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Pilarization TiO_2 onto De-oiled spent bleaching clay using *Rarasaponin* as surfactant

Pilarization TiO_2 onto De-oiled spent bleaching clay using *Rarasaponin* as surfactant

N Hindryawati, Daniel, Erwin and N D Fadillah

Faculty of Mathematic and Natural Sciences, Mulawarman University, Gunung Kelua, 75113 Samarinda, East Kalimantan, Indonesia

E-mail: ienwati@yahoo.com

Abstract. Synthesis and characterization TiO^2 pillared deoiled spent bleaching clay (DSBC) with rarasaponin as surfactant had been done. Activation DSBC have been done with H_2SO_4 1N, followed by pillarization with TiO_2 using rarasaponin as surfactant. Characterization has done with Fourier transform infrared spectroscopy showed the rarasaponin as surfactant was successfully carried out in DSBC with the presence of absorption peak C=O stretching group in a sharp 1720.50 cm-1 wavelength range. As well as the C-CH_2 stretching uptake peak is represented on wave number 1462.04 cm^{-1} and 1033,85 cm^{-1} for aromatic functional group C=C stretching. After pillared by TiO_2, the XRD pattern on DSBC showed new peak appears on 2θ = 27,4460°; 36,0850° and 55,3216° and the mineral contain on DSBC is rectorite with dioctahedral mica layer and dioctahedral smectite with ratio 2:1. This molecule have formula $Na.Al_4(Si, Al)_8.O_{20}.(OH)_4.H_2O$. Crystallinty of pillared clay showed 72,5014 % after calcination and there is some Ti suspected on the layer based on SEM.

1. Introduction

In palm oil processing there are several steps had been through such as oil removal, neutralization, tanning and odor removal. In bleaching process they are used a porous material such as clay [1]. Palm oil processing in Indonesia in 2016 touched 34 million with estimated residual clay (spent bleaching clay) are 34 thousand [2]. Spent bleaching clay (SBC) is classified as hazardous waste (B3) based on government rules no. 18 in 1999, because there is a 20-40 % oil content which is can aggravate the soil and air quality [3,4] and a lot of company dealing this problem by dumping them into landfills [2]. Bleaching clay is one of pore materials which is consist an aluminosilicate mineral as negative charge and balanced by Na, Ca, Mg or H as positive charge. Bleaching Clay can be regenerated by extraction to remove oil content and this material called deoiled spent bleaching clay (D-SBC) [1]. Since this material was used before, the active site of this material become inactive. There are several steps to activated this material and acid treatment is the best way [5]. Hydrogen ions that produced by adding some acid will charge the alluminosillicate in interlayer region. This charge will activated the active site and alters the structure, chemical composition and physical properties of the DSBC, afterwards this material called DSC-A [6]. The presence of ion hydrogen in interlayer of DSBC-A could be replaced by another ion with different size and similar charge [7,8]. To hence ions exchanged in interlayer DSBC-A there is needed support by another substance. Using polyoxypropylene (POP) as surfactant had been reported can hence ion exchange in interlayer area [9]. However, by using synthetic surfactant also impact environment because they are non biodegradable and toxic. Klerak fruit contain

rarasaponin as main substance has been reported can be used as natural surfactant, this natural surfactant also performed similar properties such as synthetic surfactant [10]

To overcome this phenomenon, in this work a novel approach to utilize DSBC as support material and pillaring with TiO_2. SBC needs some handling before those material can be used, first oil contained in the material need to remove with extraction step, SBC will turn to deoiled spent bleaching clay (DSBC) after these process. This work will perform synthesis and characterization of deoiled spent bleaching clay (DSBC) by addition rarasaponin as surfactant to increase the basal spacing of the material [10] which is expected these material can be used as photocatalyst material of liquid textile waste. In the process, the photocatalyst material will characterized using X-ray fluorescence, X-Ray diffraction, Fourier transform infrared spectra (FTIR) and scanning electron microscopy (SEM).

2. Method

2.1 Rarasaponin Extraction

Rarasaponin was extracted from Klerak fruit was find from Yogyakarta. Klerak fruits dried for 4 days, then crushed until 80 mesh. The ration of distillate water (mL): klerak frutis (g) is 2:1. The extraction was done with soxhlet extractor at 70 ^oC for 180 minutes. The results will separated by evaporator at 100 ^oC.

2.2 Oil extraction on SBC

Spent bleaching clay heated in an oven at 105 ^oC for 150 minutes. The ration between SBC and hexane used is 1:2 (g/g). The mixture was put into an ultrasonic cleaner (using a frequency of 42 kHz, a voltage of 235 W) at 55± 2 ^oC for 60 minutes. The results will be separated with centrifuged at 1000 rpm for 5 minutes. % oil content in SBC will calculated after this process and SBC will be named DSBC (deoiled spent bleaching clay). The oil content was determine using the following formula:

$$\% \text{ oil content} = \left(\frac{M_1}{M_0}\right) \text{x } 100 \quad (1)$$

M_1 and M_0 are the masses of the oil and SBC in g, respectively. The extraction of oil from SBC via ultrasound extraction yield about 21 wt% within 60 mins which was more efficient than that of soxhlet extraction. Furthermore, it was reported by Khaeng et al. [2] that extraction of oil using soxhlet extraction showed the yield about 21 wt% within 4 h. Soxhlet extraction is associated with high energy consumption, involves longer extraction time (3 h for extracted O-DC) and the use of large quantities of organic solvents. For these reasons, an improved or better extraction technique is desirable. Thus, in agreement with Maniam et al. [11], the ultrasound-assisted extraction is explored because it can enhance the extraction efficiency through acoustic cavitations and some mechanical effects.

2.3 Synthesis TiO_2 pillared DSBC

Deoiled spent bleaching clay need to activated first using H_2SO_4 1N with ration 2:1 (g/g) and then refluxed for 2 hours with temperature 96-98 ^oC, activated spent bleaching clay washed with distillate water up to pH 7 then dried into oven with temperature 105 ^oC for 1 hour afterward this is named DSBC-A. Subsequently DSBC-A need to add *rarasaponin* as surfactant with ration *rarasaponin*, aquades and DSBC-A is 1(g):50(g):10(g). the mixture as refluxed for 24 hours at 28 ^oC. The results will be separated and named DSBC-S. After add some surfactant DSBC-S will pillared by TiO_2 with mixed 04 g of TiO_2 into 100 mL on beaker glass filled with 1 g DSBC-S, added with 6 mL of 95% ethanol and stirring used magnetizer for 5 hours. The results will be separated by centrifugation followed by drying at 120 ^oC for 5 hours. Afterward proceed at calcination at 500 ^oC for 2 hours.

3. Results and discussion

3.1 XRF Analysis of DSBC and DSBC-A

Table 1 showed that there is an increase of Si metal and reduction of Ca and Mn metal. That is because the metal was dissolved during the activation process by H_2SO_4 solution. The activation of DSBC using acid treatment was aim to open active site of the DSBC by dissolving small ion [9].

Table 1. XRF result analysis of DSBC and DSBC-A

No	Sample Name	Compound									
		Fe_2O_3	CaO	K_2O	SiO_2	MnO	SO_3	ZnO	P_2O_5	Cr_2O_3	CuO
1.	DSBC	28,618	21,713	3,599	29,363	0,522	2,276	0,059	13,711	0,105	0,034
2.	DSBC-A	28,077	2,346	4,076	63,493	0,143	1,674	0,071	-	0,097	0,024

Other impurities such as SO_3, P_2O_5, Cr and Cu metals also decreased. This phenomenon suspected because the metal was dissolved in activation process resulted the material got bigger pore. DSBC-A will be further pillaritation.

3.2 Fourier Transform Infrared Analysis of DSBC-S and Ti-DSBC

Fourier transform infrared analysis (FTIR) is one of the important analyses to confirm formation of DSBC-A after adding of surfactant and pillarization of TiO_2 on DSBC. The FTIR spectrum of deoiled spent bleaching clay with *Rarasaponin* as surfactant and DSBC after pillarization with TiO_2 was shown in Figure 1.

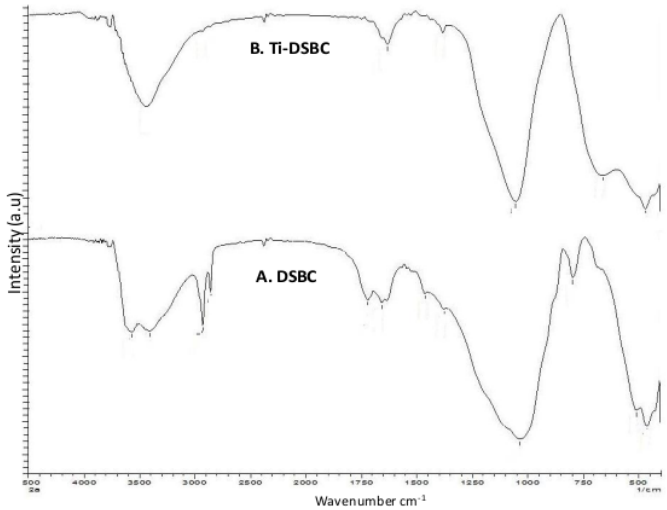

Figure 1. FTIR analysis result of (A) DSBC and (B) Ti-DSBC.

FTIR analysis showed functional group of material by interpreting absorption peaks of the infrared spectrum. *Rarasaponin* as surfactant was successfully carried out in the presence of carbonyl group absorption peak is C=O stretching group in a sharp 1720.50 cm^{-1} wavelength range. As well as the C-CH_2 stretching uptake peak is represented by spectrum with absorption peak of wave number 1462.04 cm^{-1} and 1033,85 cm^{-1} for aromatic functional group C=C stretching [10]. The structure of montmorrilonite also unchanged with the presence of spectra with absorption peak of 511.14 cm^{-1} and 462 cm^{-1} which is typical of Al-OH stretching and Si-O stretching. This information also reinforced by the presence of SiO_2 with absorption wavelengths 796.60 cm^{-1} [10]. The functional groups of C=O and

C-O esters are the main functional groups of *rarasaponin* and based on these information adding *rarasaponin* as surfactant had been successes. After Ti pillared to material DSBC-S this material losses some functional group like C=O marked with no absorption in 1720.50 cm^{-1}. There is some losses H_2O molecule with absorption wavelength only appeared in 3429.50 cm^{-1} and 1631.76 cm^{-1}.

3.3 X-ray Diffraction Analysis of DSBC-A and Ti-DSBC

Based on Figure 2 (A) showed XRD pattern on DSBC-A with peak on 20,8595°, 25,5835, 26,6393°, 35,1356, 36,5431° and 50,1375° with *hkl* value; [101], [012]; [104]; [110] and [112] indicated kind of this mineral contain on this material is rectorite. There is 2θ = 20,8595°, 26,6393°, 36,5431° with *hkl* value on [100], [110] and [101] indicated hexagonal crystal of SiO_2, furthermore 2θ = 25,5835°, 35,1356 °, 50,1375° with *hkl* value [012], [104] and [112] indicated Al_2O_3 with rhombohedral crystal. Rectorite is one of Na-montmorrilonite with dioctahedral mica layer and dioctahedral smectite with ratio 2:1. This molecule have formula $Na.Al_4(Si , Al)_8.O_{20}.(OH)_4.H_2O$ or allevardite for common name [12]. Rectorite layer have thickness around 40 µm and wide around 5 µm. This size cause rectorite has bigger layer size than montmorrilonite. On Figure 2 we can conclude this material was ready for pillared because the amorphous value showed 55,8946 %. This material tends to amorphous so that possible to substitute another TiO_2 to this layer material.

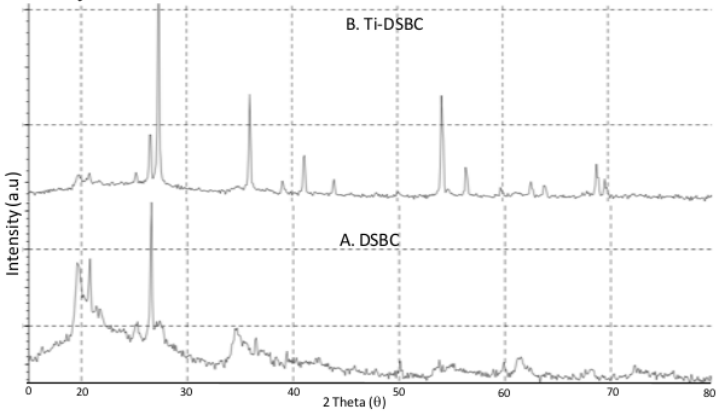

Figure 2. XRD results on (A) DSBC-A and (B) Ti-DSBC.

Based on Figure 2 (B) showed XRD Ti-DSBC result. JCPDS no. 88-1175 showed this material have rutile Ti with tetragonal geometric, this information can seen with new peak appears on 2θ = 27,4460°; 36,0850 ° and 55,3216 ° with *hkl* value [110], [101] and [211]. Otherwise, the main component of DSBC (rectorite) SiO_2 and Al_2O_3 appears on 2θ = 42,4490°, 68,3161 with *hkl* value [111] and [311] showed shifted of SiO_2 and 2θ = 25,5779° with *hkl* value [012] showed there is Al_2O_3. TiO_2 in this XRD pattern which is crystalline phase and perform as sustain for the metal oxide in the catalyst. After pillarization the crystallinity of Ti-DSBC was increased (72,50%). In line with Schneider et al. and Thamaphat et al.[7,13], the material also has different cristallinity before and after calcinated.

3.4 Scanning Electron Microscopy (SEM) of DSBC-A and Ti-DSBC

The micrograph of DSBC-A showed that DSBC-A has porous with irregular particle shape and small particle in the surface where this indicated its has specific surface area.

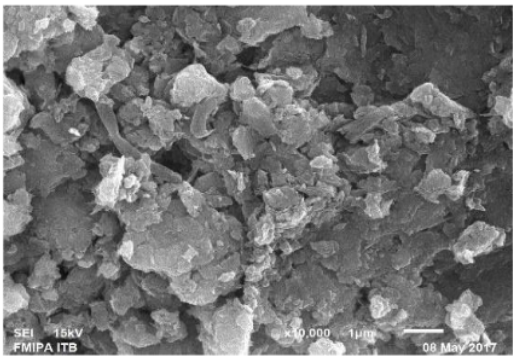

Figure 3. SEM image of DSBC-A 10.000 expand.

Figure 3 showed layer morphology of DSBC-A, there is have same size particle distribution. From this Figure also seen there is cavity for some metal into. This layer suspected as rectorite and has possibility to add TiO_2.

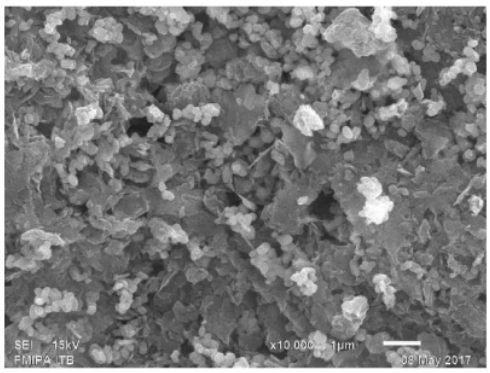

Figure 4. SEM image of Ti-DSBC 10.000 expand.

Figure 4 showed morphology Ti-DSBC had some difference and expected there is Ti with white colour stick on the layer DSBC-S. Form this Figure also seen the particle have uniform size if compared with DSBC-A, it happened because these material had calcination process.

4. Conclusion

XRD analysis showed crystallinity had increase to 72.5014 % which is only 50.0556% before treatment. Based on JCPDS no.88-1175 this material have rutile Ti various. This information reinforced by SEM analysis showed surface morphology on DSBC-A had equal particle size and presence of cavities in the material. However, in Ti-DSBC material the particle size become smaller and there are other white particles in Ti-DSBC pore suspected as Ti.

Acknowledgement

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