Photolysis, Sonolysis and Ozonolysis for Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D)

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ABSTRACT. 2,4-dichlorophenoxyacetic acid (2,4-D) is well known as inexpensive herbicides, but it can give rise to undesirable pollution. The objective of this investigation was to compare effectivity of photolysis, sonolysis and ozonolysis methods for degradation of 2,4-D. Photolysis method were performed using an irradiation of UV light λ= 365 nm, sonolysis using an ultrasound with output power of 60 Watt, and ozonolysis using an bioozone generator. The optimum condition for degradation of 2,4-D by photolysis, sonolysis, and ozonolysis without anatase-TiO_2 were found at pH = 3,5; while degradation of 2,4-D by photolysis and sonolysis with addition anatase-TiO_2 was optimum at pH = 2,5. Percentage degradation of 2,4-D by sonolysis, photolysis, and ozonoliysis without anatase-TiO_2 after 180 minutes was 71,85%, 76,12%, and 77,40% respectively. With addition anatase-TiO_2, the percentage degradation of 2,4-D by sonolysis was 78,98% while 82,59% of degradation was achieved by photolysis within 180 minutes treatment. This investigation finding shows that for degradation of 2,4-D without anatase-TiO_2 effectivity of ozonolysis better than photolysis and sonolysis methods, while whit addition anatase-TiO_2 photolysis better than sonolysis methods.

Keywords: *photolysis, sonolysis, ozonolysis, 2,4-dichlorophenoxyacetic acid*

1. INTRODUCTION

The utilization of pesticides in agriculture have caused a large number of residues in the environmental such as in the air, water and soil. Finally, This residu will be accumulated in the water. (Spiro and Stigliani, 2003). Utilization of 2,4-dichlorophenoxyacetic acid (2,4-D), one of the active material in a few herbicide formulation that widely used to control broadleaf bug, rises undesirable pollution. 2,4-D is classified in a compound with medium toxicity level and with maximum levels of 2,4-D in drinking water by 30 µg/ L (Peller, et al., 2004). However, if the compound 2,4-D residues in the environment present in large numbers will also be at risk to the health of living things to disrupt the endocrine system. Therefore, the waste residues of pesticides needs to be addressed to the fullest.

Advanced Oxidation Process (AOPs) is one of the popular methods to degradate any pollutant in the environmental. Some methods of Advanced Oxidation Process that used frequently are photolysis, sonolysis, radiolysis, ozonolysis and Fentons reaction (Peller, et al., 2001).

Advanced Oxidation Process (AOPs) is a technology that used very reactive hydroxyl radical as oxidative agent to break organic contaminant like this herbicides. Hydroxyl radical can be formed through some of methods like high frequency ultrasonic wave, gamma ray, TiO_2 and UV light, H_2O_2 and UV light, O_3 and UV light, Fenton's reaction (H_2O_2/ Fe^{2+}) and any combination of this process.

Photolysis is degradation process of compound that used light as agents. If the compound received amount of ray, this compound will be absorb photon that caused chemistry reaction. Photolysis that used catalyst is known as photo catalyst. One of catalyst that popular is TiO_2 (Yulianto, et al., 2005).

Sonolysis is one of method that used to degradation organic contaminant in water medium with ultrasonic wave helped. Acoustic cavitations in the sonolysis process produce radical species from the H_2O molecule that act as destructive agent of contaminant in the aqueous solution. Degradation of organic pollutant with ultrasonic wave needs high energy and the long time. To accelerate the reaction, usually this process used catalyst like this TiO_2 (Weng, et al., 2006).

Ozonolysis is advanced oxidation process whereas the reaction initiated by ozone. In the aquous solution ozone will be dissociated by hydroxide ions (OH^-) or conjugate base of the peroxide hydrogen (HO_2^-) to $HO_2^\cdot$ and $^\cdot OH$ radicals that can act as agent for organics contaminant degradation (Xian-wen, et al., 2005).

Single advanced oxidation process or combination of this process gets variety effectiveness. The affectivity of this process depends on some factors like pH, temperature, time and concentration of catalyst. Jafari and Marofi (2005) that degradated 2,4-D with fotolisis found that this process effectively on 2,5 until 3,5pH range. Sonolysis that used 640 kHz frequency can degradate 2,4-D with pH 2,2 in the 21 minutes (Yasman, et al., 2004). The goal of this study is to compare effectivity of photolysis, sonolysis and ozonolysis methods for degradation of 2,4-D

2. MATERIALS AND METHODS

Materials that used on this study like the 2,4-dichlorophenoxyacetic acid (2,4-D) get from Santamin 865 SL pesticides, TiO_2 anatase (Ishihara Sangyo, Ltd, Japan), chloride acid, sodium hydroxide and aquades.

Some of instrument that used on this study consist of a set of photolysis apparatus (irradiated box with 10 Watt UV lamp, 365 nm wavelength Germicidal CE G13 Base 8 FC11004), sonolysis apparatus (Ultrasonik VC-1, 45 kHz 60 Watt; As One Comp, Japan), ozonolysis apparatus (Bioozone space age sterilizer, Natural Health Science

Sdn, bhd, Malaysia), UV-Vis Spectrophotometer, pH meter, analytical neraca, magnetic stirrer, sentrifuce and a set of glasses apparatus.

Optimum wavelength for 2,4-D compounds determined by measurement absorban 2,4-D 30 mg/L standard solution on the 230 – 400 nm wavelength range, until got the maximum absorban.

Optimum concentration of TiO_2 catalyst determined throught degradated 20 mL 2,4-D 50 mg/L standart solution by photolysis and sonolysis in 90 minutes with variety of amount TiO_2, until maximum degradation percentage have got.

Optimum pH determined throught varieted pH by sodium hydroxide or chloride acid addition to the 2,4-D 50 mg/L standart solution that will degradated by photolysis, sonolysis and ozonolysis until founded the maximum degradation percentage. Determination optimum pH for photolysis and sonolysis done with and whitout TiO_2 catalyst, whereas for ozonolysis without TiO_2 catalyst only.

Effectivity photolysis, sonolysis and ozonolysis methods to degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) determined by compare degradation percentage have got from each methods on this optimum pH and concentration of TiO_2 catalyst in variety of time.

3. RESULT AND DISCUSSION

From this experiments known that 283,4 nm gave maximum absorban to the 2,4-dichlorophenoxyacetic acid (2,4-D) compound.

Optimum concentration of TiO_2 catalyst to the 2,4-dichlorophenoxyacetic acid (2,4-D) degradation fotolisis dan sonolisis determined by varieted amount of TiO_2 that is 0,0; 0,5; 1,0; 1,5; 2,0; 2,5; dan 3,0 mg. This results presented by figure 1.

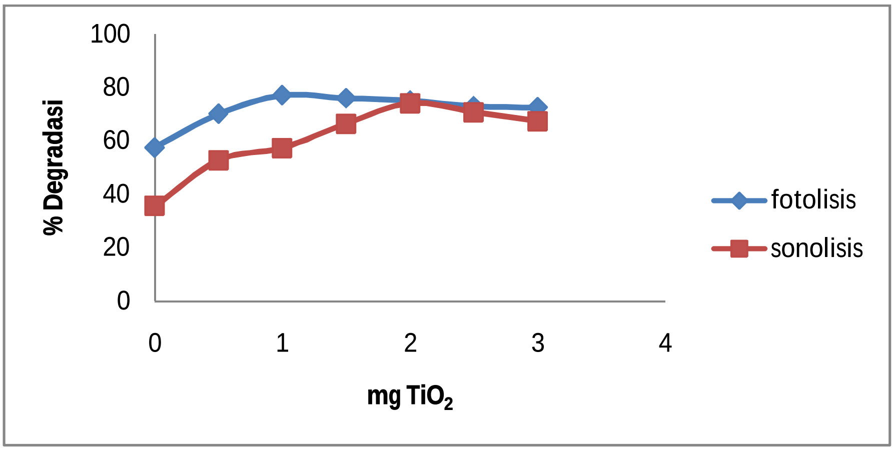

Figure 1. Influence of amount TiO_2 to 2,4-D degradation with photolysis and sonolysis $[2,4\text{-D}]_0$ = 50 mg/L, t = 90 minutes

From the figure 1 we know that maximum degradation percentage for photolysis and sonolysis raised with addition 50 mg/L and 100 mg/L TiO_2 respectively. In general, addition TiO_2 be increased degradation percentage, but in the higher concentration this caused decreased of degradation percentage because their activity is not maximum.

Decreased catalytic activity of the TiO_2 caused light difraction by suspended catalyst. Other factor is catalyst surface can't absorb foton and 2,4-D, so catalytic reaction can't be done (Guettai and Amar, 2005). On the sonolysis process, decreased activity of catalyst caused agglomeration formed and collision catalyst partickel one and other with the present of wave that resulted cavitation effect (Suslick, 1994).

Determination influence of pH to the degradation with photolysis, sonolysis and ozonoliysis without TiO_2 gave results that presented figure 2, while influence of pH to the degradation with photolysis and sonolysis with TiO_2 gave results that presented figure 3.

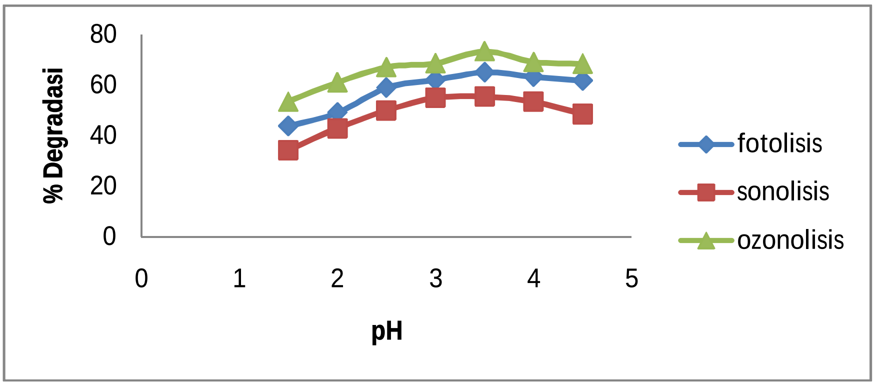

Figure 2. Influence of pH to the degradation with photolysis, sonolysis and ozonoliysis without TiO_2 $[2,4\text{-D}]_0$ = 50 mg/L, t = 90 minutes

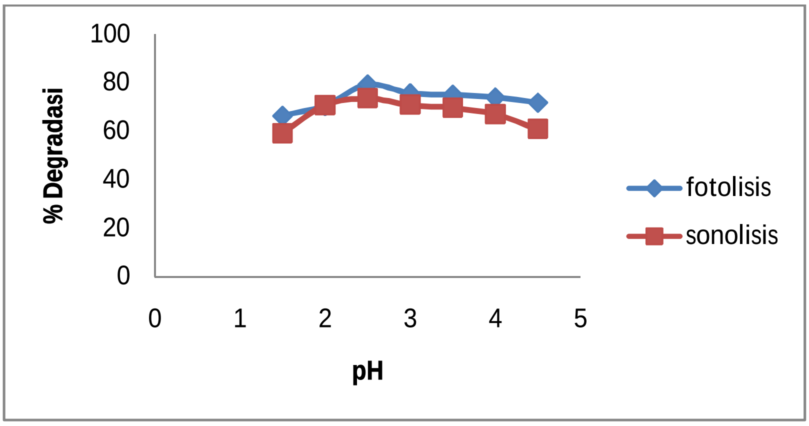

Figure 3. Influence of pH to the degradation with photolysis, sonolysis and ozonoliysis with TiO_2
$[2,4\text{-D}]_0$ = 50 mg/L, t = 90 minutes, $TiO_{2\,(f)}$ = 1 mg, $TiO_{2\,(s)}$ = 2 mg

Figure 2 shown that maximum degradation percentage for photolysis, sonolysis and ozonolysiswithout TiO_2 raised on the pH 3,5. Figure 3 presented that pH 2,5 gave maximum degradation percentage by photolysis and sonolysis with TiO_2.

Initial pH of solution influence the degradation process by photolysis, sonolysis and ozonoliysis. Jafari and Marofi (2005) found that 2,4-D can degraded in acid condition with pH 2,5 or 3,5; while in the higher pH hydroxil radical can be loose and reaction will be decreased. While Guettai and Amar (2005) found that degradation of metil orange by photocatalyst can be raise maximum on the pH 3.

Figure 4 shown effectivity photolysis, sonolysis and ozonolysis methods for 2,4-D degradation whitout TiO_2. Whereas effectiveness ozonolysis method more than photolysis and ozonolysis.

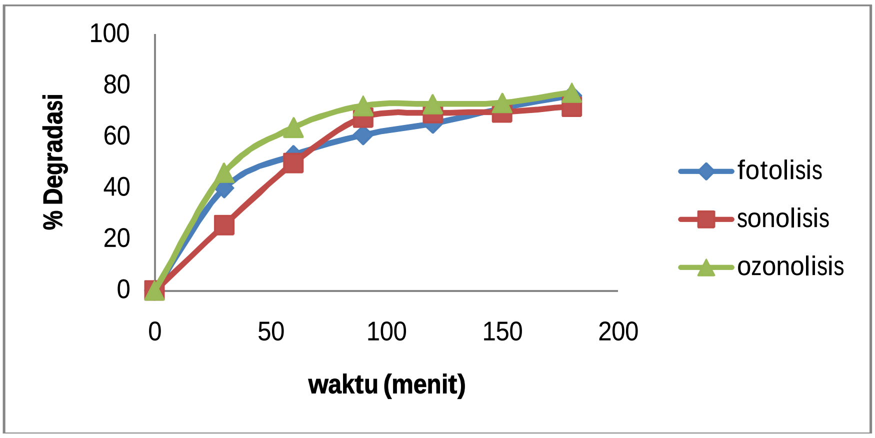

Figure 4. Influence of time to the 2,4-D degradation by photolysis, sonolysis and ozonolysis without TiO_2
$[2,4\text{-}D]_0$ = 50 mg/L, pH = 3,5

While efectivity photolysis and sonolysis methods for 2,4-D degradation with TiO_2 presented by figure 5.

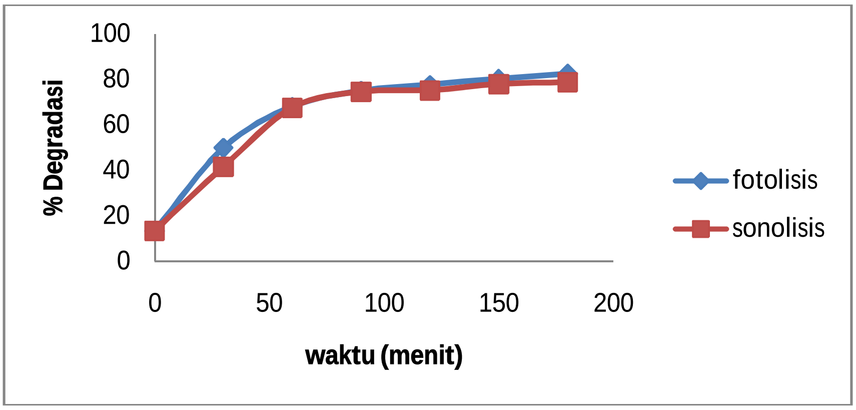

Figure 5. Influence of time to the 2,4-D degradation by photolysis and sonolysis with TiO_2
$[2,4\text{-}D]_0$ = 50 mg/L, pH = 2,5 ; $TiO_{2\,(f)}$ = 1 mg, $TiO_{2\,(s)}$ = 2 mg

From the figure 5 we know that efectivity photolysis methods more than the sonolysis one. This caused TiO_2 catalytic activity on the photolysis whereas light as energy resource more than sonolysis process, where ultrasound act as energy resource

4. CONCLUSIONS

This investigation finding shows that for degradation of 2,4-D without anatase-TiO_2 effectivity of ozonolysis better than photolysis and sonolysis methods, while whit addition anatase-TiO_2 photolysis better than sonolysis methods.

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