Synthesis of TiO$_2$ pillared clay and its application to the decolourization of crystal violet dyes

Suhartana$^{1,*}$, Atikah Ayu Janitra$^1$, Choiril Azmiyawati$^1$, Adi Darmawan$^1$

Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia

* Corresponding author: suhartana@live.undip.ac.id

Abstract. In this study the synthesis of TiO$_2$ pillared clay was carried out through clay activation and pillarisation. The clay activation process was carried out using H$_2$SO$_4$ in the reflux system, then continued with pillarisation then calcined. Natural, activated and TiO$_2$ pillared clay were characterized using FTIR and XRD, respectively to determine functional groups and basal spacing of these three materials. Clay decolourization ability to Crystal violet dye was measured based on changes in Crystal violet concentration before and after treatment using UV Vis Spectrophotometer. The results obtained in this study indicate that clay activation and pillarisation can cause a decrease in the SiOH/SiOTi ratio functional groups and increase in basal spacing. The biggest changes occurred in of TiO$_2$ pillared clay with TiCl$_4$: ethanol of 1: 45 against natural clay, in which SiOH/SiOTi ratio decreased from 0.68 to 0.57 and basal spacing increased from 19.19 Å to 29.17 Å. The optimal ability of clay to decolorize Crystal violet occurred at 45 minutes’ contact time.

Keywords: TiO$_2$ pillared clay, TiCl$_4$, Crystal violet, Decolourization

1. Introduction

Clay is one of Indonesia's abundant natural resources and has not been utilized optimally. The clay consists of uniform layers with octahedral coordinating atoms, which are between two layers of tetrahedral coordinating atoms [1]. Between the layers of clay there are exchangeable cations that can be exchanged. Because of the clay structure in the form of layers, clay has a high adsorption capacity and is able to adsorb metal ions, organic molecules, gases and liquids. This is because the clay interlayer can expand or contract because there is no rigid support between the layers. The clay layer can change if the clay is given a treatment with the insertion of certain ions or molecules hence the clay interlayer is enlarged. This causes clay adsorption capabilities can be engineered [2]. To increase the potential of clay as an adsorbent, clay can be activated or pillarised. Clay activation is one method used to improve clay adsorption ability by cleaning the area between the layers of clay from impurities [3]. Whilst, pillarisation is conducted by intercalating the hydroxy polycation in the clay, then calcined to form a metal oxide pillar [4, 5]. Clay pillarisation has been extensively studied, including polycation of aluminium [6], chrome, iron and others. On the other hand, Ti in the form of TiO$_2$ compounds has been known to have good photocatalytic capabilities, affordable prices, inert chemical properties, photostable and biocompatible [7]. TiO$_2$ is often used in photocatalyst degradation of pollutants [8, 9]. In this study, acid activation was carried out on clay followed by pillarisation using TiO$_2$. The TiO$_2$ pillared clay produced was then tested for its decolourisation ability on Crystal violet dyes.
2. Methodology

2.1 Clay Preparation

Natural clay fractionation was conducted by suspending clay in water. Then suspension clay was left to stand for 24 hours until the heavy fraction settles and light fractions could be separated. The light fraction was the clay fraction floating in the clay suspension. Then the suspension from the light fraction was let stand again until the precipitate was formed and then decanted and the precipitate obtained was dried. Clay samples that have been dried, then smoothed and sieved with a 170 mesh sieve.

2.2 Clay activation

The 20 grams of natural clay samples prepared were then refluxed by adding 200 mL of 0.5 M H$_2$SO$_4$, for 3 hours at 60ºC [3]. Then washed with distilled water to obtain a neutral pH and to remove SO$_4^{2-}$ ions which tested using AgNO$_3$. The activated clay was then heated for 6 hours at 120ºC followed by grinding and sieving with a 170 mesh sieve.

2.3 Preparation of pillarisation agents

Preparation of pillarising agent in the form of Ti-polycation solution was carried out by slowly adding 3.5 mL of TiCl$_4$ with 52.5 mL ethanol (ratio of TiCl$_4$: ethanol = 1:15) with stirring for 3 hours to form a yellow homogeneous solution [10]. The same procedure was conducted for the ratio of TiCl$_4$: ethanol of 1:30 and 1:45.

2.4 Clay pillarisation

10 grams of activated clay were added gradually to the TiO$_2$ pillarising solution, while stirring with a magnetic stirrer at room temperature for 18 hours until a homogeneous suspension was obtained. The TiCl$_4$ clay suspension was then washed using 96% ethanol until the pH was neutral and free of Cl$^-$ ions by testing using AgNO$_3$. The TiCl$_4$ clay was then dried overnight in an oven at 70ºC, then calcined using a furnace at 200ºC for 4 hours with a ramp rate of 2ºC/minute [11]. The calcined sample was crushed and sieved with a 170 mesh sieve.

2.5 Crystal violet decolourization test

Each 0.1 gram of natural clay, activated natural clay and TiO$_2$ pillared clay (ratio of TiCl$_4$: ethanol = 1:45) was added to 10 mL of 50 ppm crystal violet solution [12] and stirred with a magnetic stirrer. The solution was then separated between the filtrate and the residue with a centrifuge and the filtrate was analyzed using UV-Vis. Variations in contact time were carried out which were 1; 3; 5; 7; 10; 15; 30; 60 and 90 minutes. For TiO$_2$ pillared clay, decolourization was also carried out with or without irradiation with a 20 watt UV lamp.

3. Results and Discussion

3.1 Functional group analysis

From the results of FTIR characterization, spectra are obtained which show the emergence of certain peaks at certain wave numbers where the wave number indicates a particular functional group. The spectra of natural clay and activated clay are shown in Fig. 1.
Fig. 1 shows an increase in absorbance in activated clay compared to natural clay before being activated for wave numbers between 950-1050 cm\(^{-1}\) which indicates Si-O groups in the form of Si-O-Si and Si-OH. While the wave number between 3400-3800 cm\(^{-1}\) which characterizes the -OH group there is an increase in absorbance due to loss of some noise. Increased peaks in the frame area as well as in the free OH area and reduced noise imply a cleaner and more non-interference structure. This indicates that the activation process can significantly reduce the impurities in the clay. In clay layers there are several impurity metals that are detected at wave numbers around 800 cm\(^{-1}\), which were AlFeOH and AlMgOH. The activation process removed Fe\(^{3+}\), Mg\(^{2+}\) and other impurities from the structure lattice, hence physically the clay becomes more active [2]. With activation, the cations on the clay interlayer could be replaced by H\(^{+}\), as H\(^{+}\) is a small cation which generally replaces larger cations. Because of the similar form of spectra, to conduct a quantitative analysis of FTIR spectra, FTIR spectra deconvolution was carried out using “fityk” software. Deconvolution was carried out by looking for derivative spectra with the same FWHM for each particular peak. The results of the calculation of the ratio of SiOH/Si-O-Si and the ratio of SiOH/Si-O-Ti are presented in Fig. 2.

The acid activation process results in the exchange of metal ions in the interlayer clay region in the form of Na\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\) and other metals with H\(^{+}\) ions from acids, this caused an increase in the Si-OH (silanol) group [13]. While the presence of pillarisation before calcination, an increase in the Si-OH ratio to Si-O-Si was due to the addition of metals as a pillar in large quantities to the cations between clay layers [14]. Whereas after calcination, the Si-OH-Si-O-Si ratio decreased because the calcination process caused dehydration, dehydrogenation and condensation of the Si-OH group to Si-O-Si. After the clay underwent pillarisation, the peak appeared at the wave number 1010 cm\(^{-1}\) [15] with greater absorbance intensity indicating the vibration of “Si-O...O-Ti” from Si-O polarization. Allegedly formed Ti-O bonds with Si-OH [16]. Initially in the clay there is a bond between Si-OH or silanol, then by adding Ti-Polyhydroxy then the hydrogen in silanol will break up and bind to Ti [17].
3.2. Basal spacing analysis

The natural, activated and TiO₂ pillared clay were analyzed using XRD and it was observed there was a shift in reflection of the basal spacing of clay with a value of 2θ, indicating an increase in basal spacing due to the process of activation and pillarisation. This indicates that the activation process enlarges the area between layers which may be due to the replacement of impurity.
ions with H\(^+\) ions. This H\(^+\) ion facilitates water molecules to be absorbed in the clay interlayer hence the interlayer becomes larger. Basal spacing was further increased when clay was intercalated with TiO\(_2\) pillaring solution. This is due to the inclusion of large amounts of Ti-polyhydroxy into the inter-layer clay. Calcination conducted transformed Ti-polyhydroxy into a TiO\(_2\) pillar. The resulting titania oxide acts as a pillar while modifying the clay into a photocatalyst in the decolourization of dyes. What's interesting is that the ratio of TiCl\(_4\): ethanol of 1:45 shows the highest increase in basal spacing compared to the ratio of TiCl\(_4\): ethanol of 1:15 and 1:30. Possible reasons to explain this is first, more amount of ethanol solvent making it easy for Ti\(^{4+}\) ions to enter the clay interlayer. Second, a high solvent content produces better conditions for the formation of Ti\(^{4+}\) polycation in the process of making a pillarisation agent.

3.3. Decolourization of crystal violet dyes

![Figure 3](image)

Fig. 3 shows that the percentage of crystal violet decolourization increases with increasing contact time. The decolourization process occurs very quickly in the early minutes which is a common characteristic of an adsorption process. Even for natural clays and activated clays, they have achieved optimum decolourization performance in the first minute. While for pillared clays, the adsorption process takes longer. For all materials, the absorption process reaches optimum up to 45 minutes then constant and only a slight increase until the contact time of 90 minutes. Natural clay and activated clay show a higher percentage of decolourization compared to pillared clay at all times. This shows that the natural clay and activated clay kinetically absorb faster than pillared clays. This is understandable because natural clays have less rigid pores, while pillared clays are stiff because of the pillars in the interlayer of clay, so it is easier for natural clays to absorb crystal violet dyes.

Activated clays show better decolourization performance than natural clay. This is easy to understand because the activation process causes the clay gallery to be cleaner from impurities and causes the clay to absorb better. From this fact it can be concluded that the decolourization mechanism is predominantly caused by the adsorption process. Another interesting thing is that the decolourization performance in TiO\(_2\) pillared clay which was given UV light was higher than that without UV for the entire contact time tested. This indicates that the photocatalytic process is functioning properly by TiO\(_2\). TiO\(_2\) did not only serve as a pillar in clay interlayer but also as a photocatalyst.

This happens because TiO\(_2\) can function as a photocatalyst to speed up reactions that are induced by light because it has a semiconductor structure that is an electronic structure characterized by the presence
of a filled valence band (vb) and an empty conduction band (cb). The two bands are separated by bandgap energy \((E_g)\) [18]. Hole \((h^+)\), hydroxyl radicals \((\cdot OH)\) and superoxide ions \((O_2\cdot)\) formed can decolorize most organic molecules, especially dyes, because they are very strong oxidizers. When photons from UV hit the surface of \(TiO_2\), electron excitation occurs from the conduction band to form a positively charged hole in the valence band. Electrons in the conduction band and holes in the formed valence band migrate to the surface of \(TiO_2\) where \(O_2\) and/or \(OH/\)\(H_2O\) molecules form reactive oxygen such as \(O_2\cdot\), \(HOO\cdot\) and \(OH\cdot\) radicals, which attack the dye molecules which change the structure of the dye and cause decolourization [16].

Then the data-based adsorption model was made based on Fig. 3. The results were approached with the Langmuir and Freundlich models. The correlation coefficient \((R^2)\) is an important characteristic for measuring the proximity of data to the model produced. In this study, \(R^2\) value was 0.732 for Langmuir isotherm, whereas for Freundlich isotherm \(R^2\) value was 0.987. \(R^2\) value shows a good model if the value of \(R^2\) approaches 1 [19], so it can be concluded that the type of adsorption isotherm for crystal violet dyes in clay was the type of Freundlich isotherm. The adsorption coefficient of crystal violet dye based on Freundlich adsorption isotherm in Table 2 was 12.07 and the value of \(n\) obtained was 1.14. The relative ability of an adsorbent to adsorb the adsorbate can be seen from the \(K_f\) value, the greater the \(K_f\) value the greater the ability of an adsorbent to adsorb, as well as the interaction strength between adsorbent and adsorbate can be seen from \(1/n\), the smaller the value \(1/n\) the stronger the interaction between the adsorbent and the adsorbate [20]. Because the \(K_f\) value was not too large, this indicates that the adsorption that occurs was a physical adsorption.

### Table 2. The value of the isotherm constant

| Isotherm  | Symbol | Value       |
|-----------|--------|-------------|
| Langmuir  | Qm     | 61.74 mg/g  |
|           | \(K_1\) | 0.24        |
|           | \(R^2\) | 0.732       |
| Freundlich| \(n\)  | 1.14        |
|           | \(K_f\) | 12.07       |
|           | \(R^2\) | 0.987       |

### 4. Conclusion

Activated clay and \(TiO2\) pillared clay were obtained which were characterized by an increase in basal spacing and a decrease in \((SiOH)/(SiOTi)\) ratio. The lower the ratio of \(TiCl_4\): ethanol, the greater the increase in basal spacing, which may be caused by the ease of the \(Ti^{4+}\) polycation entering the clay interlayer because of the large amount of solvent. The percentage of Crystal violet decolourisation increases in activated clays but in \(TiO_2\) pillared clays it is lower. UV light irradiation in \(TiO2\) pillared clay has a significant effect which indicates a photocatalyst reaction by pick up. It was also found that the optimum contact time was 45 minutes.

### 5. References

[1] Darmawan A 2004 Hidrorengkah Fraksi Berat Minyak Bumi Menggunakan Katalis Lempung Terpilar Aluminium Berpengemban Nikel. *J. Kim. Sains Apl.* 7 1 6-9
[2] Nascimento A R d, Alves J A B L R, Melo M A d F, Melo D M d A, Souza M J B d and Pedrosa A M G 2015 Effect of the acid treatment of montmorillonite clay in the oleic acid esterification reaction *Materials Research* 18 2 283-7
[3] Bhattacharyya K G, SenGupta S and Sarma G K 2014 Interactions of the dye, Rhodamine B with kaolinite and montmorillonite in water *Applied Clay Science* 99 7-17
[4] Yuan P, Annabi-Bergaya F, Tao Q, Fan M, Liu Z, Zhu J, He H and Chen T 2008 A combined study by XRD, FTIR, TG and HRTEM on the structure of delaminated Fe-intercalated/pillared
Kurniawan A, Suseno A and Darmawan A 2017 Sintesis Lempung Terpilar Polikation Alumunium Sebagai Adsorben Indigo Karmina J. Kim. Sains Apl. 20 3 146-50

Taslimah T, Kusumawardani R and Azmiyawati C 2008 Pilarisasi Lempung dengan Al2O3 untuk Agen Pemucat Minyak Sawit J. Kim. Sains Apl. 11 2 48-51

Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, Anpo M and Bahnemann D W 2014 Understanding TiO2 photocatalysis: mechanisms and materials Chemical reviews 114 19 9919-86

Nakata K and Fujishima A 2012 TiO2 photocatalysis: design and applications Journal of Photochemistry and Photobiology C: Photochemistry Reviews 13 3 169-89

Barbosa L V, Marçal L, Nassar E J, Calefi P S, Vicente M A, Trujillano R, Rives V, Gil A, Korili S A and Ciuffi K J 2015 Kaolinite-titanium oxide nanocomposites prepared via sol-gel as heterogeneous photocatalysts for dyes degradation Catalysis Today 246 133-42

Shaheed M and Hussein F 2012 Synthesis and photocatalytic activity of TiO2 Nanoparticles Journal of Babylon University 22 1 423-30

Darmawan A, Suseno A and Agus Purnomo S 2005 Sintesis Lempung Terpilar Titania J. Kim. Sains Apl. 8 3 61-8

Gil A, Assis F, Albeniz S and Korili S 2011 Removal of dyes from wastewaters by adsorption on pillared clays Chemical Engineering Journal 168 3 1032-40

Ketaren S 1986 Pengantar teknologi minyak dan lemak pangan (Jakarta: UI Press)

González-Rodríguez B, Trujillano R, Rives V, Vicente M, Gil A and Korili S 2015 Structural, textural and acidic properties of Cu-, Fe-and Cr-doped Ti-pillared montmorillonites Applied Clay Science 118 124-30

Ninness B, Bousfield D and Tripp C 2003 Formation of a thin TiO2 layer on the surfaces of silica and kaolin pigments through atomic layer deposition Colloids and Surfaces A: Physicochemical and Engineering Aspects 214 1-3 195-204

Liu J, Dong M, Zuo S and Yu Y 2009 Solvothermal preparation of TiO2/montmorillonite and photocatalytic activity Applied Clay Science 43 2 156-9

Innocenzi P 2003 Infrared spectroscopy of sol–gel derived silica-based films: a spectr-microstructure overview Journal of Non-Crystalline Solids 316 2-3 309-19

Wang R, Sakai N, Fujishima A, Watanabe T and Hashimoto K 1999 Studies of surface wettability conversion on TiO2 single-crystal surfaces The Journal of Physical Chemistry B 103 12 2188-94

Delle Site A 2001 Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review Journal of Physical and Chemical Reference Data 30 1 187-439

Auta M and Hameed B 2013 Acid modified local clay beads as effective low-cost adsorbent for dynamic adsorption of methylene blue Journal of Industrial and Engineering Chemistry 19 4 1153-61