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The Influence of Calcination Temperatures in TiO₂ Impregnated Ouw's Natural Clay on Its Degradation Activity of Methylene Blue Dye

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Abstract

The influence of calcination temperatures in TiO₂ impregnated Ouw's natural clay on its degradation activity of methylene blue dye has been done. Calcination process was conducted at various temperatures of 200, 300, and 400 °C. The characterization of TiO₂ impregnated clay's structure was examined by IR analysis. The result showed that Ouw's natural clay has characterized vibrations of montmorillonite and thermal effect didn't affect the structure of TiO₂ impregnated clay. The highest result of methylene blue's degradation occurred in the addition of TiO₂ impregnated clay calcinated at 200 °C (98.69%). This result was found that calcination temperatures of impregnation process were significantly affect the degradation activity of TiO₂ impregnated clays.

Keywords: *Calcinations; Degradation; Impregnation; Ouw's natural clay; Photocatalyst*

ARTICLES

1. INTRODUCTION

Clay minerals are well-known as one of phyllosilicate mineral abundant in Indonesia. Clays are usually used in the ceramic industry. Besides that, clays are used as catalysts, metal-supported catalysts, ion exchangers, and adsorbents. The clay distribution in Moluccas is founded in Ambon Island and Saparua Island (especially in Ouw Village). As the one of reported in previous research, the major component of Ouw's natural clay is montmorillonite [1], the valuable clay, that is usually used as raw materials in some industry due to its advantage properties.

On the other hand, natural clay possess low ability, therefore the structural modification was needed to increase the ability of natural clay in order to produce metal-supported catalyst with high surface area. The method that can be used to enhance clay's performance as metal-supported catalyst is impregnation process

using active metal which active metal will be the impregnator and also the catalyst [2].

On impregnation process, the calcination step plays important role to activate the catalyst that dispersed on the surface of natural clay. Besides that, the thermal effect can also affect the structure of clay, increasing the acidity and surface area, but the higher temperature can change the physical and chemical properties of natural clay [3-5]. Study about calcination temperature was also investigated in another research in order to get cyanide biosensor with the best performance [6].

Titanias (TiO₂) are well-known as semiconductor materials that are usually used in wastewater treatment because they are nontoxic, chemically and also biologically inert [7]. All this time, titanias are used in slurry form, but they present several disadvantages, such as catalyst agglomeration and difficult recovery, which result ineffective application of the catalyst [8]. One of the method that can be used to solve this problem is immobilization of TiO₂ on the stable and inert supported materials, like clay [9,10]. It has been reported in previous research that the use of clay as supported

material can improve the photocatalytic activity of TiO₂ in methylene blue degradation process up to 93.93% [2].

Coloring is important step in textile and paper-making industries. As the growth of the both industries increase, the release of wastewater containing dyestuff also drastically increase, where in the percentage of dye lost in wastewater is 50% of the dye because of the low levels of dye-fiber fixation [11]. Methylene blue is one of the cationic dye that is usually used in coloring process. Methylene blue is stable and recalcitrant to biodegradation of microorganism due to its complex chemical structure with the presence of benzene ring. Dye contamination in wastewater can cause several environmental problems and may be carcinogenic to aquatic life [12]. Besides that, the Chemical Oxygen Demand (COD) decrease with the increase of dye pollutant in wastewater. This condition is really dangerous for organism, like plants and fishes, and humans will also get the indirectly impact [13]. Dye pollutant in wastewater can naturally degrade by UV-rays, but the intensity of UV-rays is small on the surface of the Earth that make the rate of degradation process is really slow, therefore the use of the photocatalyst was needed to increase the rate of degradation process [9, 12].

2. MATERIALS AND METHODS

2.1. Materials

Chemicals used in this research were : NaCl (p.a Merck), AgNO₃ (p.a Merck), H₂SO₄ (p.a Merck), BaCl₂ (p.a Merck), TiO₂, absolute ethanol (p.a Merck), methylene blue dyestuff (p.a Merck), H₂O₂, and distilled water.

2.2. Sample Preparation

Samples of natural clays were collected from Ouw Village, Saparua, Moluccas. The samples were washed with distilled water and dried at 120 °C. Clays were crushed and sieved to a particle size of 100 mesh. The characterization was examined by IR analysis.

2.3. Acid Activation

The acid activation was conducted by mixing dry Na-Clay with H₂SO₄ 2 M for 24 h. Solid was separated from the slurry, rinsed with warm distilled water till sulfate free, and dried at 100-110 °C.

2.4. Impregnation Process

The impregnation was performed by adding TiO₂ and absolute ethanol with ratio 1:1 (clay : absolute ethanol). The stirring was continued for 4 h. The clay suspensions were dried at 110 °C for 2 h. Impregnation clays were crushed, sieved to a particle size of 100 mesh, and finally calcined at various temperatures of 200, 300, and 400 °C for 5 h. The characterization was examined by IR analysis.

2.5. Degradation of methylene blue dye

The photocatalytic activities of various samples (TiO₂, TiO₂ impregnated clay uncalcined, TiO₂ impregnated clay calcined at 200 °C, TiO₂ impregnated clay calcined at 300 °C, and TiO₂ impregnated clay calcined at 400 °C) were evaluated on their performance as catalyst in degradation of methylene blue in aqueous solution under UV irradiation. 50 mg of each sample was suspended in 50 mL of the methylene blue (25 mg/L) aqueous solution. Before illumination, the suspension was magnetically stirred in the dark condition for 1 h to achieve adsorption equilibrium. The reaction was started when the UV lamp was turned on and 2 mL of 15% H₂O₂ was added to the each reaction system before the irradiation. Degradation process was occurred for 3 h at UV reactor. The degradation of methylene blue aqueous solution was tested by UV-Vis absorption spectrum at its maximum absorption wavelength of 665 nm. The degradation of methylene blue in the absence of catalyst (only UV irradiation and H₂O₂) was performed under the same condition.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the natural clay and TiO₂ impregnated clay

Infrared spectroscopy is a very important tool for investigating the structural changes of natural clay. From the result, it was found that the Ouw's natural clay showed some characteristic vibrations corresponding to the montmorillonite, i.e. 534.28 ; 912.33 ; 794.67 and 3622.32 cm⁻¹. The band at 534.28 cm⁻¹ is attributed to bending vibration of Si-O-Al which also confirmed by Si-O plane stretching at 1029.99 cm⁻¹. The band at 912.33 cm⁻¹ is attributed to vibration of Al-Al-OH bending. The band at 794.67 cm⁻¹ is attributed to SiO₂, which also confirmed by Si-O-Si at 468.7 cm⁻¹. IR spectrum of Ouw's natural clay also shows the band at 3622.32 cm⁻¹ in OH stretching region, which is assigned to hydroxyl groups coordinated to octahedral cations. The band at 692.44 cm⁻¹ shows the presence of quartz admixtures present in the sample. The bands at 1641.42 and 3412.08 cm⁻¹ are the bending and stretching vibrations for the hydroxyl groups (-OH) of water molecules present in the clay [14-16]. Figure 1 presents the IR spectrum of Ouw's natural clay.

Figure 1. IR spectrum of Ouw's natural clay.

Acid activation with H₂SO₄ was conducted to increase the surface area and pore volume of natural clay. According to the previous research, activation with 2 M H₂SO₄ resulted the clay with higher surface area and pore volume when compared to other concentrations

[14]. The wet impregnation process was used to modify the structure of Ouw's natural clay in order to become metal-supported catalyst. TiO₂ acted as impregnator and also catalyst, while absolute ethanol acted as solvent. The mixture was stirred to disperse TiO₂ on the surface of catalyst. The calcination process was needed to activate the catalyst (TiO₂). In this study, the effect of calcination temperatures to the character of TiO₂ impregnated clays is focused.

The result of IR analysis showed that impregnation process didn't change the structure of natural clay. What can be noticed from natural clay and TiO₂ impregnated clay is the shift of vibration corresponds to Si-O and O-Al-O bands to the higher wavenumber. This suggests that TiO₂ impregnation process gives higher vibrational energies. IR spectra of TiO₂ impregnated clay uncalcined and after calcination process at various temperatures are depicted in **Fig. 2** and **Fig. 3**.

Figure 2. IR spectrum of TiO₂ impregnated clay uncalcined.

Figure 2 and **Fig. 3** show the absorption peaks in the area of the wavenumber 400-1250 cm⁻¹ which is the characteristic of the bond O-Ti-O, while the peaks at region 1625-1650 cm⁻¹ are the peak related to -OH bending vibrations from the water that is still trapped in crystal structure of TiO₂ [17,18]. Besides that, the intensity of Si-O plane stretching on TiO₂ impregnated clay is wider than natural clay. According to the previous research, the reason can be explained that vibration of Ti-O and/or Ti-O-Ti, formed at around 400-800 cm⁻¹, were overlap [19]. Overall, the spectrum of TiO₂ impregnated clays gave almost similar trends. This

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suggests that thermal effect didn't affect the structure of TiO₂ impregnated clay.

Figure 3. IR spectrum of TiO₂ impregnated clay calcined at various temperatures.

3.2. The results of degradation process

Degradation of methylene blue dye was performed using various catalysts, i.e TiO₂ (A), TiO₂ impregnated clay uncalcined (B), TiO₂ impregnated clay calcined at 200 °C (C), TiO₂ impregnated clay calcined at 300 °C (D), and TiO₂ impregnated clay calcined at 400 °C (E). While, the degradation of methylene blue in the absence of catalyst (only UV irradiation and H₂O₂) was showed as F condition. In the degradation process, H₂O₂ acted as acceptor of irreversible electron and source of HO[•] radicals. The result of degradation methylene blue is presented in **Table 1**.

As described in **Table 1**, it was found that different catalyst gave different result. The highest result was showed by C condition (98.69%), with using TiO₂ impregnated clay calcined at 200 °C as photocatalyst. While, the lowest result was showed by F condition (20.76%), in the absence of photocatalyst. The lowest result is due to the absence of photocatalyst. Therefore, the degradation process only depended by UV-ray and H₂O₂. Without e⁻_{VB} from TiO₂, H₂O₂ couldn't produce very reactive hydroxyl radicals (HO[•]), which this radicals play important role to conduct the partial or complete mineralization of organic pollutants [20].

Table 1. The results of methylene blue degradation.

Type of treatment	Abs.	C ₀ (ppm)	C _e (ppm)	C ₀ - C _e (ppm)	D (%)
A	0.411	25	2.9848	22.0152	88.06
B	0.077	25	0.5714	24.4286	97.71
C	0.041	25	0.3265	24.6735	98.69
D	0.09	25	0.6957	24.3043	97.22
E	0.149	25	0.9909	24.0091	96.04
F	2.096	25	19.8106	5.1894	20.76

The degradation efficiency increases when photocatalyst was used in the degradation process. It has been established that degradation of organic pollutants in aqueous solution is initiated by the photoexcitation of TiO₂, formed an electron-hole pair (h⁺_{CB} and e⁻_{VB}) on the surface of catalyst [20]. Therefore, HO[•] radicals can be formed by following reaction:

From the data listed in **Table 1**, TiO₂ impregnated on clay is more active than pure TiO₂ powder. It can be

seen that the degradation efficiency using pure TiO₂ only reached 88.06%. The result can be explained by the different properties and morphologies of these materials. The surface of TiO₂ impregnated clays is porous hence they have photocatalytic activity and also adsorption properties. While, TiO₂ particles exhibit smooth surface. Similar result has been also reported in the previous research [21].

According to the data from **Table 1**, calcination temperature at TiO₂ impregnated clay was responsible for the result of methylene blue's degradation. It can be seen that the degradation of methylene blue using TiO₂ impregnated clay uncalcined as photocatalyst (B condition) only reached 97.71% while the result for degradation process using TiO₂ impregnated clay calcined at 200 °C (C condition) was 98.69%. These percentages of methylene blue's degradation can be related to different distribution of TiO₂ on the surface of catalyst. Besides that, the photocatalytic activity of TiO₂ impregnated clay decreases with the increase of calcination temperature. According to the previous research, the increasing calcination temperature leads to the collapse of some pores in samples and the decrease of specific surface area and pore volume [8].

4. CONCLUSION

In this research, the major component of Ouw's natural clay is montmorillonite. TiO₂ impregnated clays with various calcination temperature were successfully prepared. Here we observed that impregnation process didn't change the structure of natural clay and different temperatures gave almost similar trends of spectrum of TiO₂ impregnated clays. Degradation of methylene blue using various photocatalyst displayed high photocatalytic activity in a efficiency range from 88.06 % to 98.69%. The degradation efficiency decreased with the increasing calcination temperature of impregnation process. While, the degradation efficiency of methylene blue only reached 20.76% in the absence of catalyst.

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