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KEGGIN TYPE POLYOXOMETALATE $H_4[\alpha SiW_{12}O_{40}].nH_2O$ AS INTERCALANT FOR HYDROTALCITE

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ABSTRACT

The synthesis of hydrotalcite and polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ with the ratio (2:1), (1:1), (1:2) and (1:3) has been done. The product of intercalation was characterized using FT-IR spectrophotometer, XRD, and TG-DTA. Polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ intercalated layered double hydroxide was optimised to use as adsorbent Congo red dye. Characterization using FT-IR was not showing the optimal insertion process. The result using XRD characterization was showed successful of polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ inserted layered double hydroxide with a ratio (1:1) which the basal spacing was expanded from 7,8 Å to 9,81 Å. Furthermore, the thermal analysis was performed using TG-DTA. The result show that the decomposition of polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ intercalated hydrotalcite with ratio (1:1) was occured at 80°C to 400°C with a loss of OH in the layer at 150°C to 220°C, and then the decomposition of the compound polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ at 350°C to 420°C.

Keywords: Hydrotalcite, Layered Double Hydroxide, Polyoxometalate, Intercalation

INTRODUCTION

The layered material based on its existence is divided into layered material found in nature and synthesized. Hydrotalcite is a class of synthetic anionic clays whose represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}$•$nH_2O$ with the identities of M^{2+} and M^{3+} are divalent and trivalent metal cation and A^n is interlayer anion (Zhao *et al*, 2011).

Hydrotalcite is modified to aim the increasing the interlayer so that it can be more effectively used. Hydrotalcite modification was done by intercalation anion macro. The macro anion used is polyoxometalate Keggin type, i.e. $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$. Hydrotalcite intercalation by polyoxometalate used ion exchanged method. The anion macro intercalated in the hydrotalcite causes the loss of the OH^- and was located on the interlayer so it can be expected to increase the distance between the layers of the hydrotalcite.

In this research, synthesis and characterization of hydrotalcite, polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ and hydrotalcite intercalated by polyoxometalte $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ to know the functional group and the success of intercalation process used Fourier characterization Transform Infra Red (FT-IR), X-Ray Diffractometer (XRD) and Thermo Gravimetric-Differential Thermal Analysis (TG-DTA).

EXPERIMENTAL SECTION

Materials

The chemicals used are qualified materials such as sodium metasilica, sodium tungstate, hydrochoric acid, pottasium hydroxide, pottasium chloride, diethyl ether, sodium hydroxide, sodium carbonate, magnesium nitrate and aquadest.

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Methods

Synthesis Hydrotalcite

Hydrotalcite was synthesized in a solution with a concentration of 50 mL of $Mg(NO_3)_2$ 1M and 20 mL of $Al(NO_3)_3$ 1M wa s added by rapidly stirring into 250 mL of distilled water at pH value 10 of 5 mL of NaOH 2M at teazmperature 40̊ C. The reaction was maintained at a pH value of 10 then simultaneously added 20 mL of Na_2CO_3 2M and 10 mL of NaOH 2M. The product obtained is white suspension and is still stirred for 3 hours at 40˚C and left at 70̊ C for 40 hours. The obtained product is filtered, washed with aqua dest and dried at room temperature. The structure, term stability and product texture of hydrotalcite were characterized by FT-IR Spectrophotometer, XRD, and TG-DTA.

Polyoxometalat $H_4[\alpha\text{-}SiW_{12}O_{40}]$•$nH_2O$

Polyoxometalat $H_4[\alpha\text{-}SiW_{12}O_{40}]$•$nH_2O$ was synthesized by dissolving methanolic sodium as much 2,75 grams into 25 mL of aqua dest was used as solution A. 45,5 grams of sodium tungstate dissolve into 75 mL of boiled aqua dest and this solution becomes B solution. 41,25 mL of HCl 4M was added slowly for 5 minutes with strong stirring to dissolve the precipitate of tungstic acid. Then, solution A was added rapidly into solution B with an addition of 12,5 mL of HCl 4M. The solution was kept for an hour at 100˚C at pH value of 5 to 6. 12.5 mL of sodium tungstate and 20 mL of HCl 4M are added to the solution rapidly. This solution is filtrated after cooling at room temperature. The solution is used to obtain a salt or α-$[SiW_{12}O_{40}]^{4-}$ acid. Potassium salt was obtained by adjusting the solution to a pH value of 2 using a KCl of 12.5 grams rapidly to obtain a white sediment from potassium salt to form $K_4[\alpha\text{-}SiW_{12}O_{40}]$.

To obtain $H_4[\alpha\text{-}SiW_{13}O_{40}]$ polyoxometalate acid by extraction of a white sediment from potassium salt to form $K_4[\alpha\text{-}SiW_{12}O_{40}]$ using 20 mL diethyl ether and 30 mL of diethyl ether and concentrated hydrochloric acid (1: 1) which had previously been cooled to Temperature 0˚C. The bottom layer is taken and concentrated to obtain white crystals which are recrystallized using quads so as to obtain polyoxometalate acid $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$. The characteristic of $H_4[\alpha\text{-}SiW_{13}O_{40}]$ was performed using FT-IR spectroscopy and XR analysis.

Preparation of Hydrotalcite intercalated by Polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$

Intercalated hydrotalcite by polyoxometalate $H_4[\alpha\text{-}SiW_{13}O_{40}]$ used ion exchanged method with weight variation ratio of each hydrotalcite : polyoxometalate (2:1), (1:1), (1:2) and (1:3) is by preparing a solution of 1 grams polyoxometalate $H_4[\alpha\text{-}SiW_{13}O_{40}]$ 1 M distilled with 50 mL of aqua dest and 1 grams hydrotalcite was added to 25 mL of NaOH 1M.. Solution A and solution B were mixed rapidly under conditions of N_2 gas sterilized for 24 hours. The suspension is cooled and the product is washed with water and dried at room temperature. The structural analysis and the thermal stability of intercalated product are identifed using XRD, FT-IR, and TG-DTA.

RESULTS AND DISCUSSION

Characterization of Hydrotalcite and Polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ and the result using FT-IR Spectrophotometer

The FT-IR spectrum of hydrotalcite is presented in Figure 1a. It is seen that the widespread vibration peak between the wave number 3800-3300 cm^{-1} is the vibration of the OH group within the hydrotalcite structure. The presence of a detected peak at the 1635 cm^{-1} is a bending OH vibration. In the wave number 1381 cm^{-1}, there is a vibration which is an asymmetrical stretch of nitrate and a nitrate bend at wave number 671 cm^{-1}. Vibration Al-O and Mg-O are at wave numbers 601 cm^{-1} dan 408 cm^{-1} (Handayani, et al.2014)

Polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ has the vibration at 3448 cm^{-1}. In Figure 1b, identifies the presence of H_2O contained in the polyoxometalate $H_4[\alpha SiW_{12}O_{4t0}].nH_2O$. characteristic of polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ has shown in the wave number 925 cm^{-1} for Si-O vibration and wave number 794 cm^{-1} for W-O-W vibration.

Hydrotalcite intercalated by polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ ratio 2:1; 1:1; 1:2; and 1:3 is presented in Fig. 1c, d, e, and f. Hydrotalcite intercalated by polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ ratio 2:1; 1:1; and 1:2 did not show the characteristic of polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ wherein 3 peaks at wave number 980-770 cm^{-1}, but only the widespread nitrate bending of wavenumber 820-550 cm^{-1} was shown. As for hydrotalcite intercalated by polyoxometalate ratio 1:3, the FT-IR spectra shown the vibration at wavenumber 833 cm^{-1} indicated the presence of polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ and then more identified using X-ray Diffraction.

Characterization of Hydrotalcite and Polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ and The Intercalation Result Using X-ray Difraction

Polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ was characterized using XRD. The pattern is shown in Fig. 2. Polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ has a diffraction at 2θ is 8, 9, 18 and 27°. Distractions for polyoxometalate is generally present at 6-10°, 15-20°, 22-25° and 35-40° (Yang et al, 2011). Hydrotalcite and Hydrotalcite intercalated by polyoxometalate are shown in Fig 3.

Hydrotalcite pattern of XRD has shown the layered structure is located at the diffraction at 2θ is 11° intensity 106 and the basal spacing is 7,4 Å and the peak in the diffraction pattern 2θ of 60° indicates that the presence of anions on the interlayer (Dolidovich and Palkovits, 2015).

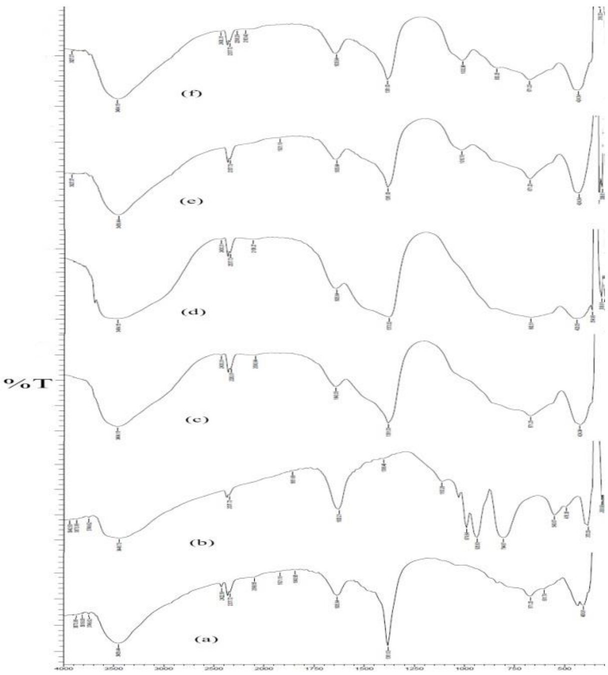

Figure 1. FT-IR Spectra a) Hydrotalcite, b) polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$, c) hydrotalcite intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ 2:1, d) 1:1, e) 1:2 dan f) 1:3.

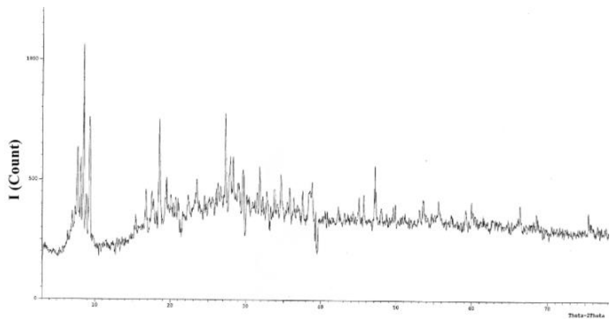

Figure 2. Pattern of polyoxometalat $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$

Hydrotalcite intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ with ratio 2:1; 1:1; 1:2; and 1:3 have been characterized and the result is shown in Fig 3. The diffraction at 2θ is 11,2° intensity 265 and basal spacing 7,87 Å. The presence of a new diffraction peak occurring in the region of 22.9° denotes the typical peak of polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ intensity 116 and basal spacing 3,8 Å is shown Fig 3a. In addition, Fig 3b has explained the highest diffraction at 2θ is 10,8, intensity is 342 and basal spacing is 9,81 Å, and diffraction at 22,5 which is the diffraction peak of a polyoxometalate intensity 141 and basal spacing 3,6 Å. Fig 3c and 3d were showing the same diffraction as hydrotalcite. This condition shows that hydrotalcite intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}].nH_2O$ ratio 1:1 more better than others because this ratio has the better diffraction and the highest basal spacing which shown polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}].nH_2O$ has intercalated into hydrotalcite and caused increased the basal spacing.

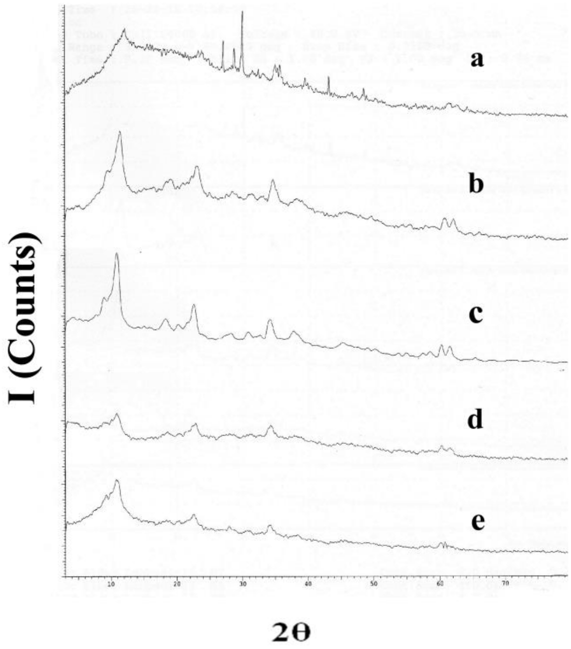

Figure 3. XRD Pattern a) Hydrotalcite, , b) Hydrotalcite intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ 2:1, c) 1:1, d) 1:2 dan e) 1:3.

Characterization of Hydrotalcite and Hydrotalcite intercalated by Polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ Usi ng TG-DTA

Hydrotalcite and Hydrotalcite intercalated by Polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ has characterized using TG-DTA analysis by program temperature starting from 25°C to 950°C using N_2 gas yielding thermogram pattern as presented in Figure 4 and Figure 5

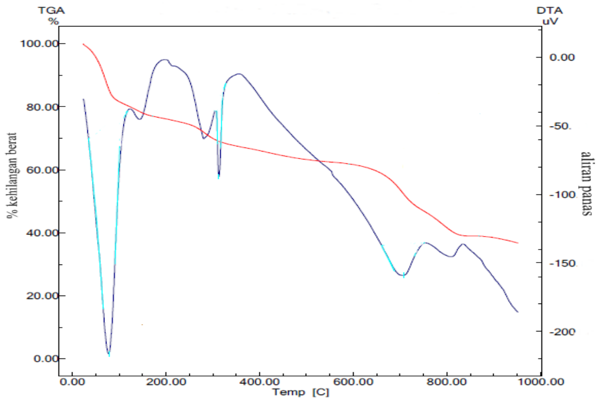

Figure 4. Thermogram of Hydrotalcite

Figure 4 shows that the hydrotalcite decomposes with the loss of water molecules with an endothermic peak at temperatures of 50-100°C with a mass loss of 23%. (Xie, 2006). At temperature 200-320°C has showing decomposes OH^- of hydrotalcite at interlayer was marked widening endothermic peak along loss the carbon dioxide at temperature 270-330 °C a total lost mass is 15,21%. The results of this TG-DTA measurements show similarities with the research conducted by Frost et al (2005) which shows the loss of OH groups in the interlayer layer along with the loss of CO_2 at temperature 300-400°C. At temperature 650-770°C, there is a decomposition of hydrotalcite in the presence of an endothermic peak marked by loss of carbonate anion attached to chemically bonded Mg^{2+} and Al^{3+} is 22,89 % (Lin et al, 2001).

Figure 5 shows the decomposition at temperature 150-220°C with the loss OH in interlayer (Zhang et al, 2012). According to Khozhevnikov (2002), thermogram pattern has shown decomposition at 350-420°C is decomposition of polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ with the loss hydrogen bonding of polyoxometalate $H_4[\alpha\text{-}SiW_{12}O_{40}]\bullet nH_2O$ of ion hydroxide.

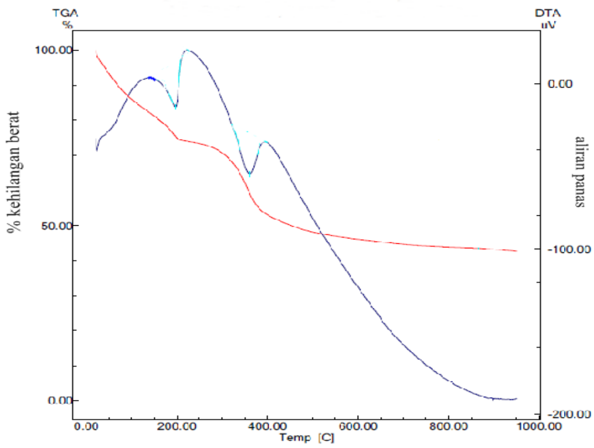

Figure 5. Thermogram Hydrotalcite intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ ratio (1:1).

CONCLUSION

Hydrotalcite has been successfully intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ ratio of mass hydrotalcite: polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ which optimum is ratio 1:1. Hydrotalcite intercalated by Polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$, with mass ratio 1:1 has characterization using FT-IR spectrophotometer, XRD, and TG-DTA. The result of FT-IR spectrophotometer have not shown the optimal intercalated process, characterization of XRD was shown that the diffraction at 2θ is 10,8 with intensity 342 dan basal spacing is 9,81 Å, and diffraction at 22,5 is characterized of polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$. the thermal analysis was carried out using TG-DTA into hydrotalcite intercalated by polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ was decomposition at 80oC until 400oC with loss OH in interlayer at 150-220°C while for decomposition of polyoxometalate $H_4[\alpha SiW_{12}O_{40}]\bullet nH_2O$ at temperature 350-420°C.

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