AJChE 2009, Vol 9, No. 2, 25 – 34

Photolysis Reaction of Linear Alkhylbenzene Sulphonate in Saturated Soil: Kinetics Parameters Evaluation

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Fate of detergent of linear alkhylbenzene sulphonate (LAS) in the soil can be described if the values of kinetics parameters are known. The objectives of the study were to determine the kinetics parameters of photolysis reaction of LAS in saturated soil system, to identify variables affecting the parameters, and to set-up empirical equations correlating parameter to the pertinent variables.

The experimental works were performed in batch reactor which was equipped with ultraviolet of 53 or 789 lumens. One hundred grams of soil was mixed with 1000 ml of water and then the mixture was left for 24 hour in the reactor. A certain amount of LAS was then added to the soil solution and stirrer was put on, so that the LAS concentration in the mixture became 20 ppm. Before the light put on, the soil solution was analyzed its biomass content using a plate count method and LAS concentration using Methylene Blue Active Substances (MBAS) method. Subsequently the slurry were stirred and lighted continuously. At a certain time interval, 5 cubic centimeters of solution was taken from the reactor then its biomass content and LAS concentration were analyzed. The variables studied were different soil type and the light intensity. When effects of one variable studied, the other variables were kept constant.

Photolysis reaction of LAS in saturated soil took place both in soil solution and particle. The kinetics parameters are the function of soil organic matter (%OM) and clay mineral (%CM) content, as well as light intensity. The photolysis reaction rate constants of LAS in soil solution and particle for light intensity of 53 lumens are described as follows:

$$k_{PS} = 3.79x10^{-4}(\%OM) + 4.41x10^{-3}(\%CM)$$
$$k_{PL} = 7.73x10^{-3}(\%OM) + 1.18x10^{-3}(\%CM)$$

For the light intensity of 789 lumens, the kinetics parameters are

$$k_{PS} = 16.3x10^{-4}(\%OM) + 0.075x10^{-3}(\%CM)$$
$$k_{PL} = 49.3x10^{-3}(\%OM) + 1.46x10^{-3}(\%CM)$$

The sorption coefficient soil and water of LAS is expressed as:

$$K_d = 8.06x10^{-4}(\%OM) + 7.39x10^{-5}(\%CM)$$

Keywords: fate, photolysis, methylene blue active substances, detergent of linear alkhylbenzene sulphonate, saturated soil

INTRODUCTION

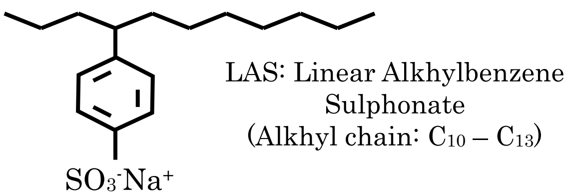


Figure 1. Linear Alkhylbenzene Sulphonate Detergent Structure

The structure of linear alkhylbenzene sulphonate (LAS) detergent is shown in Figure 1. Linear alkhylbenzene sulphonate is a mixture of isomers and homolog, each isomer and homolog has a para sulphonate aromatic ring and the linear alkyl chain. Linear alkhylbenzene sulphonate has C linear chain in the range of 10 to 13, the mole ratio of C_{10}: C_{11}: C_{12}: C_{13} in the LAS is 13:30:33:24 with average C close to 11.6.

Table 1. Physical and chemical data of the commercial $C_{11.6}$ LAS (EHC 169, 1986)

LAS	Protocol	Results
Molecular description	Solid organic acid sodium salt	-
Molecular weight (g/M)	$(C_{11.6}H_{24.2})C_6H_4SO_3Na$	342.4
Vapour pressure at 25°C (Pa)	Calculated as C_{12}	$(3–17)10^{-23}$
Boiling point (°C)	Calculated as C_{12}	637
Melting point (°C)	Calculated as C_{12}	277
Octanol-water partition coefficient (log K_{ow})	Calculated as $C_{11.6}$	3.32
Organic carbon-water partition coefficient K_{oc} (1/kg)	Calculated as $C_{11.6}$	2500
Water solubility (g/L)	Experimental	250
Sorption coefficient between soil/sediment and water, K_d (1/kg)	Experimental	2 – 300
Density (kg/L)	Experimental	1.06 (relative)
		0.55 (bulk)
pH (5% LAS water solution)	Experimental	7-9
Henry's constant (Pa.m^3/mole)	Calculated as C_{12}	$6.35.10^{-3}$

Table 1 shows the range of physical chemical data of the commercial LAS. From Table 1, it can be seen that sorption coefficient value is very wide, while reaction rate constants, for biotic as well as abiotic are not available. In environment, LAS can be degraded or transformed simultaneously both biochemically (biotic) and chemically (abiotic) (Wolfe et al., 1980). The transformation of abiotic consists of hydrolysis and photolysis. Hydrolysis and photolysis reactions occur both in soil solution and soil particle (sediment) phases (Sekizawa and Eto, 1992). The ultraviolet light from sunlight will cause a dispersion process of pesticide in environment (Schnoor, 1992). The photolysis of a compound in water is affected by pH and the energy from ultraviolet light (Miyamoto, 1977), as well as sunlight intensity (Mikami et al., 1969). The light intensity absorbed by a media as a function of distance from the surface (Valsaraj, 1995).

$$I_{abs} = I_0 - I = I_0(1 - 10^{-\varepsilon v(c)^2}) \quad (1)$$

The quantum of light accepted by specific molecule, for example B, will form a species of active B and furthermore it will cause a transformation process, and can be expressed as follows (Valsaraj, 1995).

$$B + hv \rightarrow B^* \quad (2)$$

The rate of formation of B^* is:

$$\frac{d(B^*)}{dt} = k(B^*) \quad (3)$$

The concentration of B^* was influenced by

B concentration in medium and light intensity absorbed in medium.

$$(B^*) = (I_{abs})(B) \quad (4)$$

Substituting equation (4) into equation (3), it gives:

$$\frac{d(B^*)}{dt} = k(I_{abs})(B) \quad (5)$$

The rate of B consumption can be expressed as:

$$-\frac{dB}{dt} = \emptyset k_{total}(I_0)(B) \quad (6)$$

In its implementation, the rate of photolysis of a compound on a specific coming light intensity can be stated in following formulation:

$$\frac{dB}{dt} = -k_p(B) \quad (7)$$

Where $k_p = \emptyset k_{total} I_0$

The LAS that comes into unsaturated soil will experience sorption, photolysis, hydrolysis, and biodegradation processes simultaneously. The biodegradation reaction is slower compared with photolysis and hydrolysis reactions. Therefore, the biodegradation reaction can be neglected especially in the first few minutes of the degradation because the amount of microorganism available is not enough (Rahayuningsih et al., 2007).

Rahayuningsih et al. (2007) found that the rate of LAS hydrolysis, both in soil solution and soil particle, follows first order reaction. Sorption equilibrium condition was achieved very quick, so that the reaction of hydrolysis and photolysis controlled the system (Rahayuningsih et al., 2002). Because of LAS concentration in the saturated soil system is very low (20 ppm) at equilibrium state, therefore the relation of LAS in soil and water follows a linear correlation, as shown in equation 8.

$$C^*_{LAS} = \frac{X}{K_d} \quad (8)$$

Previous study found that the rate of biodegradation of organophosphor pesticide (Rahayuningsih et al., 2001) and of LAS (Rahayuningsih et al., 2007) at the early process in a system soil solution using sterilized soil could be neglected. Therefore mass balance of LAS in the soil particle can be described as follow;

$$m\frac{dX}{dt} = k_{C1}\frac{m}{\frac{4}{3}\pi R^3 \rho_s} 4\pi R^2 (C_{LAS} - C^*_{LAS}) - mk_{hs}X - mk_{ps}X \quad (9)$$

Rahayuningsih et al., (2001) studied the fate of organophosphor pesticide in the flooded soil system. It was found that the rate of mass transfer was very fast compared with the rates of photolysis and hydrolysis reactions. By assuming that the same phenomenon took place for saturated system, the first terms on the right side of equation (9) can be neglected.

$$m\frac{dX}{dt} = -mk_{hs}X - mk_{ps}X \quad (10)$$

LAS concentration in soil solution is determined through mass balance of LAS in the reactor:

$$VC_{LAS1} + mX_{t1} = VC_{LASt} + m\int_{t1}^{t} k_{hs}X dt + V\int_{t1}^{t} k_{hL}C_{LAS} + m\int_{t1}^{t} k_{ps}X dt + V\int_{t1}^{t} k_{pL}C_{LAS} \quad (11)$$

Boundary conditions for the equation (11) are:

At t=25 hours, $C_{LAS} = C_{LAS0}$ and $X = X_0$ (12)

The values of k_{hS} and k_{hL} were evaluated using emperical correlations that were formulated by Rahayuningsih et al. (2007). The values of k_{pS} and k_{pL} were determined by a curve fitting method by comparing calculated LAS concentrations that were found from equations 10, 11, and 12 and experimental data.

EXPERIMENTAL METHOD

Experiments were performed in a 1000 mL glass Erlenmeyer used as a batch reactor. The reactor was equipped with ultraviolet lamp with light intensities were 53 or 789 lumens.

Soil was taken from 3 different places in Yogyakarta region those were Bantul, Sukoharjo, and Godean. The physical and chemical properties of the soils were analyzed (Rahayuningsih et al., 2001). Soil preparation consists of drying and then screening processes. One hundred grams of soil was mixed with 1000 ml of water and then the mixture was left for 24 hour in the reactor. A certain amount of LAS was then added to the soil solution and stirrer was put on, so that the LAS concentration in the mixture became 20 ppm. Before the light put on, the soil solution was analyzed its biomass content using a plate count method and LAS concentration using Methylene

Blue Active Substances (MBAS) method. Subsequently, the slurry were stirred and lighted continuously. At a certain time interval, 5 cubic centimeters of solution was taken from the reactor then its biomass content and LAS concentration were analyzed. The variables studied were different soil type and the light intensity. To evaluate the effects of variables, the variables were varied and the other variables were kept constant.

RESULTS AND DISCUSSION

The experimental results are shown in Figure 3 and Figure 4. In order to show the trend of the data clearly, Figure 5 and Figure 6 describe typical distribution of LAS and biomass concentration as a function of time for Sukoharjo soil zone II (SKH II) for the light intensities of 53 and 789 lumens. The figures show that the concentration distributions of LAS for light intensity of 53 lumens are higher than for 789 lumens. In contrary, the concentration distribution of biomass for light intensity of 789 lumens is higher than for 53 lumens. Therefore it can be concluded that the biodegradation (biotic) and photolysis (abiotic) reaction of LAS are strongly affected by the light intensity. The results are in a good agreement with the experimental results of Miyamoto, (1977) and Mikami et al., (1969).

Figure 6 shows for the time duration 5 to 25 hours, the concentration of LAS in soil solution constant for the certain value under the initial concentration value. In this period, the sorption process of LAS by soil is dominant and the other processes can be neglected, therefore the value of partition coefficient or sorption coefficient (K_d) could be evaluated. Referring to Figure 5 and Figure 6 for the duration of 25 to 300 hours, the biomass concentration is relatively constant and very small. During this time periods, the effect of biotic degradation could be neglected, because microorganism has to adapt for the new conditions. Thus the constant rate of hydrolysis and photolysis reaction can be evaluated. From 300 to 800 hours, LAS concentrations decrease rapidly compared to the previous period, meanwhile the biomass concentration slightly increase. In this time period the microorganism starts growing. It could be concluded, in this period the hydrolysis, photolysis, and the biodegradation reactions took place simultaneously. Above 800 hours, the LAS concentrations are relatively constant and the biomass concentrations decrease accordingly. This is due to the decrease of the number of the microorganisms.

Tabel 2. The values of K_d for various soil types

Soil source	% OM	% CM	Kd x 103 (L/g)
Bantul I	1.85	29.32	2.37
Bantul II	0.98	37.86	3.23
Bantul III	0.72	39.90	4.13
Bantul IV	0.75	39.85	3.76
Sukoharjo I	2.57	11.44	3.19
Sukoharjo II	1.46	9.13	1.74
Sukoharjo III	1.18	8.62	2.27
Sukoharjo IV	0.72	6.82	1.50
Godean I	4.07	13.76	4.09
Godean II	2.28	12.68	2.82
Godean III	1.27	10.94	2.82
Godean IV	0.67	10.67	1.32

The paper emphasized to evaluate kinetics parameters of photolysis reactions. Besides that, this paper also described the sorption process, because the sorption process takes place before in the photolysis reaction. In the time duration 5 to 25 hours, the value of sorption coefficient (K_d) could be evaluated. The results of sorption coefficient (K_d) are presented in Table 2 and Figure 7. From Table 2 and Figure 7, it can be seen the values of K_d is not influenced by light intensity but it is affected by soil type, which is represented by in organic matter (%OM) and clay mineral (%CM) content.

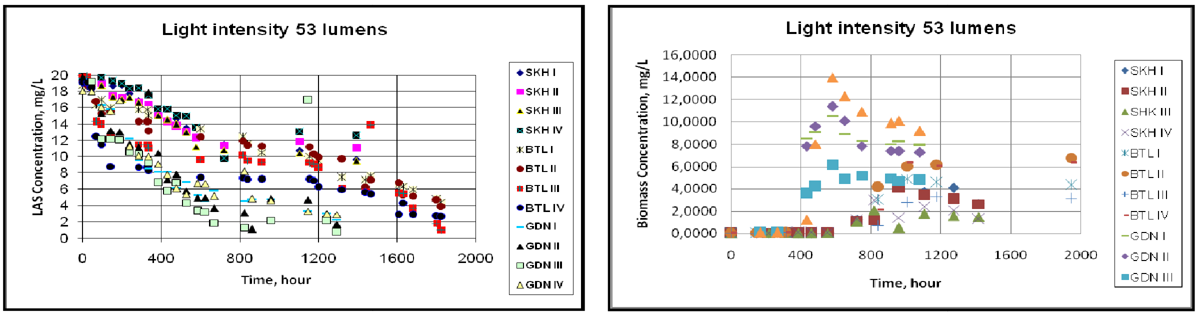


Figure 3. LAS and Biomass Concentrations in The Soil Solution as A Function of Time for Sukoharjo, Bantul, and Godean Soils Each for 4 Zones for The Same Light Intensity of 53 Lumens.

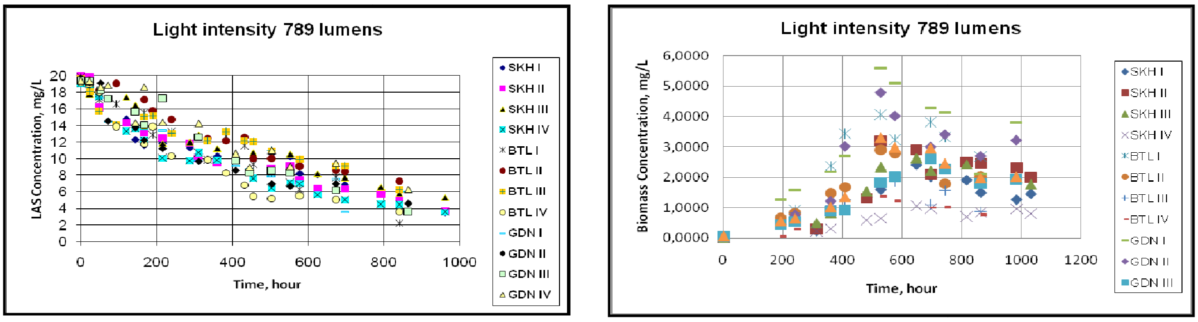


Figure 4. LAS and Biomass Concentrations in The Soil Solution as A Function of Time for Sukoharjo, Bantul, and Godean Soils Each for 4 Zones for The Same Light Intensity of 789 Lumens.

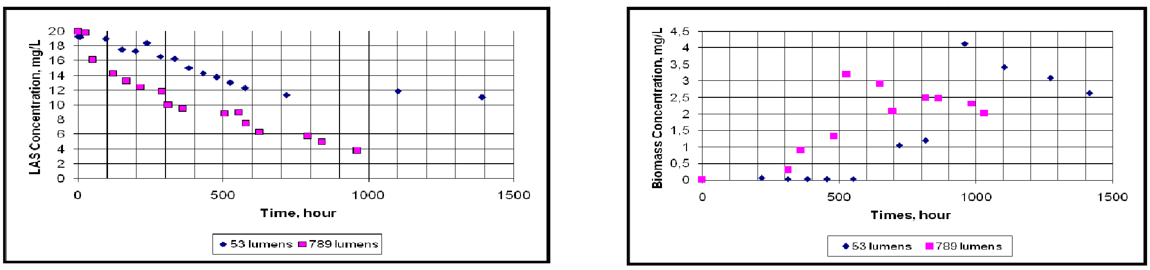


Figure 5. LAS and Biomass Concentrations in The Soil Solution as A Function of Time for Zone II of Sukoharjo Soil for Light Intensity of Ultra Violet 53 Lumens and 789 Lumens

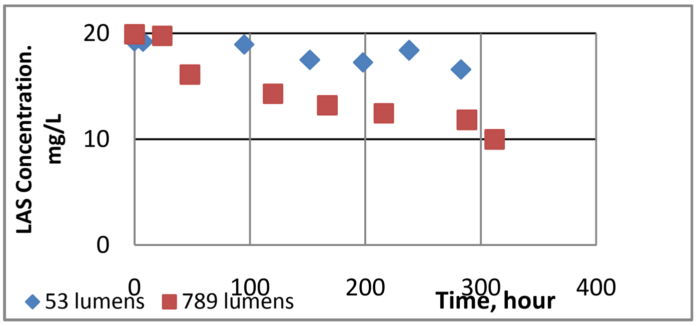


Figure 6. LAS Concentrations in The Soil Solution as A Function of Time for Zone II of Sukoharjo Soil for Light Intensity of Ultra Violet 53 Lumens and 789 Lumens

The range of K_d values is 1.33 L/kg up to 4.29 L/kg, which is in agreement with the K_d shown in Table 1 (EHC 169, 1986). The empirical correlations of the K_d as a function of organic matter (%OM) and clay mineral (%CM) content is presented in the equation 13:

$$K_d = 8.06x10^{-4}(\%OM) + 7.39x10^{-5}(\%CM) \quad (13)$$

The constant rate of photolysis reaction was evaluated by curve fitting method for the time period of 25 to 300 hours. The curve fitting for Sukoharjo, Bantul, and Godean soils each for 4 zones for the same light intensity of 53 lumens and 789 lumens are expressed in Figure 8. The values of k_{PS} and k_{PL} for various soil type for light intensity 53 lumens and 789 lumens can be seen in Table 3, Figure 9, and Figure 10. The correlation between the kinetics parameter of photolysis reaction of LAS in soil solution (k_{PL}) and soil particle (k_{PS}) versus pertinent variable are represented by equations 14, 15, 16, and 17. The kinetics parameters for light intensity of 53 lumens are described as follows:

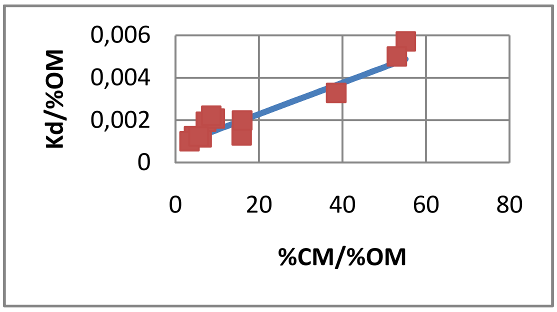
$$k_{PS} = 3.79x10^{-4}(\%OM) + 4.41x10^{-3}(\%CM) \quad (14)$$

$$k_{PL} = 7.73x10^{-3}(\%OM) + 1.18x10^{-3}(\%CM) \quad (15)$$

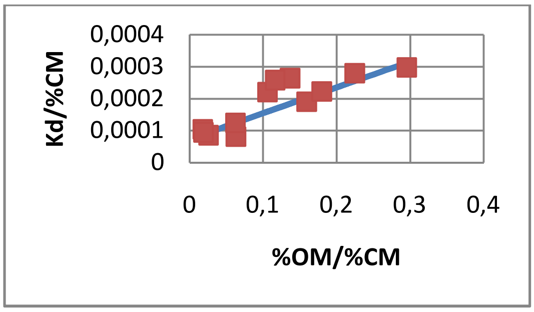
and for light intensity of 789 lumens, the kinetics parameters are;

$$k_{PS} = 16.3x10^{-4}(\%OM) + 0.075x10^{-3}(\%CM) \quad (16)$$

$$k_{PL} = 49.3x10^{-3}(\%OM) + 1.46x10^{-3}(\%CM) \quad (17)$$

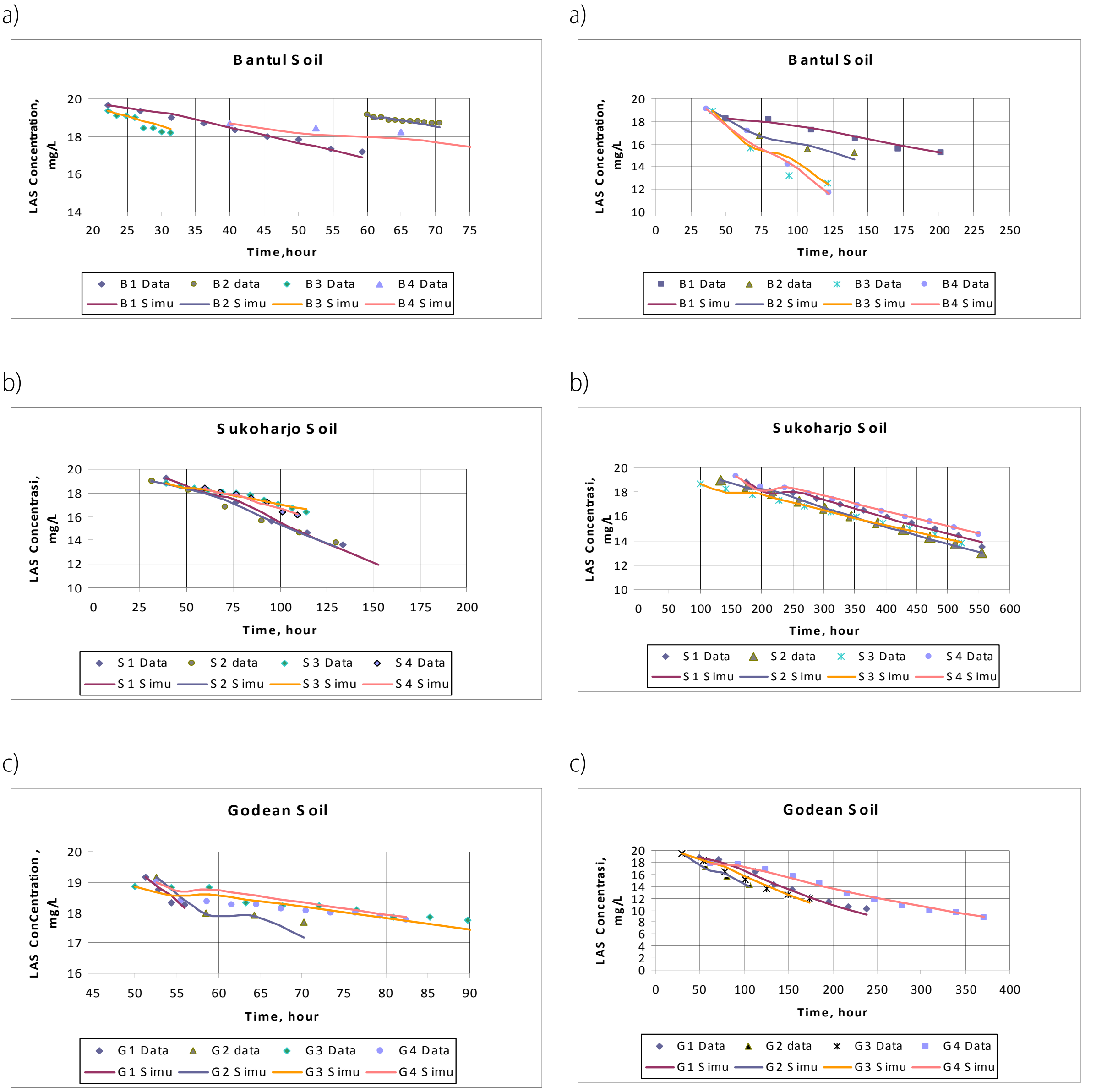


a. The correlations between $\frac{K_d}{\%OM}$ and $\frac{\%CM}{\%OM}$



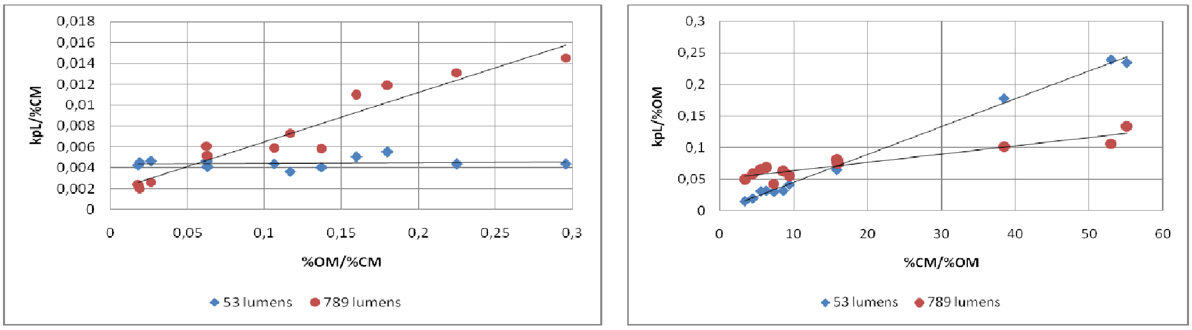
b. The correlations between $\frac{K_d}{\%CM}$ and $\frac{\%OM}{\%CM}$

Figure 7. The Correlations Between K_d and Organic Matter (%OM) and Clay Mineral (%CM) Content



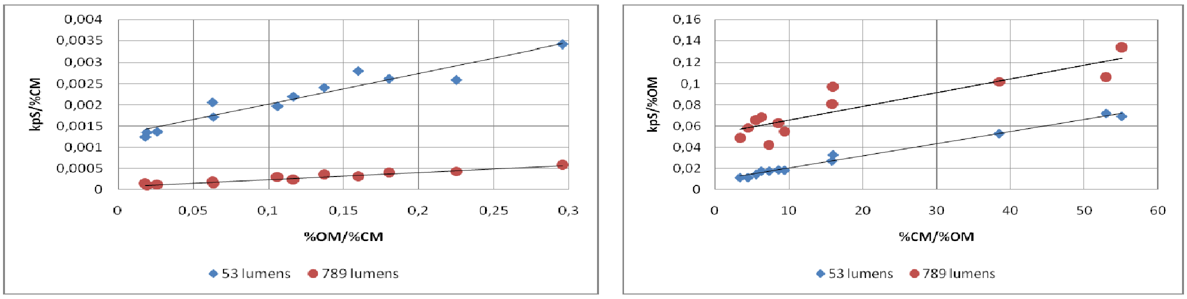
Light intensity of ultra violet 53 lumens **Light intensity of ultra violet 789 lumens**

Figure 8. The Curve Fitting for Determining of Values of k_{PS} and k_{PL} for Sukoharjo, Bantul, and Godean Soils Each for 4 Zones for The Same Light Intensity of 53 Lumens and 789 Lumens.



a. The correlations between $\frac{k_{PL}}{\%CM}$ and $\frac{\%OM}{\%CM}$ b. The correlations between $\frac{k_{PL}}{\%OM}$ and $\frac{\%CM}{\%OM}$

Figure 9. The Correlation Between k_{PL} and Organic Matter (%OM) and Clay Mineral (%CM) Content for Light Intensity 53 Lumens and 789 Lumens.



a. The correlations between $\frac{k_{PS}}{\%CM}$ and $\frac{\%OM}{\%CM}$ b. The correlations between $\frac{k_{PS}}{\%OM}$ and $\frac{\%CM}{\%OM}$

Figure 10. The Correlation Between k_{PS} and Organic Matter (%OM) and Clay Mineral (%CM) Content for Light Intensity 53 Lumens and 789 Lumens.

Table 3. The Values of Constant Rate of Photolysis Reaction (k_{PS} and k_{PL}) for Various Soil Type and Light Intensity

Soil type	Contents		Light intensity 53 lumens		Light intensity 789 lumens	
	% OM	% Clay	k_{PL}, 1/day	k_{PS}, 1/day	k_{PL}, 1/day	k_{PS}, 1/day
Bantul I	1.85	29.32	0.1200	0.0504	0.1500	0.0040
Bantul II	0.98	37.86	0.1750	0.0520	0.1000	0.0040
Bantul III	0.72	39.90	0.1700	0.0500	0.0970	0.0055
Bantul IV	0.75	39.85	0.1800	0.0540	0.0800	0.0040
Sukoharjo I	2.57	11.44	0.0500	0.0296	0.1500	0.0050
Sukoharjo II	1.46	9.13	0.0460	0.0256	0.1000	0.0028
Sukoharjo III	1.18	8.62	0.0350	0.0208	0.0500	0.0030
Sukoharjo IV	0.72	6.82	0.0300	0.0134	0.0400	0.0020
Godean I	4.07	13.76	0.0600	0.0470	0.2000	0.0080
Godean II	2.28	12.68	0.0700	0.0332	0.1500	0.0050
Godean III	1.27	10.94	0.0400	0.0240	0.0800	0.0025
Godean IV	0.67	10.67	0.0500	0.0220	0.0650	0.0020

CONCLUSIONS

From this study it can be concluded:

1. Photolysis reaction of LAS in saturated soil takes place both in soil solution and particle.
2. In this process, the kinetics parameter were describes as photolysis reaction rate constants in the soil solution and particle (k_{ps} dan k_{pl}), and sorption coefficient soil and water (K_d).
3. The kinetics parameter is influenced by the organic matter (%OM) and clay mineral (%CM) content in the soil, as well as light intensity.
4. The photolysis reaction rate constants of LAS in soil solution and particle for light intensity of 53 lumens are described as follows:
   $k_{PS} = 3.79x10^{-4}(\%OM) + 4.41x10^{-3}(\%CM)$
   $k_{PL} = 7.73x10^{-3}(\%OM) + 1.18x10^{-3}(\%CM)$
   And for light intensity of 789 lumens, kinetics parameters are:
   $k_{PS} = 16.3x10^{-4}(\%OM) + 0.075x10^{-3}(\%CM)$
   $k_{PL} = 49.3x10^{-3}(\%OM) + 1.46x10^{-3}(\%CM)$
5. The sorption coefficient soil and water of LAS is expressed as:
   $K_d = 8.06x10^{-4}(\%OM) + 7.39x10^{-5}(\%CM)$

NOMENCLATURES

B	:	Specific molecule
B^*	:	A species of active B
c	:	Concentration of absorbing species in medium, ($mg.L^{-1}$).
C_{LAS}	:	LAS concentration in liquid phase, ($mg.L^{-1}$).
C^*_{LAS}	:	LAS concentration in soil solution which is in equilibrium with LAS concentration in soil particle, ($mg.L^{-1}$).
CM	:	Clay mineral, (% mass)
I	:	Light intensity at $z = z$
I_{abs}	:	Light intensity absorbed by a media
I_o	:	Light intensity at interface ($z = 0$)
k	:	Constant rate of formation of B^*
k_{total}	:	Overall constant rate of degradation of B
k_{hL}	:	Constant rate of hydrolysis reaction at liquid phase, (day^{-1})
k_{hs}	:	Constant rate of hydrolysis reaction at solid phase, (day^{-1})
k_{pL}	:	Constant rate of photolysis reaction at liquid phase, (day^{-1})
k_{ps}	:	Constant rate of photolysis reaction at liquid phase, (day^{-1})
K_d	:	Sorption coefficient, ($L.g^{-1}$)
m	:	Soil weight, (g)
OM	:	Organic Matter, (% mass)
t	:	Time, (day)
V	:	Volume of liquid, (L)
X	:	LAS concentration in soil particle, ($mg.L^{-1}$)
Z	:	The depth of absorbing medium
εv	:	Coefficient of light absorbed
$\emptyset$	:	Quantum efficiency

ACKNOWLEDGMENT

Thanks to the Directorate General Higher Education of the Republic of Indonesia for the financial support to make this research possible. Special thanks also, I addressed to Shinta Pertiwi, Suwardiyanto, and Abd Halim for the helps so the study was running successfully.

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