reduced by phenomena (Arbeli and Fuentes, 2007). The using of pesticide caused unbalancing of pesticide in soils, water, and air environment that effect to natural degradation of chemicals in soil as biomagnifications.

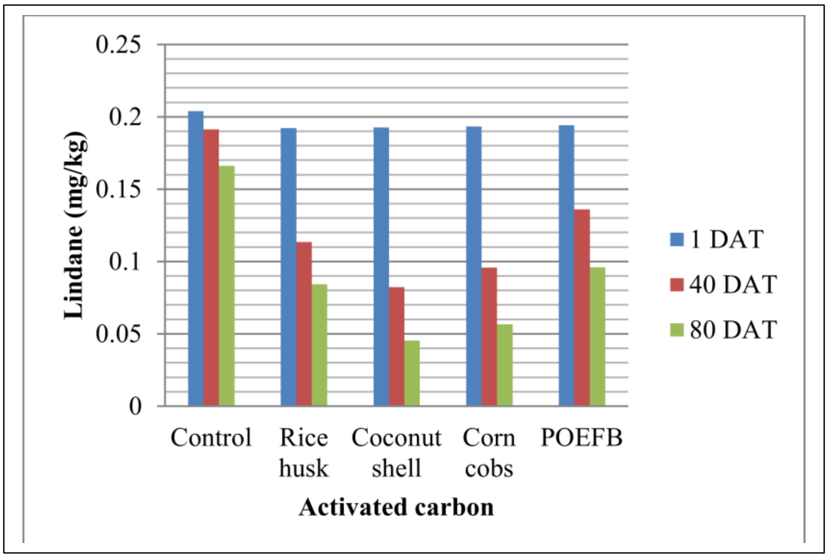

Figure 2. Concentration lindane in soil (mg/kg) after activated carbon (AC) treatment.

Microbes in the soil

Application of AC in the soil apparently affects bacterial populations because AC is used as a 'good home' for microbes. AC inthe soil has the role of reducing residual insecticides in rice and water particularly the organochlorine residues. AC could be increased degrade microbial populations such as *Citrobacter*, *Enterobacter*, *Azotobacter* and *Bacillus* sp. (table 5). Not only activated carbon but the role of microbes is very important in declined the concentration of insecticide residues, because insecticide residues as nutrient source for microbes. Gupta *et al*., (2000) reported lindane degradation using acclimatized culture of *Bacillus circulans* and *Bacillus brevis* in 5 µg/mL lindane and 80% degradation was noted within 8 days. The combination of microorganism consortia indigenous and isolated microbe from contaminated of environment will have degraded more faster. The process of bio augmentation and adding of nutrient and organic matter could accelerate the degradation of contaminant by indigenous microbe. The use of indigenous microbe effect on growing plant ecological (Verma *et al*., 2014). Ogawa (1994) reported that the use of activated carbon in paddy fields can increase the number of bacteria and bacterial nitrogen fixation (*Azotobacter*) in the soil around the roots of plants, especially food. Results of studies in Japan have said that there has been an increase in the frequency of bacterial nitrogen fixation on land use activated carbon that is, 10-15% in Hokkaido and Tohoku (northern Honshu), 36-48% in Tokyo to Hiroshima (the East-West Honshu) and Shikoku, 59-66% in Kyushu (Ogawa, 1994). Gilani *et al*., (2010) reported that 100 ppm fortification of chlorpyrifos did not affect adversely but 1000 ppm application suppressed the growth of certain colonies while count of some of the colonies was increased. Initially two types of colonies were observed in the culture identified as *Bacillus* sp., and *Klebsiella* sp.

Table 5. Influence of AC on bacterial populations in paddysoil.

No.	AC treatment[a]	Bacteria cfug^{-1}			
		Citrobacter	***Enterobacter***	***Azotobacter***	***Bacillus sp.***
1	Control	1.0×10^{10}	2.0×10^{8}	2.2×10^{9}	7.1×10^{9}
2	Rice husk	7.0.x.10^{9}	1.9×10^{9}	1.7×10^{9}	1.7×10^{9}
3	Coconut shell	2.0×10^{9}	6.0×10^{9}	2.5×10^{9}	1.2×10^{8}
4	Corn cobs	2.7×10^{10}	1.2×10^{10}	1.2×10^{10}	7.9×10^{9}
5	POEFB	9.6×10^{8}	1.0×10^{7}	2.4×10^{8}	3.8×10^{8}

[a]POEFB: palm oil empty fruit bunch

CONCLUSIONS

Activated carbon (AC of coconut shell, rice husk and corn cobs) as a potential for remediation of insecticide residue (lindane and chlorpyrifos) in soil because its could be increasedthe microbial populations (*Citrobacter*, *Enterobacter*, and *Azotobacter*) which serve as decomposers insecticide residues (chlorpyrifos and lindane).Activated carbon (AC of coconut shell, rice husk and corn cobs) as bioremediation that accelerate degradation process in soil. The process of bio augmentation and adding of nutrient and organic matter could be accelerated the degradation of contaminant by indigenous microbe. Decreasing of insecticide in soil caused desorption-desorption and biodegradation by indigenous microbe that influenced by adding the soil amendment like as activated carbon.

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