ADSORPTION OF CONGO RED USING Mg/Al HYDROTALCITE

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ABSTRACT

Mg/Al hydrotalcite and Mg/Al hydrotalcite intercalated with polyoxometalate H4[α-SiW12O40]•nH2O (1:1) was synthesized and used as adsorbent colored-dye i.e. Congo red. Adsorption was conducted using batch system. The factor that influencing adsorption such as kinetic, thermodynamic, and pH was investigated. The results showed that kinetically adsorption of Mg/Al intercalated polyoxometalate was faster than Mg/Al hydrotalcite before intercalation. On the other side, thermodynamically adsorption using Mg/Al hydrotalcite is higher than Mg/Al hydrotalcite intercalated polyoxometalate. Probably due to high molecular size of Congo red can decreased the adsorption ability of Mg/Al hydrotalcite after intercalated.

Keywords: hydrotalcite, polyoxometalate, intercalated, Congo red, adsorption

INTRODUCTION

Hydrotalcite has general formula [M2+(1-x)M3+(x)(OH)2]2(x/n)A(n-x)O. This layer materials contains divalent and trivalent metal cation with high flexibility cation exchange and easily synthesized in laboratory (Zhao, et.al, 2011). Application of hydrotalcite can be achieved optimally by modification of these material.

The modification of hydrotalcite for various applications is interesting due to ion exchange ability such as sensors, membranes, adsorbents, catalysts, and ion exchanges (Duan et.al, 2011).

Modification of hydrotalcite can be achieved by intercalation using anion such as sulfate, carbonate, or nitrate. These anions are cations with small size (Asif et.al, 2017). In order to increase the ability of hydrotalcite as adsorbent, the use of macroanion is vital. Macroanions are rarely obtained in the nature or laboratory. Thus synthesis of macroanions for intercalation of hydrotalcite is intriguing research. Lesbani et al(2008, 2015) was used polyoxometalates as macroanion for starting materials of ionic crystals and as catalysts. The advantages of polyoxometalates are high acidity, redox properties, high solubility depending on counter ions, and various structures such as Keggin, Dawson, Anderson, and Lacunary types. Among these polyoxometalates, Keggin type is commonly used in many applications due to stability of these compound. Polyoxometalates were applied as intercalant in many layer double hydroxides materials like hydrotalcite (Jia et.al, 2015, Liu et.al, 2016).

In this research, Mg/Al hydrotalcite and Mg/Al hydrotalcite intercalated Keggin type polyoxometalate of H4[α-SiW12O40]•nH2O was used as adsorbent of Congo red. In the previous research, optimization of intercalation process of hydrotalcite was conducted using polyoxometalate H4[α-SiW12O40]•nH2O (Palapa and Said, 2016). Congo red is an anionic azo dye having IUPAC name as 1-naphthalsulfonic acid, 3, 3-[4,4-biphenylebis(azo)] bis (4-aminodisodium) salt (Bhoi, 2010). The adsorption process of hydro talcite intercalated polyoxometalate H4[α-SiW12O40]•nH2O is intended to determine the effect of pH, kinetic, and thermodynamic parameters by measuring residual concentration and adsorbed amount using UV-Vis spectrophotometer.

EXPERIMENTAL SECTION

Materials

The chemicals used are qualified materials such as sodium metasilicate, sodium tungstate, hydrochloric acid, potassium hydroxide, potassium chloride, diethyl ether, sodium hydroxide, sodium carbonate, magnesium nitrate, Congo red dye and aquadest.

Methods

Synthesis of hydrotalcite, polyoxometalate H4[α-SiW12O40]•nH2O, and hydrotalcite intercalated H4[α-SiW12O40]•nH2O has been reported previously (Palapa and Said, 2016).

Application of Hydrotalcite intercalated by Polyoxometalate H4[α-SiW12O40]•nH2O as adsorbent of Congo red dye

1. pH

pH reaction of Congo red adsorption on hydrotalcite intercalated was studied by varying the initial pH of Congo red solution. 0.1 g of hydrotalcite and hydrotalcite intercalated each added into 50 mL of Congo red dye solution 50 mg/L shaker until 10 minutes using a horizontal shaker. The initial pH of Congo red was set at 3, 4, 5, 6, 7, 8, 9 and 11 with the addition of 0.1 M NaOH and 0.1 M HCl. Then the Congo red was separated and the residual concentration after the adsorption process was measured using a UV-Visible spectrophotometer.

2. Kinetic

0.1 g of hydrotalcite and hydrotalcite intercalated each added into 50 mL of Congo red dye solution 50 mg/L shaker with variations in absorption time varied start from 10, 20, 30, 40, 50,
60, 70, 80, 90, 100, 110 and 120 minutes using a horizontal shaker. The solution of the adsorbed Congo red dye substance was separated by filtration and then measured its concentration by using UV-Vis spectrophotometer. The adsorption rate can be calculated using the Langmuir Equation 1.

3. Thermodynamic

Thermodynamic adsorption of the Congo red dye into hydrotalcite and hydrotalcite intercalated of experiment series as carried out through a series of experiments by varying the concentration and the adsorption temperature. 0.1 g hydrotalcite intercalated by polyoxometalate added 50 mL of Congo red dye solution varied concentration 50, 60, 70, 80 and 90 mg/L while stirred using a horizontal shaker for 30 min at varying temperatures 30, 40, 50, 60 and 70°C. As the control, in different containers as much as 0.1 g of hydrotalcite added into 50 mL Congo red dye solution varied of concentration 10, 20, 30, 40 and 50 mg/L. The solution was filtered and Congo red separated from the adsorbent was measured using a UV-Visible spectrophotometer.

Data Analysis

Hydrotalcite and hydrotalcite intercalated by polyoxometalate were characterized using FT-IR, XRD, and TG-DTA. The result was applied as adsorbent Congo red dye. The adsorption process was studied by the kinetic and thermodynamic parameter. The kinetics of adsorption was studied by varied of time and adsorption rate was calculated with Langmuir equation:

\[
\ln \frac{C_0}{C} = k_1 \frac{t}{K} + K
\]  

Where :
- \( C_0 \) = Initial concentration of Congo red
- \( C \) = Concentration of Congo red after the time
- \( t \) = Time of adsorption
- \( K \) = The adsorption equilibrium constant

Thermodynamic Parameters was studied by varied of concentration Congo red dye, adsorption capacity and adsorption energy calculated using Langmuir eq:

\[
\frac{C}{m} = \frac{1}{bK} + \frac{C}{b}
\]  

\[
E = - RT \ln K
\]

Where :
- \( C \) = The Congo red concentration after adsorption reaches equilibrium
- \( m \) = Mol of Congo red adsorption 0.1 g hydrotalcite
- \( K \) = Equilibrium constant
- \( b \) = Adsorption capacity
- \( E \) = Adsorption Energy
- \( R \) = Boltzmann constant
- \( T \) = Temperature

Whereas to find the coefficient value of adsorbant distribution is used the equation:

\[
\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

Where:
- \( K_d \) = Coefficient ditribution adsorbat distribution (qe/Ci)
- \( \Delta H \) = Enthalphy
- \( \Delta S \) = Enthrophy
- \( R \) = Boltzmann constant
- \( T \) = Temperature

The bonds formed between the adsorbate and the adsorbent was studied by FT-IR spectrophotometer.

RESULTS AND DISCUSSION

Characterization of intercalated layered double hydroxide with \( H_4[\alpha SiW_{12}O_{40}] \cdot nH_2O \) was presented by Palapa and Said (2016) in previous published article. In this results, adsorption of congo red process was systematically reported.

Effect of Initial pH Adsorption of Congo red Dye by Hydrotalcite Mg/Al Intercalated Polyoxometalate \( H_4[\alpha SiW_{12}O_{40}] \cdot nH_2O \)

Effect of Congo red Adsorption of Time by Hydrotalcite and Hydrotalcite Intercalated

Hydrotalcite intercalated can absorb more adsorbate than hydrotalcite at the same time. At the optimum time of adsorption at 70 min it is seen that the amount of Congo red dye
stuff adsorbed by 1.5 times the adsorbent without insertion process. This is because the hydrotalcite intercalated has a larger basal spacing of 9.81 Å than the previous value of 7.4 Å. The hydrotalcite intercalated and hydrotalcite curves before the insertion process are presented in Figure 2.

The data obtained in Table 1 show that the hydrotalcite intercalated adsorbent has a higher adsorption rate than the hydrotalcite before intercalated. It causes the hydrotalcite intercalated adsorbent to have a greater reactive rate than the hydrotalcite before intercalated.

![Figure 2. Effect of Congo red Adsorption of Time by Hydrotalcite and Hydrotalcite Intercalated](image)

**Table 1. Adsorption rate values for hydrotalcite and hydrotalcite intercalated**

| Adsorbent            | Parameter | Adsorbed (ppm) |
|----------------------|-----------|----------------|
| hydrotalcite         | k (Sec⁻¹) | 13.64          |
| hydrotalcite intercalated | R²       | 0.984          |
|                      |           | 51.38          |
|                      |           | 0.999          |

**Effect of Concentration and Temperature Adsorption Congo red Dye by Hydrotalcite and Hydrotalcite Intercalated**

Adsorption temperature data by hydrotalcite adsorbent and hydrotalcite intercalated. Figures 3 and 4 show the results of the effect of adsorption temperature on the adsorbed Congo red amount of hydrotalcite adsorbent and the hydrotalcite intercalated. Figures 3 and 4 show the effect of temperature and concentration of Congo red dye by a hydrotalcite adsorbent and hydrotalcite intercalated shows that the larger the temperature the greater the amount of adsorbed Congo red, the greater the concentration. Then the amount of Congo red adsorbed will increase as well Hydrotalcite adsorbent (control) presented in Figure 3.

The adsorption capacity and adsorption energy of the Congo red adsorption process by hydrotalcite and the hydrotalcite intercalated Table 2 explains that the adsorption energy value (E) of Congo red adsorption by hydrotalcite intercalated at visible concentration variations. The greater the temperature the more decreasing the adsorption energy (E). This indicates that the adsorption process occurring at the varied temperature undergoes an exothermic condition which means the process releases energy. This state suggests for chemistry states (chemical adsorption) (Vimoses et al, 2009). The determination of the adsorption capacity (b) is determined by the equation 2 which expresses the absorbent's ability to adsorption the Congo red presented in Table 2. The table show when the temperature increases, the larger the adsorption capacity.

The subsequent thermodynamic parameters of enthalpy (ΔH) and entropy (ΔS) of the Congo red dye adsorption process by the hydrotalcite and hydrotalcite intercalated are presented in Table 3. The table shows the entropy (ΔS) of Congo red adsorption by hydrotalcite intercalated indicates the degree of irregularity that occurs where large entropy values indicate that the smaller the concentration the degree of irregularity or greater entropy. In addition to the enthalpy value (ΔH) of Congo red adsorption by the hydrotalcite intercalated presented in Table 3 indicates a decrease as concentration increases.

**Study of Adsorption Congo red Dye by Hydrotalcite and Hydrotalcite Intercalated**

The Congo red adsorption interaction study by hydrotalcite adsorbent and the hydrotalcite intercalated was carried out to determine the changes occurring in the adsorbent prior to the adsorption process and after the adsorption process. The change of each adsorbent is seen through characterization using FT-IR spectrophotometer. Figure 5 and 6 show the FT-IR spectrum, before and after the Congo red adsorption process.

Figure 5 shows the comparison of the double layer hydroxy spectrum prior to adsorption and double layer hydroxy after adsorbing Congo red differences in each bonding vibration. Figure 5 after adsorbing Congo red indicates the wave number of 3000-3500 cm⁻¹ indicated that there is a vibration peak of -OH and NH whereas for Fig. 10 before adsorbing a strong and widespread vibration Congo red is a vibration of -OH only. The presence of Congo red vibrations is amplified by a peak at 1635 cm⁻¹ which is slightly dilated with low intensity this is due to the bend vibration of OH which coincides with the vibration of the azo structure (N = N) which is characteristic of Congo red (Zvezdova, 2014). When compared to Figure 20 before adsorbing the Congo red wave numbers at 1653 cm⁻¹ with high enough intensity and sharpness indicates only OH bend vibration.

![Figure 3. Adsorption Congo red dye varied of concentration and temperature by hydrotalcite](image)
The Congo red color has a S = O vibration shown in Figure 20 after adsorbing Congo red at the peak of vibration with a very low intensity at 1072 cm\(^{-1}\) wave numbers. In addition, the aromatic C = C vibration appears at 1481 cm\(^{-1}\) wave numbers. The symmetric stretching vibration of the N-O nitrate of the double layer hydroxyl compound with reduced intensity of the double layer hydroxyl before the adsorption process is present at the wave number 1371 cm\(^{-1}\) and the vibration of the 1419 cm\(^{-1}\) wave number indicates the buckling of C-N (Kaur and Rajvir, 2016).

The double layer hydroxyl adsorbent inserted with the H\(_4[\alpha SiW_{12}O_{40}]\)\(\cdot\)nH\(_2\)O polyoxometalate compound before and after the Congo red adsorption process is shown in Figure 6. Figure 6 shows the hydroxyl of the double layer inserted prior to the adsorption process shown by the FT-IR spectrum in Fig. 6 before the Congo red adsorption process shows a wider and larger peak when compared to Figure 6 of the double layer hydroxy insertion after the adsorption process has a peak showing the characteristic of the Congo red, There is a widened and strong peak which is a vibration of -OH and NH at wave numbers 3000-3600 cm\(^{-1}\). At the same wavelength region the adsorbent before the insertion process has a widened peak which is the vibration of the OH alone is shown in Fig. 6. Figure 6 hydroxyl layer of hammer after Congo red adsorption process at wave number 2924 cm\(^{-1}\) there is a peak of aromatic benzene vibration from Congo red, peak Vibration for azo structure N = N and OH buckling is present at wave number 1635 cm\(^{-1}\), aromatic C = C vibration at wave number 1481 cm\(^{-1}\), for vibration of NO bend is at wave number 1373 cm\(^{-1}\) and vibration S = O is at number Wave 1072 cm\(^{-1}\). The presence of a characteristic peak of Congo red dyestuff vibration indicates that Congo rally absorbed into the adsorbent surface resulting in changes in the FT-IR spectrum before and after the adsorption process.

| Adsorben | Co | R\(^2\) | \(\Delta H\) | \(\Delta S\) |
|-----------|----|--------|-------------|-------------|
|          | 10 | 0,9280 | 84,511      | 0,281       |
|          | 20 | 0,9330 | 76,114      | 0,251       |
|          | 30 | 0,8910 | 64,059      | 0,212       |
|          | 40 | 0,9100 | 70,810      | 0,227       |
|          | 50 | 0,9780 | 84,387      | 0,265       |
|          | 60 | 0,9030 | 40,838      | 0,136       |
|          | 70 | 0,9290 | 38,967      | 0,127       |
|          | 80 | 0,9380 | 39,200      | 0,127       |
|          | 90 | 0,9780 | 28,242      | 0,091       |

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Tabel 3. The subsequent thermodynamic parameters of enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)) of the Congo red dye adsorption process by the hydrotalcite and hydrotalcite intercalated

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|          | 90 | 0,9780 | 28,242      | 0,091       |
CONCLUSION
Adsorption process of Congo red dye by double layer hydroxy and double layer hydroxy inserted polyoxometalate H₄[αSiW₁₂O₄₀]•nH₂O (1:1) showed adsorption rate of 13.64 and 51.38 min⁻¹. While the adsorption thermodynamic parameters for both adsorbents showed an increase in adsorption capacity along with increasing temperature. Other thermodynamic parameters such as enthalpy and entropy decrease with increasing dye concentration. The effect of pH indicates that the optimum pH for the double layer hydroxy compound is at pH 9, and the polyoxometalate-insulated double-hydroxied hydroxy is at pH 8.

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