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Degradation of methylene blue using pillared TiO₂ on de-oiled spent bleaching clay

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Abstract. Degradation of methylene blue (MB) using pillared TiO₂ onto spent bleaching clay has been conducted. Activation of deoiled spent bleaching clay (DSBC) has been done using acid, followed by pillarization with TiO₂ using *rarasaponin* from Klerak fruit as surfactant. From the X-ray diffraction results show the mineral on DSBC is rectorite with dioctahedral mica layer and dioctahedral smectite with ratio 2:1. This molecule have formula Na.Al₄(Si, Al)₈.O₂₀.(OH)₄. H₂O and after calcinations the pattern TiO₂ was appearance at 2θ: 27.4460°, 36.0850°, 54.3216° and 56.6403°. In order to test the catalytic performance of Ti-DSBC for photodegradation of MB under UV light was conducted under several reaction conditions. The highest degradation of MB was 90 % within 50 minutes and Ti-DSBC can be reused until 5 cycles with percent degradation MB was 84 %.

1. Introduction

Indonesia is one of the world's largest producers and exporter of palm oil. In terms of agriculture, Indonesian Palm Oil Producers Association has been recorded palm oil is the most important industry and the total area of oil palm plantations in Indonesia is currently around 11.9 million hectares [1]. On the palm oil process, there are three steps in the refining of edible oils. There are degumming, neutralization, bleaching and deodorization. In the bleaching process palm industries are using imported natural or acid activated clays. The local consumption of bleaching clay is estimated to be 100,000 tons per year, with annual production of crude palm oil is 18 million tons/years [2]. The residual of bleaching clay will transformed to spent bleaching clay (SBC) that containing 20-40 % oil and it may cause pollutions hazard due to the substantial oil content in clay [3]. Based on their structural as smectite, SBC possess certain properties which make them as choice as low cost adsorbent or support material because there high mechanical and chemical stability, availability, affordability, ion exchange capability and environmentally friendly material [4].

Based on their performance pillared clay has been reported that dispersion TiO₂ particles into layer clays could improve catalyst performance because their stability properties. In general, TiO₂ pillared clays will substitute several ions in the interlayers of clay [5]. Photocatalysis, in which clean and safe energy of the sun can be harnessed for sustainable, non-hazardous and economically viable technologies. These processes are all characterized by the same chemical features such as production of hydroxyl radicals (OH) and superoxide anion, which are generated when a semiconductor catalyst



absorbs radiation when it is in contact with water and oxygen and among of all semiconductor photocatalyst, titanium oxide has proven to be the most widely used do to its strong oxidizing power, non-toxicity and long-term photostability [6,7]

Before SBC used as template for TiO₂, there are several treatment to activate the SBC. Solvent extraction processes for recovery of oil from spent bleaching clay have been suggested. This is because they give a higher yield and better quality [8]. There are some extractions methods such as soxhlet but in the last research report ultrasonic extraction give more advantage such as efficiency of time and solvent. This technique used ultrasound wave to impressed the molecules [9]. The deoiled spent bleaching clay (DSBC) also needs activation to open their active side and high surface area. Kheang has reported that activation use acid treatment has a good result [10].

Otherwise, DSBC had been materials there is some report the use of high molecular weight such as polyoxypropylene (POP) or ethyl Trimethyl Ammonium Bromide (CTAB) can increase surface area of montmorillonite [5]. But, utilizing synthetic like those as modifying agent can also cause environmental hazardous because they are non biodegradable and toxic, so that an unused synthetic surfactant need to processed after modification takes place which increases operational costs [11]. Kurniawan have been reported that rarasaponin from Klerak can be performed as natural surfactant and show similar results such as surfactant synthetic [12]. Rarasaponin is sugar derivatives compound that may be found in plants, to characterize the rarasaponin could by forming foam when dissolved in water and the most widely used method to obtain rarasaponin is solid-liquid extraction. The others solvent can be used to extract rarasaponin from its solid matrices such as ethanol, methanol, and sodium methoxide [11].

In the present study, TiO₂ pillared DSBC were prepared from SBC and Titanium oxide in the presence of polymeric surfactant *rarasaponin* and the as prepared materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR) and scanning electro microscopy (SEM). The influence of optimum concentration and contact time of this material photocatalyst was investigated by evaluated methylene blue degradation. The fundamental information derived from this study is important in developing catalyst or adsorbent of pore structure from layered clays.

2. Experimental

2.1. Material and chemical

The spent bleaching clay was purified by dispersion in water, decantation and ultrasonic extraction of the oil and sieved with a particle size 100 mesh. Klerak was supplied form Yogyakarta. Klerak will be extracted using polar solvent to obtained *rarasaponin* as surfactant. Titanium oxide (II) pro analyst was obtained from sigma Aldrich, sulphuric acid (H₂SO₄ (98 %)), methanol 95 %, n-hexane were supplied by Sigma-Aldrich

2.2. Preparation technique

Modification DSBC was conducted by dissolving 0.5 g of rarasaponin in 25 mL of distilled water. Subsequently, 5 g of DSBC powder was added to the solution. The mixture was then stirred for 24 hours at 26°C. The solid was then separated from the mixture, repeatedly washed using distilled water and dried at 110°C for 24 hours. Furthermore, pillarization of TiO₂ was prepared with dissolve TiO₂ in 6 mL ethanol 98 % that contain 1 g of DSBC, the mixture was stirred for 24 hours and dried in oven at 120°C for 5 hours. Thereupon, the material crushed until have similar size and calcinated for 5 hours at 550°C and labeled as Ti-DSBC.

2.3. Characterization

X-ray diffraction (XRD) patterns of the resulting organoclays were obtained on Shimadzu 700 diffractometer using Cu K α radiation at 30 kV and 30 mA. The Fourier transform infra red (FT-IR) spectra were recorded on a spectrum 501 Shimadzu. Scanning electron microscope (SEM) (JEOL JSM

501 LA) was used to observe the crystal microstructure of as-prepared pillared clays. Surface analysis was used to observe the surface area of material.

2.4. Photocatalytic experiment

Photocatalytic activities of these materials were also evaluated on their performance as catalyst in the photocatalytic oxidation of methylene blue in water. Photocatalytic reaction was carried out in a beaker glass reactor of 40 mL capacity attached to an inner radiation type 100 W ultraviolet lamp. Aqueous suspensions of methylene blue (20 mL, with three different concentrations: 5, 10 and 15 ppm) and Ti-DSBC (1 g) were placed in beaker glass. Prior to irradiation, the suspensions were shaken with different time (10, 30, 70 and 90 minutes) to establish an adsorption/desorption equilibrium between dye and the Ti-DSBC. At given intervals of illumination, a specimen (1 mL) of the suspension was collected and centrifuged. The filtrates were analyzed by UV-Vis spectroscopy at 664.97 nm.

3. Results and Discussion

3.1. Characterization of DSBC and Ti-DSBC

The powder XRD patterns of DSBC and Ti-DSBC are shown in figure 1. The diffractograms of (fig. 1A) showed that the intense diffraction peaks found at 20,85 to 50,1375° correspond to the Miller indices [100], [101] and [110] were confirmed as SiO₂, and [112] was confirmed as Al₂O₃ as the framework of DSBC. The type of clay was confirmed as rectorite. Wang (2005) had reported that the thickness of a single sheet of rectorite is the sum of the thickness of the smectite layer and the thickness of the mica layer [13]. Additionally, the original rectorite single sheet is about 40 μm lengths and 5 μm in width whereas monmorillonite (MMT) is about 1 μm length as well as in width. As a result, the separable layer thickness and layer aspect ratio (width/thickness) of rectorite are larger than those of regular MMT [14]. The XRD patterns of Ti-DSBC show the appearance of peak at 2θ of 27.4460°, 36.0850°, 54.3216° and 56.6403° corresponding to Miller indices [101], [101], [211] and [220] were assigned as the diffraction peak of rutile. The diffraction peaks found at 2θ = 42,4490°, 68,3161 ([111] and [311]) indicates the presence of silica. The crystallinity of Ti-DSBC (72,5014 %) was increase compared to DSBC (55,8946 %).

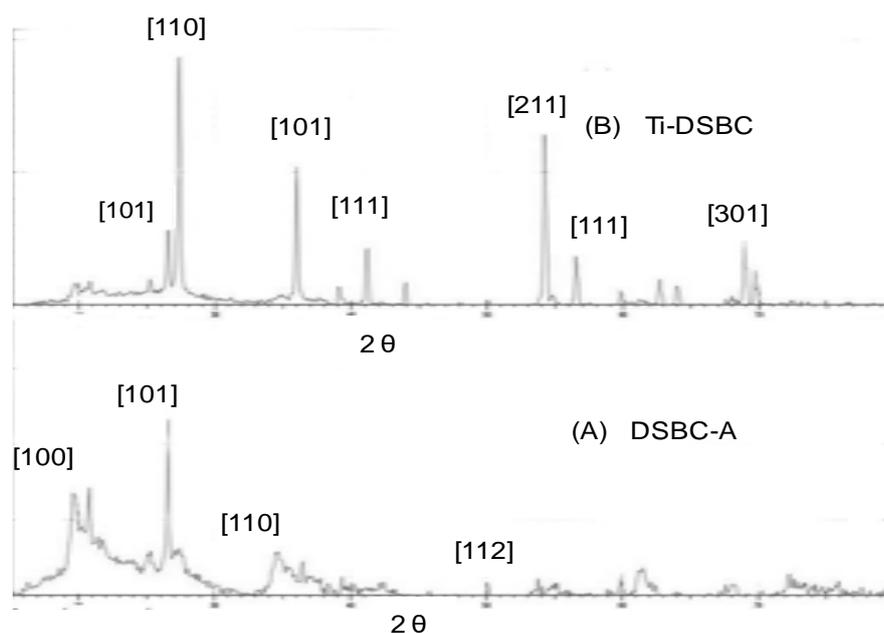


Figure 1. XRD results of Ti-DSBC and DSBC-A

The Fourier Transforms Infrared (FTIR) spectra of Ti-DSBC and DSBC-S (DSBC-Surfactant) spectrum are shown in figure 2. The FTIR spectrum of DSBC-S shown the difference of the peaks detected for DSBC after pillared with TiO₂ in wave numbers 2,900, 1,700 and 1400 cm⁻¹, which are C–H stretching, C–H bending and C=O stretching, respectively. These functional groups belong to carbon chain and carbonyl functional groups of rarasaponin. The presence of these functional groups is strong indication that intercalation of rarasaponin molecules. The weak –OH stretching vibration of water at 3570.24 cm⁻¹ and 3408.22 cm⁻¹ corresponding to the stretching vibration of hydroxyl group and interlayer water molecules from DSBC, is observed, the adsorption peak at 1462.02 cm⁻¹ appears only after adding surfactant rarasaponin, this wave number is assigned to the asymmetrical stretching vibration of C-O carbonyl group from rarasaponin. The stretching vibration C=O indicates that carbonyl group from rarasaponin was intercalated to DSBC [12]. Furthermore, the spectra of Ti-DSBC and DSBC-S shows peak at 462.92 cm⁻¹ and 470.63 cm⁻¹ that belongs to Si-O stretching [4].

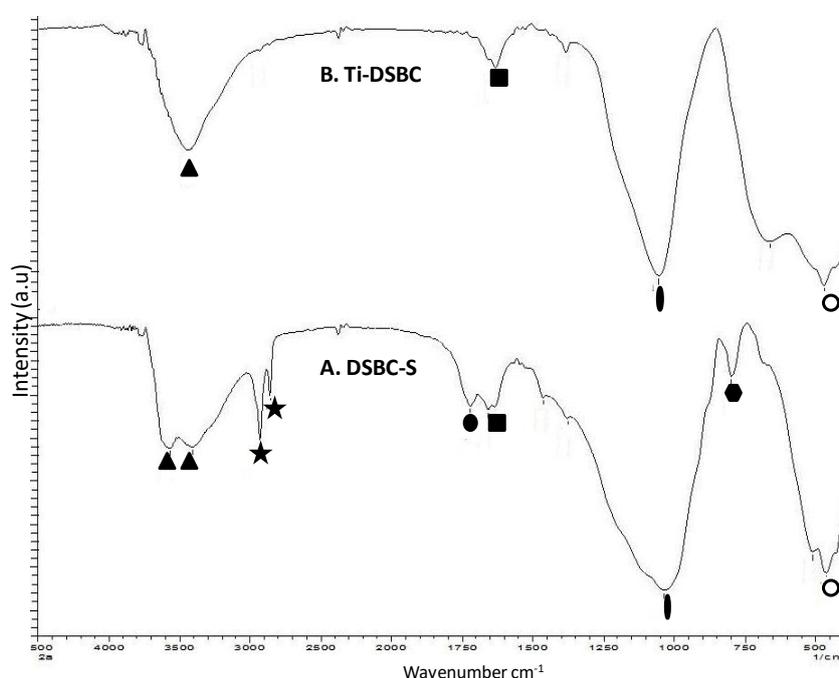


Figure 2. FTIR spectra of (A) DSBC-S and (B) Ti-DSBC; ▲:O-H; ★:C-H stretching; ●:C=O stretching; ■:H-OH bending; ◆: Si-O-Si; ▮: Si-O ; ○: Al-O-Si

The same chemical groups present in DSBC-S and Ti-DSBC are identified by the FTIR spectra as shown in fig. 2. The characteristic absorption peaks at 486 cm⁻¹ are attributed to the vibration of the Al–O–Si bond structure, and the characteristic absorption band Si–O are shown at 858 cm⁻¹, Si–O stretching are shown at 1101 cm⁻¹ and band at 1641 cm⁻¹ shows the presence of bending vibration of water molecules bound to the material.

Figure 3 (A) and (B) show the field emission scanning electron microscopy (FESEM) images of (A) DSBC-A and (B) Ti-DSBC. Advance enlargement of the image (10000 times) discovered the existence of aggregate particles. It showed that DSBC-A particles were having porous whereas after pillared with TiO₂ showed a different morphology occurred in Ti-DSBC, the small spherical crystals shown in the surface Ti-DSBC.

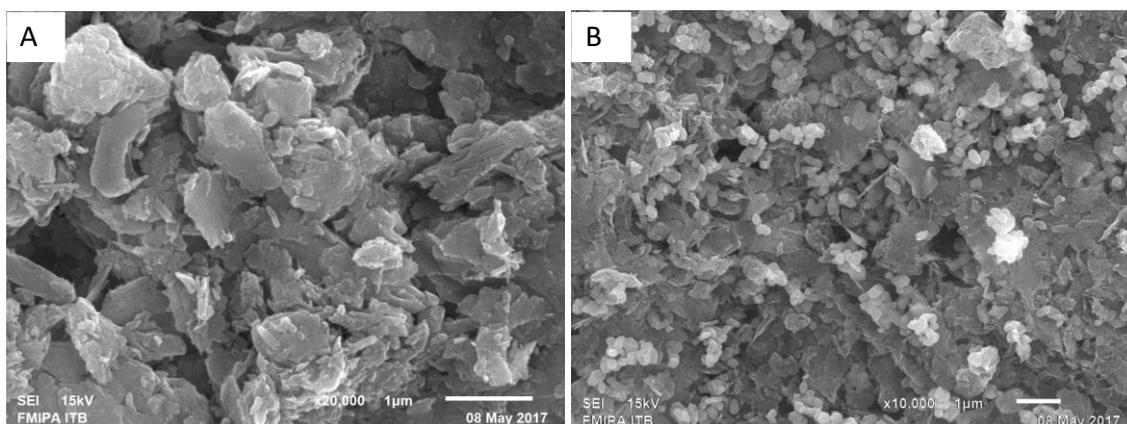


Figure 3. SEM pictures of (A) DSBC-A and (B) Ti-DSBC

3.2 Photocatalytic performance

This study investigated the effect of the contact time and the effect of methylene blue concentration in catalytic performances of Ti-DSBC under UV light is shown in figure 4. The contact time was varied in the range 10-90 min and concentration methylene blue was varied in the range 5-15 ppm.

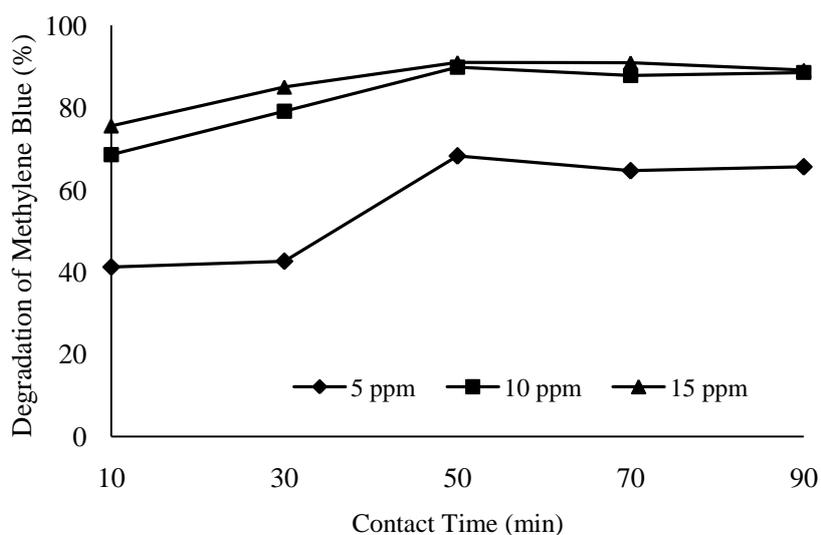


Figure 4. Photocatalytic performance of Ti-DSBC under UV light with different time

From fig.4 it can be seen that for 1 g of catalyst the photodegradation methylene blue (MB) increased within the first 10 min and reached as high as 40% , 66% and 75% for 5, 10, 15 ppm, respectively. Further, with an increase in reaction duration more than 30 min, the photodegradation of MB increased, this finding is mainly due to for longer reaction duration will increase the contact opportunity between catalyst and reactant and increase the production of electron-hole pairs on the surface of TiO₂ and the high reactive hydroxyl radicals was improved [15]. After 50 min percent degradation MB remained almost constant for 90 % at 10 and 15 ppm of MB.

The effect of catalyst dosage on degradation of MB was investigated by varying the catalyst amount (0.25 – 1.5 g) with optimal conditions 10 ppm of MB for 50 min. As shown in Fig. 5, the percent degradation MB increased as the catalyst amount increased from 0.25 to 1 g. The results obtained revealed that photocatalytic degradation performance was substantially improved with

increasing the amount of Ti-DSBC and reached a plateau at a dosage of 1 g due to the enhancement of production of hydroxyl radicals.

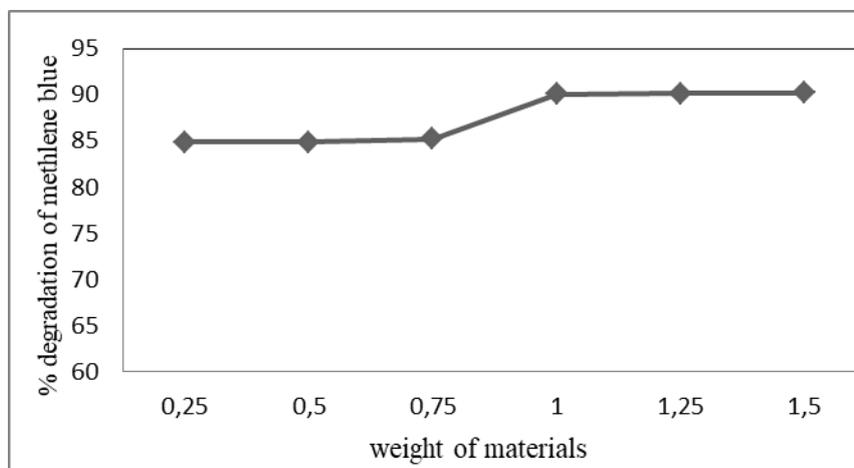


Figure 5. Effect of Ti-DSBC dosage in degradation of methylene blue by photocatalytic, initial concentration 10 ppm for 50 min reaction duration

However, the dosage of Ti-DSBC more than 1 g was not increase the photocatalytic activity due to reach the equilibrium or the agglomeration and sedimentation of TiO_2 may also occur under large amount of loadings which leads to lower surface area [15].

Reusability is one of the factors in the economical application of Ti-DSBC as the photocatalyst. The material was reused without any further activation. In order to test the reusability of the catalyst, the repeated batch experiments using the photocatalytic under UV light with optimized conditions was applied (catalyst content of 1 g, MB concentration of 10 ppm and reaction time 50 min). The results provided in Figure 6, show that the Ti-DSBC can be used up to five cycles while maintaining the activity at considerable degradation of methylene blue (84 %). This study shows that catalytic activity of catalyst has good reproducibility.

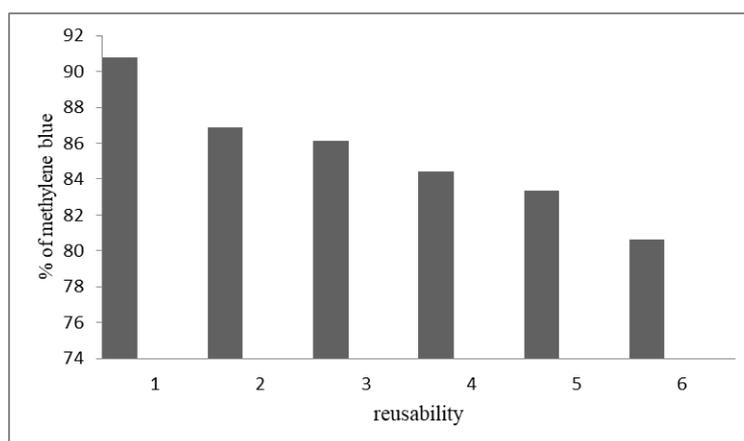


Figure 6. Reusability of Ti-DSBC

4. Conclusion

In this work, TiO_2 was pillared on DSBC in the presence of polymer *rarasaponin* as a surfactant. The XRD result proved that pillarization of TiO_2 on DSBC is a success. The morphology of Ti-DSBC

shows the some spherical crystal was distributed on the pore of DSBC. The optimum reaction condition of photodegradation methylene blue (MB) were : 1 g catalyst, 10 ppm of MB and 50 minutes reaction duration with % degradation of MB 90%. The Ti-DSBC was easily to separated and could reused five cycle while maintaining 84% degradation MB.

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