Photodegradation of Permethrin using Photocatalyst Montmorillonite-TiO₂

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Abstract

Photocatalyst Montmorillonite-TiO₂ was synthesized using template CTAB and natural clay for degradation of Permethrin. The porosity and crystalline phase of catalyst were evaluated using N₂ sorption analyzer and XRD diffraction. Permethrin photodegradation was optimized by varying reactant volume, irradiation time and initial concentration. Montmorillonite enhanced by CTAB showed typical porosity i.e. specific surface area, pore radii and pore volume for layer material. It properties decreased as this host material was impregnated with TiO₂. XRD diagram indicated that space between layers of Montmorillonite expanded up to 4.7 Å. The diffractogram also confirmed that TiO₂ formed an Anatase phase instead of Rutile. Photodegradation conducted at several condition showed relatively low photocatalytic activity. The highest photodegradation was achieved at 50 mL of Permethrin with initial concentration 10 ppm and 100 minutes’ irradiation.

Keywords: Permethrin, Photodegradation, Montmorillonite-TiO₂

INTRODUCTION

South Sumatera is one of province in Indonesia with large area of plantation, about 1,380,856 hectares of Palm Oil and Rubber plantation. Landowner tends to use pesticides to exterminate bugs and pests. Permethrin is known as an active substance founds in many commercial pesticides and widely used in fruits, vine vegetables and palm oil plantation [1]. The spreading of harmful substances in environment needs to be contained and treated in a degradation process [2]. Unfortunately, nature has limitation in degradation capacity upon huge amount of harmful substances such as permethrin. Photodegradation of pesticides using photocatalysts has been studied by several researchers.
One of well-known photocatalyst material is Titanium Dioxide (TiO$_2$). TiO$_2$ has been used and developed for years through modification of shape, size and energy band gap [3,4,6].

Application of photocatalyst TiO$_2$ in pesticides degradation requires several parameters to be considered. In order to mineralize the pesticides through photochemical reactions, it must be able to adsorbed and reacted onto surface of TiO$_2$. [7]. Many efforts have been conducted on modification of TiO$_2$ to provide optimum interaction between photocatalyst and pesticides [6, 8]. Sol-gels technique was used to synthesized TiO$_2$ using surfactant to produced porous material along with large specific surface area [9]. Another researcher has been developed TiO$_2$ photocatalyst using ultrasound agitation technique and hydrothermal treatment [6]. The reported TiO$_2$ has Nano fibers structure and crystallite size; 10.16–17.9 nm. Improvement of surface and structure morphology of TiO$_2$ can also be achieved by dispersing TiO$_2$ into host materials. Montmorillonite and latex polymer had been used as host materials for TiO$_2$ photocatalyst [3,7]. TiO$_2$ was dispersed in solid form within materials to give a synergetic effect between adsorption and photodegradation process.

Among materials were common used as a host, Montmorillonite was preferred due to its abundance in nature. Natural clay was known as main resource for layer materials such as bentonite and montmorillonite. The nature of layer materials will depend on its geological origin, for example: metal oxide as a constituent of montmorillonite has differences composition therefore metal oxides also differ in their physical properties. This research aims to prepare the layer material, montmorillonite, taken from local natural clay and then enhanced by cetyltrimethyl ammonium bromide (CTAB). The product will be used as host material for photocatalyst TiO$_2$. TiO$_2$ was introduced as oxide solid form and dispersed in various loading ratios to montmorillonite. The photocatalytic activity was investigated using Permethrin degradation in different reaction conditions to achieve the optimum result.

**EXPERIMENTAL SECTION**

**Materials**

Montmorillonite was taken from local resource at Semarang Central Java, all chemicals were used as delivered without further purification. TiO$_2$, cetyltrimethyl ammonium bromide (CTAB) and silver nitrate (AgNO$_3$) purchased from Merck whereas permethrin namely Sidamethrin 50EC was obtained from pesticides local store.

Montmorillonite was grinded and screened through sieve shaker 250 mesh size. Fine particles were washed and dried in Memmert Oven for 12 hours. Cation exchange carried out by soaking Montmorillonite in saturated NaCl solution for 24 hours. The resulting materials denoted as Na-Montmorillonite was washed thoroughly to remove Chloride ions. Prior to surfactant treatment, Na-Montmorillonite immersed in demineralized water (1g/100 mL) for 24 hours. Surfactant treatment was conducted using CTAB twice cation exchange capacity of Montmorillonite at 60°C for 48 hours. Montmorillonite which in turn has hydrophobic properties treated as host materials for photocatalyst TiO$_2$ according to previous report [7]. TiO$_2$ was added to hydrophobic Montmorillonite in weight ratios 1:4, 2:3, 3:2 and 4:1 (Montmorillonite/TiO$_2$). The mixture was stirred for 48 h and then separated from the suspension by centrifugation. The obtained composite was dried in oven at 60°C until no further decreased of weight was detected. Finally, Montmorillonite-TiO$_2$ was grinded to a size smaller than 200 mesh.

**Characterization**

The characterization of Montmorillonite-TiO$_2$ was carried out by N$_2$ adsorption and X-ray diffraction (XRD). BET surface area and pore size of catalysts were determined from their nitrogen adsorption isotherms obtained at −196°C using an Autosorb 1 apparatus (Quan-tachrome). The samples were outgassed at 250°C for 12 h under high vacuum (<10$^{-4}$ Pa) before N$_2$ adsorption. The crystalline structure was analyzed by XRD instrument (Bruker D8 Advance XRD diffractometer) equipped with a CuK radiation ($\lambda$ = 0.1541 nm). Diffraction data were collected from 20 = 20° to 80° at a scan rate 2° s$^{-1}$.

**Photodegradation of Permethrin**

Photodegradation of permethrin was carried out in a photo-reactor consisted of glass chamber (150 mL) equipped with magnetic stirrer and veil to prevent sun light. At the upper part of reactor, UV lamp ($\lambda$ = 312 nm) was installed and act as light source. Permethrin was loaded into photo-reactor in various volume with typical concentration 20 mg/L. Montmorillonite-TiO$_2$ was added accordingly in various catalyst to substrate ratios. Prior illumination, the suspension was homogenized by stirrer. Photodegradation was conducted by illuminating the suspension in a different duration. The remain permethrin was separated after reaction time achieved by centrifugation. Concentration of permethrin was determined by using
spectrophotometer UV-Vis and calibration data collected beforehand.

RESULT AND DISCUSSION

Catalysts Characterization

Figure 1 showed how CTAB affected basal spacing between layers of Montmorillonite. Na-Montmorillonite resemble layer structure with all exchangeable cation was replace by Na\(^+\) ions. As CTAB introduced and replace Na\(^+\) ions, space between layers become increase and indicated by diffractogram at 6° shifted to a lower 2\(\theta\). According to calculation, basal spacing has expanded about 4.7 Å due to this replacement. The macromolecular of CTAB successfully replace Na\(^+\) ions position within Montmorillonite layer.

CTAB is one of alkyl ammonium salt which has positive charge on ammonium end. Upon preparation process, Bromide ions was release and washed out from the suspension. Interaction between CTAB and Montmorillonite surface is likely a dipole-dipole interaction. The expansion of basal spacing in accordance with previous report conducted using Montmorillonite from Zhejiang China [7].

TiO\(_2\) dispersion onto surface of Montmorillonite obviously affect porosity and surface area of the composite. Figure 2 displays photocatalysts prepared in various ratios of Montmorillonite/TiO\(_2\). Sharp peaks showed on Figure 2 refer to crystalline TiO\(_2\) dispersed within composite. According to JCPDS 03-065-5714, peaks displayed were resemble crystal structure of Anatase instead of Rutile. Peaks on 2\(\theta\) at 25 and 48 confirmed this conclusion [10]. The formation of TiO\(_2\) Anatase was preferred on the reason that this phase is more photoactive then Rutile [6]. Ratio between Montmorillonite and TiO\(_2\) apparently affected proportionally to peaks detected by XRD instrument. Peaks with TiO\(_2\) content higher then Montmorillonite (Mont/TiO\(_2\): 2:3 and 1:4) displayed a distinct sharp peaks which belong to TiO\(_2\) crystalline. As for composites which were more Montmorillonite then TiO\(_2\) broad peak at low Bragg angle was quite obvious (2\(\theta\) = 4.6–6.2°).

Pore size of Montmorillonite-TiO\(_2\) as shown on Figure 3, was determined by gas sorption analyzer using N\(_2\) as adsorbate. Basal spacing indicated by diffractogram measured the distance between layers of Montmorillonite, whereas gas sorption measured surface which adsorbed N\(_2\) molecules in average.

Montmorillonite as layer material, can be expanded by inserting large molecule between the layers. Montmorillonite porosity on the other hand, has micro pore size on its surface (< 2 nm). Dispersing
alkyl ammonium or TiO$_2$ onto Montmorillonite gave insignificant effect to pore size of the composite. Pore size decrease in Montmorillonite-TiO$_2$ 2:3 and 1:4 simply because of larger portion of TiO$_2$ ratio on the sample prepared.

Adsorption isotherm can also be used to calculate total pore volume as reveal on Figure 4. The addition of CTAB into space between layers of Montmorillonite caused decrease in total pore volume. CTAB might have filled pores on the surface materials and leave just a smaller one which was not fitted by CTAB molecules. Dispersing TiO$_2$ caused no further decrease in total pore volume of Montmorillonite-TiO$_2$.

Figure 4. Total pore volume of samples calculated by BET

![Figure 4](image)

Total pore volume is directly proportional to specific surface area hence displays data trend similarity as shown on Figure 5. Na-Montmorillonite showed large surface area compare to others. Layers within untreated Montmorillonite provide surface area which available for any adsorption. Montmorillonite treated with CTAB and TiO$_2$ on the other hand has lower specific surface area. The decrease in surface area is due to occupation of sites available by adsorbate molecule which were CTAB and TiO$_2$.

**Photodegradation of permethrin**

Photodegradation of permethrin was conducted on glass reactor in laboratory scale. Figure 6 represent 1 g Montmorillonite-TiO$_2$ mixed into various volumes of permethrin 20 mg/L. The catalyst to substrate ratio determined how effective catalyst can drive corresponding reaction into significant rate.

Figure 5. Specific surface area of sample calculated by BET

![Figure 5](image)

Figure 6. Effect of permethrin volume to degradation percentage using Montmorillonite-TiO$_2$ 1:4.

![Figure 6](image)

Theoretically, catalyst 2% of substrate or reaction mixture is considered as effective. Figure 6 showed 1 g Montmorillonite-TiO$_2$ dropped its photocatalytic activity if more than 5 mL permethrin is used. Ineffectiveness of the catalyst can be caused by several reason. Low surface area of Montmorillonite-TiO$_2$ for example could reduce amount of substrate adsorbed by catalyst. Although the catalyst used in experiment had higher ratio of TiO$_2$, lower available site for photocatalysis reaction hindered maximum conversion. Increasing volume of permethrin in such situation make photodegradation process gave minimum result.

Irradiation time by UV light onto surface of photocatalyst undoubtedly is important factor (Figure 7). Photocatalysis recorded at the beginning of process might happen due to direct photolysis reaction of permethrin [11]. Photocatalysis by TiO$_2$ is using indirect process involving photo reacted species.

Indirect process carried out by photocatalyst TiO$_2$ involved photolysis of H$_2$O molecules to produce free...
This highly active species reacted further in reduction-oxidation process lead to pesticides mineralization. Optimum time obtained according to experiment is 100 minutes after irradiation process. This result is in accordance with previous report of photocatalytic using TiO$_2$-anatase [12]. Other researcher by using typical Montmorillonite impregnated with TiO$_2$ obtained maximum removal of pesticides after 180 minutes [7]. Time needed for irradiation to initiate photocatalysis can be longer if TiO$_2$ particles were positioned within Montmorillonite layers. The photocatalyst cannot exposed by UV-light hence photodegradation result in minimum removal.

### CONCLUSION

Photodegradation of Permethrin could be carried out by Montmorillonite-TiO$_2$. Photocatalysis activity need various condition in order to achieve optimum process of pesticides mineralization. Montmorillonite-TiO$_2$ prepared still need proper modification and optimum reaction condition indicated by degradation percentage below 10%. The modification conducted by using appropriate synthesis precursors and improved method of preparation.

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