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Synthesis of Al/Fe Pillared Bentonite: Characterisation and Analysis of Thermodynamic Parameter

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Abstract. The modification of bentonite by pillarization process of Al/Fe metal oxide has been carried with metal oxide with ratios 1:2 and 2:1. The product was characterized by FT-IR, XRD and pHpzc analysis. Thus, this optimal pillarization product was used as an adsorbent of Congo red and Direct green dyestuffs. The FTIR characterization does not show optimum pillarization processes for any metal oxide ratios, while the XRD analysis shows the optimum pillarization processes at ratio 2:1 i.e. 17.1 Å. In addition, the optimum pH for absorption of Congo red took place at 2 while for Direct green at 3. At 70°C, the highest adsorption capacity (Q_e) reached 57.34 and 72.06 mol/g; and the highest adsorption energy (E) was found 3.23 kJ/mol and 4.14 kJ/mol for Direct green for Congo red and Direct green, respectively. Vice versa, the enthalpy (ΔH) and entropy (ΔS) values decreased as the increase of both Congo red and Direct green concentration.

Keywords: Bentonite, Pillarisation, Al/Fe, Adsorption, Congo Red, Direct Green

1. Introduction

Dyes can have a bad effect on waters, among others, can inhibit the activity of living organisms because of its nature. The Congo red and Direct green as a famous dyes, also have a high level of toxicity and are difficult to degrade. These materials, if they do not get a good handling will potentially pollute the environment. Adsorption still the best used methods in wastewater treatment [1]. Several previous studies have always used activated carbon as an adsorbent, whereas activated carbon has the disadvantage of its single-use use [2]. Therefore, we need another type of adsorbent that is cheap, easy to obtain and reusable.

Bentonite is a natural clay mineral with a layered structure containing exchangeable inorganic cations [3]. Cations that can be exchanged, are contained in the structure of the bentonite layer, besides having the ability to expand, they are also widely available in Indonesia. This is the reason why this material is suitable for application as an adsorbent and catalyst [4]. However, bentonite has one disadvantage, i.e. the small distance between layers and unreliable porosity.

Bentonite modification is done by increasing the distance between layers by inserting material or what is known as pillarization. Pillarization involves ions, molecules or compounds insertion in the interlayer of bentonite [5]. In this research, we used macro-anion of Al/Fe as inserted material. Besides being inside the bentonite, thus making the distance between the layers even greater, metal oxides are also on the surface of the bentonite. Since it is known that bentonite has a negatively charge on the surface, and the Congo red is a cationic dye, it will easier to make an interaction between them [6].

In this research, we investigated the properties of natural and pillared bentonite using XRD, FTIR and pHpzc analysis. In addition, Thermodynamics parameter (enthalpy, entropy and Gibbs free energy) are also determined in order to adsorb Congo red and Direct green.

2. Materials and Methods

2.1. Materials

The chemicals used are qualified materials such as natural bentonite, sulphuric acid (H_2SO_4), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), Congo red and Direct green, sodium hydroxide (NaOH), sodium chloride (NaCl), aquades (H_2O), and hydrochloric acid (HCl).

2.2. Methods

2.2.1. Preparation and Activation of Bentonite

A total of 50 g of natural bentonite is added 500 mL the distilled water was mixed in a 1000 mL beaker and stirred for 24 hours. To control the acidity was by adding 250 mL sulphuric acid (H_2SO_4) 2M and a distiller for 10 h at $65^\circ C$. The suspension formed was settled to precipitate and washed repeatedly with distilled water up to pH above 5 and centrifuged at speed 5000 rpm for 15 minutes. The solids in the oven were $100^\circ C$ for 6 hours and the bentonite was crushed and sieved with a 200 micron mesh sieve. The prepared bentonite bit is called activated bentonite. Bentonite is characterized using FT-IR, and XRD spectrophotometer.

2.2.2. Preparation Al/Fe Solvent Solution

Preparation of Al/Fe pillar solution was done by making Al/Fe pillar solution with 2:1 and 1:2 ratios. A polyhydroxy polarization solution of 2:1 Al/OH was prepared by adding $Al(NO_3)_3 \cdot 9H_2O$ 0.5 M of 80 mL and a Fe/OH pillar solution was prepared by adding $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 M as much as 40 mL mixed in a 500 mL beaker and dropped 0.5 M NaOH solution of 240 mL. The mixture of Al/Fe polymer solution was distilled for 2 h then sterilized for 2 days at room temperature and obtained polyhydroxy pillar solution of 2:1 ratio. Subsequently, the preparation of a polyhydroxy pillar solution of 1:2 ratios was prepared by adding Al/OH 40 mL 0.5 M and adding Fe/OH 80 mL 0.5 M was mixed in a 500 mL beaker and dropped 0.5 M NaOH solution of 240 mL. The mixture of Al/Fe polymer solution was distilled for 2 h then sterilized for 2 days at room temperature and obtained polyhydroxy pillar solution of 1:2 ratio.

2.2.3. Pillarization of Bentonite with Metal Oxides Al/Fe

The Al/Fe pillared bentonite was first synthesized by preparing a 1% of bentonite suspension by adding 12 g of bentonite to 120 mL of distilled water for 2 hours. The Al/Fe pillared bentonite was prepared with different Al/Fe comparisons covering 2:1 and 1:2 and then inserted into two different flasks with a predetermined ratio. The mixture is then distilled for 24 hours at room temperature. The same procedure was done in Al/Fe 1:2 ratio with the addition of Al/Fe pillar solution according to each comparison. The formed solid is dried at $100^\circ C$, and then calcination is done using furnace with temperature $400^\circ C$ for 2 hours. The Al/Fe pillared bentonite was characterized by XRD, FT-IR and pHpzc.

2.2.4. Thermodynamic Parameters

The effect of thermodynamic adsorption of the dyestuff by the natural and the pillared bentonite compound is carried out through a series of experiments by varying the concentration of dye and the adsorption temperature. A total of 0.05 g of natural bentonite was mixed with 50 mL of dye at concentration 20, 40, 50, 70 and 90 mg/L. Adsorbents that have been mixed with dyestuffs are stirred using a horizontal shaker for 1 hour at temperatures varying by 30, 50 and $70^\circ C$. The mixture was separated, and then the dye solution separated from the adsorbent for measured the absorbance value using a UV-Vis spectrophotometer to determine the residual dyestuff concentration after the adsorption process. The same procedure is performed for pillared bentonite adsorbent. The result data

was used to calculate the adsorption capacity (Q_e), adsorption energy (E), adsorption enthalpy (ΔH), and adsorption entropy (ΔS) can be calculated using thermodynamic equation.

3. Results and Discussion

3.1. Characterization of the Natural and Pillared Bentonite and the Adsorbed Congo red dye Using FT-IR Spectrophotometer

The FT-IR spectrum of natural bentonite is presented in figure 1a. It can be seen that the widespread vibration peak between the wave numbers 3626.1 and 910.4 cm^{-1} indicate vibration of the Al-O-(OH)-Al strain and Al-O-(OH)-Al buckling as the octahedral layer on bentonite. The detected peak at 1033.8 cm^{-1} indicates the vibration of the Si-O-Si strain as the tetrahedral layer on bentonite, whereas the Si-O-Si bend vibration appears at 470.6 cm^{-1} . Al-O-Si bending vibrations appear at 532.3 cm^{-1} wave numbers. The absorption bands appearing at wave numbers 686.6 cm^{-1} show vibrations of the feldspar minerals, which are associated with bentonite minerals [7].

The pillared bentonite with a ratio of 2:1 is presented in figure 1b. The pillared bentonite has visible band that absorbs of metal oxide at wave number 373.4 cm^{-1} which shows the stretch vibration of Al-O-(OH)-Al and bend Al-O-(OH)-Al as the octahedral layer on bentonite. In a while, HOH group and bend HOH bentonite Al/Fe 2:1 is shown at wave numbers 1632,55 cm^{-1} which indicates a buckling vibration. In the figure, there is a strong absorption band at wave number 1003.57 cm^{-1} which indicates the presence of a loose vibration of Si-O-Si which is a tetrahedral layer of bentonite [8]. Furthermore, FT-IR spectrum of pillared bentonite that absorbed dye do not produce significant peak change. Figure 1c shows the vibration of the Si-O-Si strain of a shift in the wave number 1002.12 cm^{-1} and the bending vibration of the Si-O shifts to the 547.8 cm^{-1} wave number. In order to further identification, it is done using XRD.

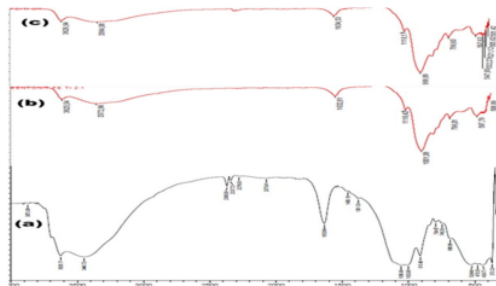


Figure 1. Spectrum FT-IR a) natural bentonite, b) pillared bentonite, c) pillared bentonite adsorbed Congo red.

3.2. Characterization of Natural and Pillared Bentonite using XRD

The natural and pillared bentonite are characterized using XRD. The diffraction pattern is shown in figure 2. The diffraction angle on bentonite indicating montmorillonite were observed on the corner (2θ) of the area 3-10 θ which is the typical angle of bentonite [9]. The natural bentonite has an XRD diffractogram that shows shifted diffraction angles (2θ) seen in the mineral montmorillonite (2θ) at 6:39 shifts to a larger diffraction angle (Figure 2a) According to Wang [10] the diffraction angle is a specific characteristic of bentonite material that indicating the presence of anions present between layers of natural bentonite and yielding the intercellular spacing of 13.82 Å.

Fig 2b and c show the pillared bentonite with a ratio of 2:1 and 1:2. From the figure it shown that both of pillared bentonite have the diffraction angle at (2θ) of 5.18 and 6.97 Å, respectively. It is similar to yielding of the intercellular spacing of 17.1 Å for pillared bentonite with ratio 1:2 and 11.876 Å for ratio 2:1. From this data, we conclude that the Al-Fe pillared bentonite with an optimum ratio 2:1 will be applied as a mixture of Congo red and Direct green dye mixtures.

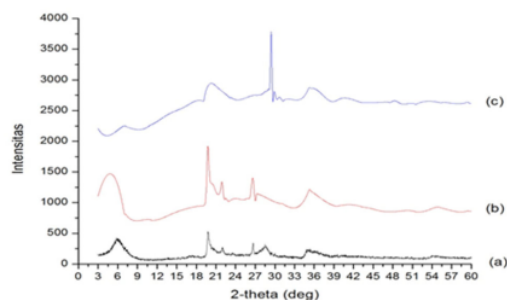


Figure 2. XRD spectra (a) natural bentonite; (b) Al/Fe pillared bentonite ratio 2:1; (c) Al/Fe pillared bentonite ratio 1:2

3.3. Point Zero Charge Measurements on Natural and Pillared Bentonite

The pZC analysis is a condition at a pH point in which the surface of the adsorbent has no charge. The purpose of this pZc pH measurement is to know the effect of pH on bentonite surface charge. Based on Alfin Kurniawan and Diyana [11], the pH PZC analysis was conducted using drift pH (pH shift) as presented in figure 3.

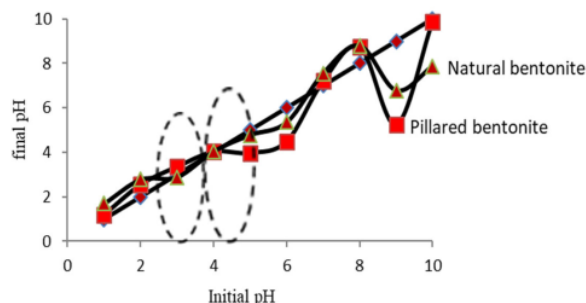


Figure 3. pH pzc of Natural and Pillared Bentonite

Figure 3 show that the natural bentonite and pillared bentonite Al/Fe 2:1 has the same pH PZC between the initial pH and the final pH. In natural bentonite, pH pH 3 and alkene Fe 2:1 were obtained in pH 4. According to Fabryanty [12], bentonite is an anionic clay type or a coated material having a negative surface property, so at a pH below the pHpzc of the bentonite surface will be positively charged at a pH less than pHpzc the bentonite surface condition has an excess of H^+ . Conversely, if the pH above the pHpzc the bentonite surface will be negatively charged, this is because at a pH greater than pHpzc the surface condition of bentonite has an OH^- excess.

3.4. Thermodynamic Parameters ¹

The adsorption energy, enthalpy and entropy of the Congo red dye adsorption process by natural and pillared bentonite was listed in Table 1 and 2. Tables 1 explains the data on adsorption with natural bentonite while Table 2 by pillared bentonite.

Table 1. The data of adsorption energy (E), enthalpy (ΔH), entropy (ΔS), and adsorption capacity (Q_e) on Congo red adsorption with natural bentonite

Concentration (mg/L)	T (K)	Q_e (mg.g ⁻¹)	ΔH (J/mol)	ΔS (kJ/mol)	E (kJ/mol)
20	303	1.6271	153.15	51.85	5.4492
	323	8.3537			2.3862
	343	9.7099			0.6788
40	303	3.9977	129.48	45.02	5.7957
	323	7.8298			3.2061
	343	19.0028			0.6165
60	303	6.9960	157.20	53.18	53.189
	323	12.999			2.4138
	343	36.798			0.7301
80	303	7.9549	145.30	49.15	49.150
	323	30.899			2.2167
	343	40.987			0.6894
90	303	6.9488	160.54	54.18	54.185
	323	38.998			2.3304
	343	44.783			0.8803

Table 2. The data of adsorption energy (E), enthalpy (ΔH), entropy (ΔS), and adsorption capacity (Q_e) on Congo red adsorption with pillared bentonite

Concentration (mg/L)	T (K)	Q_e (mg.g ⁻¹)	ΔH (J/mol)	ΔS (kJ/mol)	E (kJ/mol)
20	303	4.32070	115.23	38.14	3.2316
	323	8.35370			0.9270
	343	12.3370			1.3775
40	303	16.6875	87.24	27.21	0.7853
	323	24.0002			0.9595
	343	28.6241			2.7043
60	303	29.6070	92.98	18.66	0.4883
	323	32.2930			1.3713
	343	47.3790			3.2310
80	303	41.8602	46.32	13.89	0.1432
	323	46.3685			1.0697
	343	54.1770			1.9962
90	303	45.8523	38.33	11.43	0.1787
	323	54.3685			0.9453
	343	57.3409			1.7119

Tables 1 and 2 show the value of adsorption capacity (Q_e) increases with increasing temperature for the natural and the pillared bentonite. The adsorption capacity also increases with increasing concentration. It is also seen that the adsorption capacity of the pillared bentonite has a higher value than natural bentonite. From Table 1 and 2 showing the adsorption energy data (E) shows that natural bentonite occurs an increase in adsorption energy (E) as temperature increases. The same phenomenon exist to the pillared bentonite as the temperature of the adsorption energy (E) increased as well. This matter caused at high temperatures, the higher the interaction between adsorbent and adsorbate to produce higher energy [13]. The subsequent thermodynamic parameters of enthalpy (ΔH) and entropy (ΔS) of the Congo red dye adsorption process by natural and pillared bentonite are also presented in Tables 1 and 2. From the tables, the enthalpy (ΔH) and the entropy (ΔS) has irregularity values. The degree of irregularity that occurs where the large entropy value indicates that the smaller the concentration, the greater the degree of irregularity or entropy. In addition, the enthalpy value (ΔH) of

adsorption of Congo red by natural and pillared bentonite shows a decrease with increasing concentration.

Meanwhile, the adsorption energy, enthalpy and entropy of the Direct green adsorption process by natural and pillared bentonite are listed in Tables 3 and 4. Tables 3 explains the data on adsorption with natural bentonite while Table 4 by pillared bentonite.

Table 3. The data of adsorption energy (E), enthalpy (ΔH), entropy (ΔS), and adsorption capacity (Q_e) on Direct green adsorption with natural bentonite

Concentration (mg/L)	T (K)	Q_e (mg.g ⁻¹)	ΔH (J/mol)	ΔS (kJ/mol)	E (kJ/mol)
20	303	0.9977	91.10	35.43	7.8328
	323	1.4027			6.0107
	343	4.3343			4.1886
40	303	1.5642	118.27	44.56	8.7323
	323	2.0171			6.3669
	343	9.9638			4.0014
60	303	12.739	-16.47	-0.53	4.4532
	323	3.589			4.7827
	343	13.097			5.1123
80	303	11.967	31.92	14.97	5.3047
	323	5.9457			4.6663
	343	21.579			4.0279
90	303	1.9582	108.54	42.74	9.8576
	323	3.9124			7.6867
	343	12.627			5.5159

Table 4. The data of adsorption energy (E), enthalpy (ΔH), entropy (ΔS), and adsorption capacity (Q_e) on Direct green adsorption with pillared bentonite

Concentration (mg/L)	T (K)	Q_e (mg.g ⁻¹)	ΔH (J/mol)	ΔS (kJ/mol)	E (kJ/mol)
20	303	7.6224	161.96	51.74	2.6664
	323	5.3405			0.5728
	343	17.586			3.8121
40	303	23.825	99.48	29.97	0.1690
	323	21.209			2.1587
	343	34.409			4.1484
60	303	38.262	56.55	16.18	0.9487
	323	35516			2.0797
	343	47546			3.2108
80	303	43.906	86.90	26.56	0.2308
	323	38.963			1.5072
	343	64.965			3.2452
90	303	44.106	94.71	29.78	1.0865
	323	33.259			0.8076
	343	72.064			2.7018

Tables 3 and 4 show the value of adsorption capacity (Q_e) increases with increasing temperature of the natural and the pillared bentonite. The adsorption capacity also increases with increasing concentration. It is also seen that the adsorption capacity of the pillared bentonite has a higher value than natural bentonite. From Table 3 and Table 4 at the natural bentonite occurred the increasing of adsorption energy data (E) linear with the increasing temperature. The same phenomenon exist to the pillared bentonite. This is due to high temperatures, the higher the interaction between adsorbent and

adsorbate to produce higher energy. The subsequent thermodynamic parameters were enthalpy (ΔH) and entropy (ΔS). From the tables, it is shown the entropy (ΔS) of Direct green has the degree of irregularity where the smaller the concentration the higher of the degree of irregularity. In addition to the enthalpy value (ΔH), it shows a decreasing as concentration increases [14].

4. Conclusion

The pillarization of bentonite was success as characterized using FT-IR and XRD spectrophotometers. The results of FT-IR spectrophotometer has not shown the optimum pillarization pattern. The XRD characterization showed the optimal ratio (2:1) with shift diffraction angle (2θ) at 5.180 with the diffraction angle peak of 17.1 from 13.8 Å. The presence of pH influences shows that the optimum pH for natural and pillared bentonite for Congo red dye is 2, while for Direct green dye is 3. The thermodynamic parameters of Congo red and Direct green adsorption process by natural and pillared bentonite showed an increasing values of adsorption capacity along with increasing temperature. In addition, the others thermodynamic parameters i.e. enthalpy and entropy decreased with increasing dye concentration.

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