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Synthesis of chromium pillared clay for adsorption of methylene blue

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Abstract. Synthesis of chromium pillared clay and its application for methylene blue adsorption has been conducted. Chromium pillared clays were prepared through intercalation of chromium polycation in the area between clay silicate layers. Whereas chromium polycation was synthesized by hydrolysis of $CrCl_3.6H_2O$ solution with NaOH. The intercalated clay then dried and calcined at 200°C for 4 hours. The resulting chromium pillar clay was characterized by X-Ray Diffraction (XRD) and Surface Area Analyser (SAA). Furthermore, natural clays and chromium pillared clay were used as adsorbents for methylene blue adsorption. Chromium pillared clays showed better characteristics than natural clays. Basal spacing increased from 15.08 Å to 16.28 Å, surface area from 41.636 m^2/g to 130.555 m^2/g, average pore diameter from 30.516 Å to 30.590 Å, and pore volume from 0.067 mL/g to 0.128 mL/g. The adsorption results displayed that the optimum adsorption conditions occurred at pH 2 and there was no significant difference in adsorption ability due to time variation. The optimum efficiency for methylene blue adsorption was at a concentration of 180 ppm for natural clay and of 120 ppm for chromium pillared clay.
Keywords: pillared clay, chromium, adsorption, methylene blue

1. Introduction

Organic dyes are a large group of pollutants in wastewater discharged by the textile, paper, plastic, food and other industries. In 70,000 tons of production with around 10,000 types of dyes and pigments worldwide every year, it is estimated that around 1-15% of the dye is lost as waste during the colouring process [1]. Organic dyes, especially cationic dyes are widely used due to their ease of application, durability, and not easily wear off, however the adverse effects are also very large. Cationic dyes are recognised to be carcinogenic, mutagenic and have high staining effects throughout the ecosystem when disposed of as waste into the environment, even in low concentrations [2]. Therefore, reducing the concentration of dyes in wastewater before being discharged into the environment becomes a serious problem and becomes an important concern hence the development of appropriate treatment processes is needed [3]. One of the cationic dyes that has a very wide application that becomes one of the common pollutants or elements of waste color is methylene blue.

Among several chemical and physical methods for waste treatment, the adsorption process is an effective and efficient technique for removing dyestuffs in wastewater using various adsorbents such as bentonite [4], moroccan clay [1], montmorillonite [5] and others. Similar studies were also developed through the modification of clays to improve the adsorption ability of adsorbents, such as plasma-surface modification on bentonite clay [6], hydrothermal modification of bentonite [7], pillared clay [8] and

others. In recent years, clay has received special attention to continue to be developed as an adsorbent, especially the study of interactions between dyestuffs and clay [8].

Clay is an attractive material to be used as an adsorbent due to its abundance, low price, high absorption ability, wide surface area, and ion exchange capability. Moreover, clay is a good adsorbent since it contains active sites on its surface, which are Bronsted and Lewis acid sites and ion exchange sites [9, 10]. The character of the adsorbent surface is important for adsorption, because the adsorption process is about specific interactions between the target molecules and the surface of the adsorbent. Increasing the character of the adsorbent surface through thermal or chemical modification is expected to improve the adsorption ability of the adsorbent [6]. One modification of clay that can be done is by pillarisation[11-13]. Pillarisation was carried out to improve thermal stability, specific surface area, basal spacing, porosity, and acidity of clay surfaces [14, 15].

The pillared clay is synthesized by adding metal-hydroxy polycation into the clay layer. Furthermore, with calcination it will change the polycation into a rigid metal oxide cluster thus inhibiting damage to the interphase space [16]. The application of pillared clay for environmental pollution control, especially for removal of dyes from water media received little attention [8]. Chromium pillared clay has been widely synthesized but with the use of cause as a catalyst [17-19] and metal adsorbent [20], so that chromium pillared clay for methylene adsorption applications can be interesting to study. The chromium pillared clay can increase the character of clay surfaces such as surface area and pore structure [15, 17, 21, 22], hence it is hoped that chromium pillared clay provides better adsorption ability for dye adsorption.

2. Methodology

Natural clays are washed and cleaned of gravel, roots, and other impurities. It is dried using an oven at 100°C, then crushed and sieved with a 170 mesh sieve. Then, 100 g of clay dissolved in 1000 mL of distilled water, stirred with a magnetic stirrer for 24 hours at room temperature. Meanwhile, the pillaring solution was prepared by dissolving 66.7 grams of $CrCl_3.6H_2O$ in 500 mL of distilled water. Previously 20 grams of NaOH were dissolved in 500 mL of distilled water. Then, NaOH solution was added to the solution of chromium dropwise while stirring until homogeneous, then left to stand at a temperature of 90°C for 24 hours.

The pillar solution was then added to the clay suspension dropwise while stirring with a magnetic stirrer until it was homogeneous and stirred at room temperature for 36 hours. Then, the suspension of clay was washed until it was obtained free of Cl^- ion by testing it with $AgNO_3$ solution until no white precipitate was formed. The intercalated clay was then dried, crushed and sieved with a 170 mesh sieve, then calcined at 200°C for 4 hours at a heating rate of 2°C/minute.

The characterization was carried out to determine the characteristics of the natural clay surface and chromium pillared clay. X-Ray Diffraction was used to determine the peak shift of basal spacing (d_{001}). Whereas, surface Area Analyser was used to determine the character of pore structures such as surface area, pore diameter and pore volume.

The adsorption test was carried out in a methylene blue solution, where 0.2 g of the adsorbent (natural clay and chromium pillared clay) were put in 100 mL of 30 ppm methylene blue solution with a contact time of 30 minutes. Methylene blue solution varied in pH of 2, 5, 7, 10 and 12. The conditions before and after adsorption were analysed using a UV-VIS spectrophotometer. Variations in contact time were also carried out at 5, 10, 30, 60, 120 minutes and variations in the concentration of methylene blue solution at 60, 90, 120, 150, 180 ppm.

3. Results and Discussion

3.1. XRD analysis

The diffractogram pattern of natural clay and chromium pillared clay is shown in Fig. 1. Fig. 1 shows that natural clay has a reflection peak d_{001} at $2\theta = 5.86°$ with a basal spacing of 15.08 Å. According to Tan and Goenadi [23], natural clay species of montmorillonite minerals have basal spacing between

12Å - 15Å hence it can be assumed that this natural clay contains montmorillonite minerals. Whereas Fig. 1 also shows that the chromium pillared clay has a reflection peak d_{001} at 2θ around 5.42° with a basal spacing of around 16.289 Å. Shifting the reflection peak d_{001} towards a smaller 2θ angle indicates an increase in basal spacing and the effectiveness of metal intercalation for clays [17]. This implies that the chromium pillar can maintain the basal spacing of the clay even though the clay is heated to 200°C.
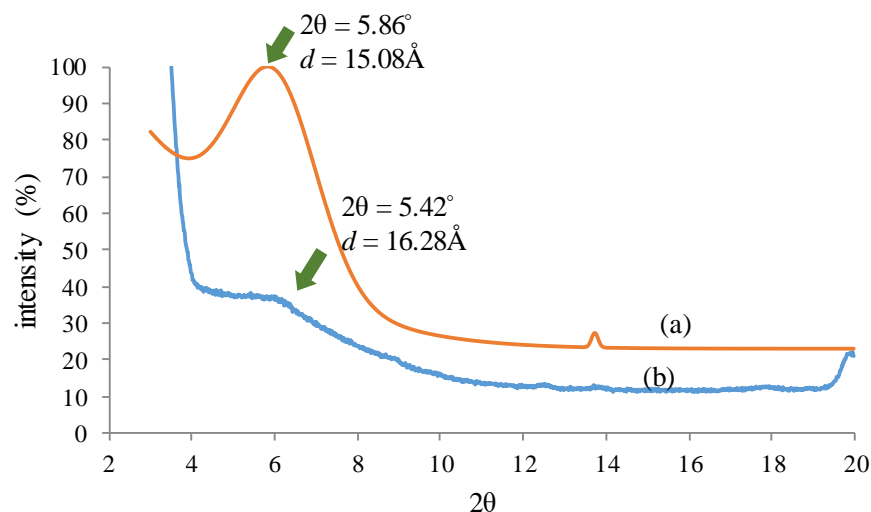

Figure 1. Diffractogram (a) natural clay pattern and (b) Cr pillared clay

Fig. 2 shows the diffraction pattern for natural chromium clay in the region of $2\theta = 3°-72°$. The appearance of peaks which are the peak patterns of chromium oxide indicate that Cr_2O_3 has been formed. The strong intensity of the Cr_2O_3 peak also implies that some of the Cr^{3+} ions inserted during the intercalation process are outside the clay interlayers. This is in line with Ding *et al.* [21] which described that the Cr_2O_3 mineral may form outside the clay interlayer. The same was reported by Mata *et al.* [17]. Sharp peaks and heights at 2theta = 28 ° are peaks of quartz which are still present in natural clays

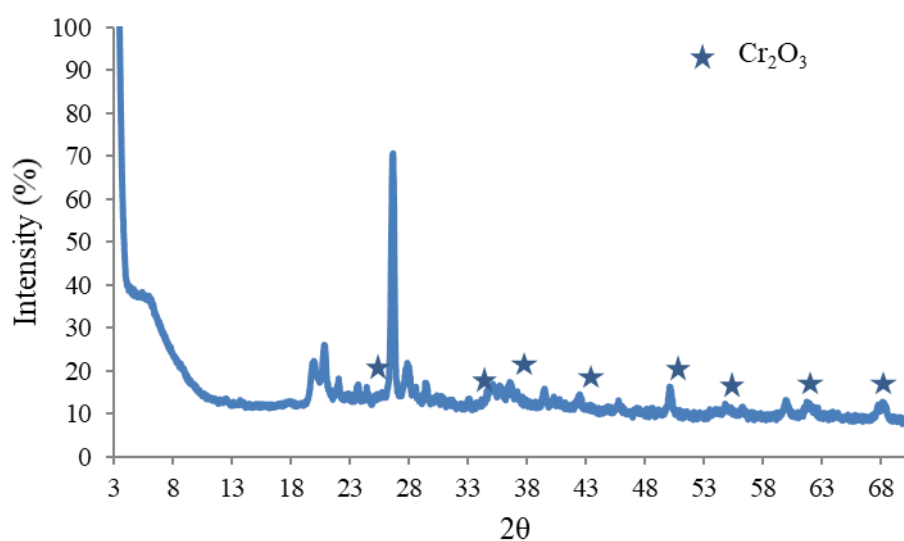**Figure 2.** The diffractogram pattern of Cr pillar clay in the range $2\theta = 3°-72°$

The drastic decrease in intensity in the diffractogram pattern of chromium pillar clay, according to Mata *et al.* [17] showed a decrease in the crystallinity of the pillared clay structure. Clay mineral is a micro-crystalline that has a neat structure. However, in conditions of excess water, the clay structure will turn random due to the nature of the plastic and the possibility of swelling on the clay. Making clay suspension at the initial stage before the pillarisation process allowed the polycation of chromium to enter the random clay structure during the pillarisation process. So that when dried, the structure of the resulting chromium pillar clay becomes more amorphous. According to Roulia [15], several factors might influence the decrease in the crystallinity of the pillar clay structure including the influence of solvent molecules which cause irregular buildup of clay particles as described by Misaelides *et al.* [24]. The heterogeneity of the clay layer due to the presence of balancing elements and the non-uniformity of the polycation of chromium in the synthesis process of pillar agents may also influence the ion exchange process during the intercalation process. Uneven distribution of polycation results in the formation of incomplete pillar phases during calcination, and the possibility of polycation is absorbed on the surface so that it covers the pore.

3.2. Surface characteristics of adsorbents

N_2 adsorption-desorption isotherms for natural clay and chromium pillared clay are shown in Fig. 3. The isotherm pattern was identified as Type IV [25] with H3 type loop hysteresis [26] according to the IUPAC classification. Type IV shows that the material has mesopore character and the H3 type loop hysteresis shows the characteristics of a layered material with gaps like pores formed by a plate-like layer with a space between plate arrays [27, 28]. The adsorption capacity of natural clay is much smaller than that of chromium pillared clay which is indicated by pore volume and small surface area, such as the data presented in Table 1. This indicates that the pillarisation process increases the pore character of the clay. This is very useful because the expected adsorbent is a material that has a high pore volume and surface area. This also implies that the Cr^{3+} ion can maintain the area between the clay layers to remain supported so as to produce a wider gallery.
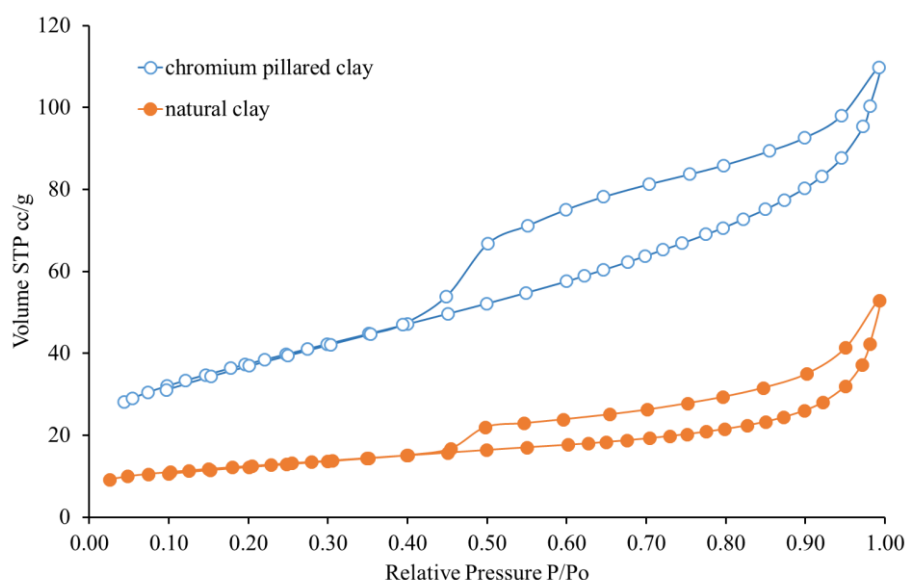

Figure 3. N_2 adsorption-desorption isotherm natural clay and Cr pillared clay

Fig. 4 shows that the distribution of natural clay pores is not uniform. For the pore size of 30-54 Å, the porous volume is quite high but continues to decrease from the volume of 4.17 x 10^{-4} to 1.47 x 10^{-4} mL/g. At a pore size of 58 Å there is a slight increase in pore volume to 1.69 x 10^{-4} mL/g. In chromium pillared clays, the pore distribution is also uneven but there are changes where small pores increase in

volume and are much higher than natural clays. These results indicate that pillarisation produces many small pores. This is easy to understand because the existence of the pillars produces barriers in the clay gallery, so that the barriers form new pores in the gallery. This pore distribution curve also shows that uniform pore formation cannot be produced. This indicates that the Cr_2O_3 pillar is not well distributed. Indeed, making a uniform pore from natural clay theoretically is not easy
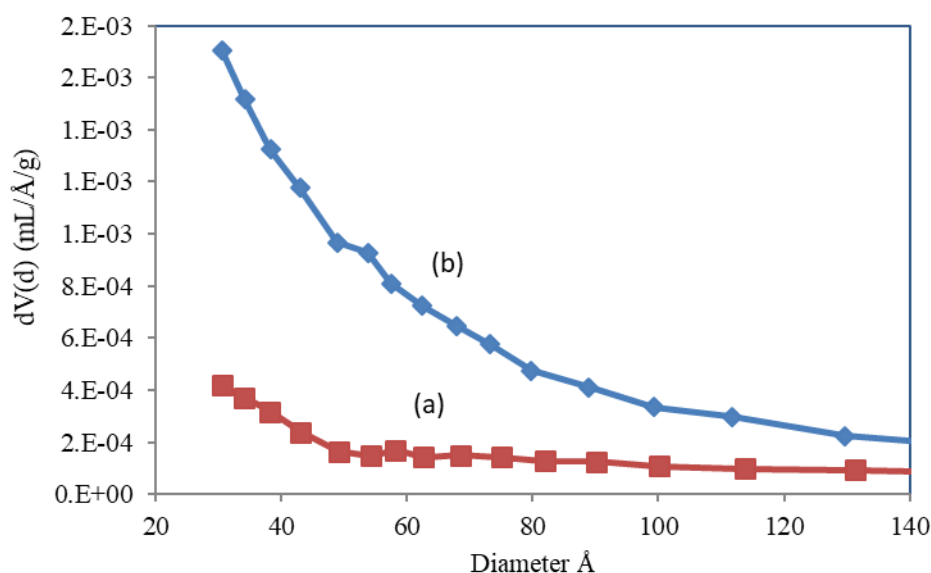

Figure 4. Pore distribution of (a) natural clay and (b) chromium pillared clay

Table 1. Surface area, pore diameter and pore volume of natural clay and chromium pillared clay

Type of adsorbent	Surface area	Pore diameter	Pore Volume
Natural clay	41.626 m^2/g	30.516 Å	0.067 mL/g
Chromium pillared clay	130.555 m^2/g	30.590 Å	0.128 mL/g

The synthesized pillar chromium clay is mesopore material, although several similar studies have been carried out that have different results. Ding *et al.* [21] reported that the synthesized pillared chromium clay had a surface area of 109 m^2/g, a pore volume of 0.12 mL/g and an average pore size of 48.4 Å. Kar and Mishra [22] reported that the chromium pillared clay produced a larger surface character, namely surface area and pore volume of 272 m^2/g and 0.22 mL/g. This difference in results is easily understood because the character of pillared clay is strongly influenced by the type of clay origin, the size of the polycation of chromium produced, which is strongly influenced by the conditions of the synthesis of pillar agents and the pillarisation process itself [15, 17, 21, 22]. Even so, the results of surface character analysis showed that the presence of Cr2O3 minerals still had an effect on the pillared pillar synthesized in the form of increasing surface area, average pore diameter and pore volume.

3.3. Methylene Blue Adsorption
Adsorption is described as a condition of a series of complex formation reactions between fluid molecules and functional groups of surface adsorbents. This surface functional group is an active site that will interact directly with the adsorbate in the adsorption process. This active site depends on the structure and chemical composition of the surface. These active sites include hydroxyl and silanol groups [29].. Surface area, pore distribution and pore volume are part of the active surface physical site which also plays an important role in the adsorption process [6]. The clay pillarisation process will

improve the character of existing active sites. The structure of methylene blue shows that the active site that might play a role in the adsorption process is the lone pair of N atoms. The adsorption mechanism is a complicated process and depends on several interactions. Several models of dye adsorption mechanisms on adsorbents have been proposed by several researchers, including the diffusion of adsorbates into the pore structure of the adsorbent and adsorption on the surface area [8], electrostatic interactions [30], hydrogen bonds [31], ion exchange [32] and others.

3.3.1. Variation in pH. pH is an important factor that influences the adsorption process, because pH can affect the surface load of the adsorbent, the degree of ionization of the adsorbate functional group, and the adsorption mechanism at the same time. Variations in pH were carried out to determine the optimum pH conditions for methylene blue adsorption. Fig. 5. shows that the methylene blue adsorption by natural clay and pillared clay has a similar pattern in which the amount of methylene blue adsorbed continues to decrease with increasing pH. But starting from pH = 10, adsorption increases again. Methylene blue adsorbed on natural clay decreased from 99.979% to 90.889% and adsorbed methylene blue in pillar chromium clay decreased from 99.958% to 95.38%. These results indicate that the chromium pillared clay has a higher adsorption ability than natural clay. The results of this adsorption are in line with the results of morphological characterization which shows that the chromium pillared clay has a higher pore volume and surface area than natural clay.
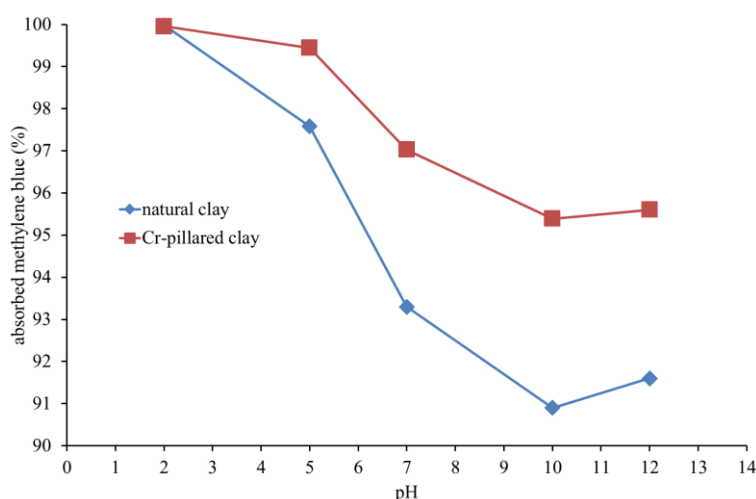

Figure 5. Effect of pH on methylene blue adsorption

The content and surface structure of pillared clay may be more stable under acidic and basic conditions so that the ability of adsorption is better, whereas in natural clays it may be affected by acidic and alkaline conditions. Methylene blue is positively charged in acidic conditions resulting in electrostatic interactions with negatively charged adsorbents. Whereas in alkaline conditions, methylene blue is negatively charged so that rejecting occurs which causes a decrease in adsorption ability [33]. A small increase that occurs under pH 12 may be due to other interactions that also influence the increase in adsorption.

3.3.2. Variation in contact time. Fig. 6 shows that the ability of methylene blue adsorption by natural clay and chromium pillared clay to variation in contact time has similar results in which methylene blue adsorbed is stable at 97% - 98% for both adsorbents. This means that the two adsorbents have the same speed of absorbing methylene blue when the operating conditions are the same. In addition, the adsorption process may be said to have been completed in the initial minutes of contact between the absorbent and the methylene blue solution because additional time does not increase the amount of methylene blue adsorbed. The number of active sites on the empty adsorbent makes the adsorption

process occur quickly at the beginning which then becomes constant as the number of active sites decreases [30].
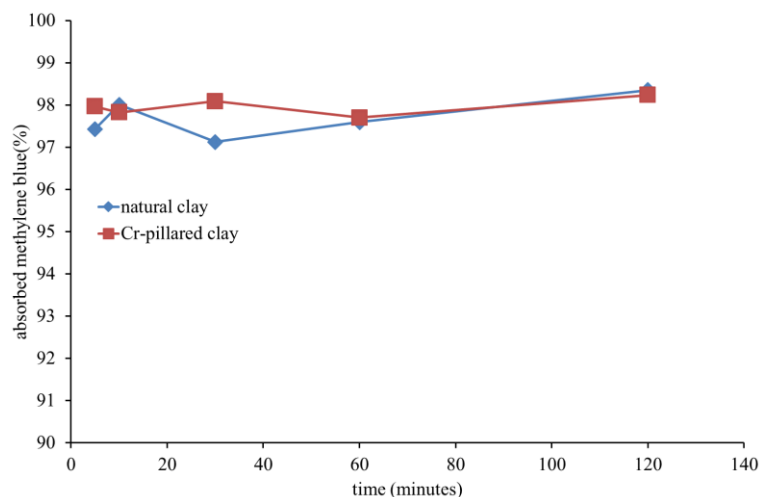

Figure 6. Effect of time on methylene blue adsorption

3.3.3. Variation of concentration. Fig. 7 shows the efficiency of adsorption of methylene blue for natural clay and chromium pillared clay. The increase in the percentage of methylene blue adsorption with an increase in the concentration of methylene blue is possible because at low concentrations the adsorption capacity of the adsorbent is not maximal. This can be understood as the entropy balance between the attraction of the adsorbent to the methylene blue and methylene blue molecules which want to be in the bulk phase, so that at higher concentrations the adsorption will be greater. But when the adsorption capacity has reached its maximum point, the addition of concentration does not increase the amount of methylene blue adsorbed. The optimum adsorption efficiency of natural clay occurs at a concentration of 180 ppm, while the clay pillar is chromium at a concentration of 120 ppm.

What is interesting is that the amount of methylene blue absorbed in natural clay is higher than that of chromium pillared clay at high methylene blue concentrations. This implies that the absorption capacity of natural clay is greater than that of chromium pillared clay. This is understandable because natural clay still has a rigid gallery, which can expand when infiltrated by blue methylene molecules. On the other hand, in chromium pillared clays, although it has a higher pore volume, but because the pillars inside produce stiff pores, the clay gallery cannot increase or expand. This is a logical reason why the pillared clay has a lower percentage of methylene blue uptake at high concentrations of methylene blue
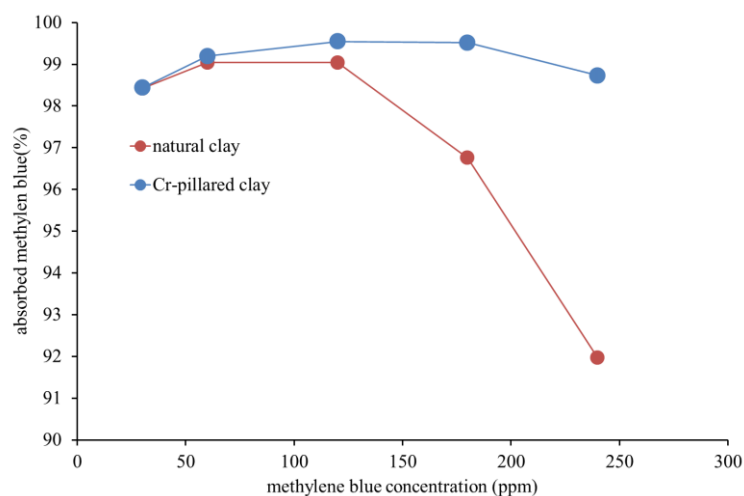
Figure 7. Effect of concentration on methylene blue adsorption

According to Attia *et al.* [34], the kinetic diameter of the methylene blue molecule is 13-15 Å, the average pore diameter of natural clay and chromium pillared clay in this study is 30.52 Å and 30.59 Å. According to Li *et al.* [35] adsorption of solute molecules can take place in pores with a diameter of 1.3-1.8 times the diameter of the solute so that the solute diffuses into the adsorbent's pore structure. This also makes accessibility of methylene blue easier to enter the adsorbent pores [32]. It is hypothesized that the mechanism of methylene blue adsorption is through diffusion of methylene blue into the pore structure. Because natural clay has a gallery that can expand, the opportunity for methylene blue molecules to enter into natural clay galleries is greater than that of pillared clay, which further implies that adsorption in natural clay is greater

4. Conclusion
Chromium pillar clay has been obtained with a better surface character than natural clay. An increase in basal spacing from 15.08 Å to 16.28 Å, surface area from 41.63 m^2/g to 130.56 m^2/g, pore diameter from 30.516 Å to 30.59 Å, and pore volume of 0.067 mL/g to be 0.128 mL/g. Methylene blue adsorption by both adsorbents tends to decrease with increasing pH. The maximum adsorption for methylene blue in natural clay is at a concentration of 180 ppm and in chromium pillared clay at 120 ppm.

5. Reference
[1]   Elmoubarki R, Mahjoubi F Z, Tounsadi H, Moustadraf J, Abdennouri M, Zouhri A, El Albani A and Barka N 2015 Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics *Water Resources and Industry* **9** 16-29
[2]   Tan I A W, Ahmad A L and Hameed B H 2008 Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies *Desalination* **225** 1–3 13-28
[3]   Auta M and Hameed B H 2014 Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue *Chemical Engineering Journal* **237** 352-61
[4]   Hong S, Wen C, He J, Gan F and Ho Y-S 2009 Adsorption thermodynamics of Methylene Blue onto bentonite *Journal of Hazardous Materials* **167** 1–3 630-3
[5]   Almeida C A P, Debacher N A, Downs A J, Cottet L and Mello C A D 2009 Removal of methylene blue from colored effluents by adsorption on montmorillonite clay *Journal of Colloid and Interface Science* **332** 1 46-53
[6]   Şahin Ö, Kaya M and Saka C 2015 Plasma-surface modification on bentonite clay to improve the performance of adsorption of methylene blue *Applied Clay Science* **116–117** 46-53
[7]   Gupta V K, Sharma M and Vyas R K 2015 Hydrothermal modification and characterization of

bentonite for reactive adsorption of methylene blue: An ESI-MS study *Journal of Environmental Chemical Engineering* **3** 3 2172-9

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

[9] Tanabe K and Hölderich W F 1999 Industrial application of solid acid–base catalysts *Applied Catalysis A: General* **181** 2 399-434

[10] Varma R S 2002 Clay and clay-supported reagents in organic synthesis *Tetrahedron* **58** 7 1235-55

[11] Geraldina G, Taslimah T and Nuryanto R 2016 Pemanfaatan Montmorillonit Terpilar Al-Cr pada Adsorpsi Zat Warna Rhodamin B dengan Variasi Massa Adsorben dan Waktu Adsorpsi *J. Kim. Sains Apl.* **19** 3 99-106

[12] Darmawan A, Azmiyawati C and Nababan P 2007 Lempung Terpilar Silika untuk Penghilangan Fenol dalam Air *J. Kim. Sains Apl.* **10** 2 54-60

[13] 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

[14] Gil A, Korili S A, Trujillano R and Vicente M A 2011 A review on characterization of pillared clays by specific techniques *Applied Clay Science* **53** 2 97-105

[15] Roulia M 2005 Synthesis and characterization of novel chromium pillared clays *Materials Chemistry and Physics* **91** 2–3 281-8

[16] Monash P and Pugazhenthi G 2011 Effect of TiO$_2$ addition on the fabrication of ceramic membrane supports: A study on the separation of oil droplets and bovine serum albumin (BSA) from its solution *Desalination* **279** 1 104-14

[17] Mata G, Trujillano R, Vicente M, Belver C, Fernández-García M, Korili S and Gil A 2007 Chromium–saponite clay catalysts: preparation, characterization and catalytic performance in propene oxidation *Applied Catalysis A: General* **327** 1 1-12

[18] Choudary B M, Prasad A D, Swapna V, Valli V L K and Bhuma V 1992 Chromium pillared clay catalysed allylic oxidation and oxidative deprotection of allyl ethers and amines: a simple and convenient procedure *Tetrahedron* **48** 5 953-62

[19] Sychev M, de Beer V H J, Kodentsov A, van Oers E M and van Santen R A 1997 Chromia- and Chromium Sulfide-Pillared Clays: Preparation, Characterization, and Catalytic Activity for Thiophene Hydrodesulfurization *Journal of Catalysis* **168** 2 245-54

[20] Okoye I P, Obi C and Otolo S E 2012 A Study of The Adsorption Kinetics of Chromium Pillared Bentonite Clay Mineral *Journal of Applied Technology in Environmental Sanitation* **2** 3 145-54

[21] Ding M, Zuo S and Qi C 2015 Preparation and characterization of novel composite AlCr-pillared clays and preliminary investigation for benzene adsorption *Applied Clay Science* **115** 9-16

[22] Kar P and Mishra B G 2013 Silicotungstic acid nanoparticles dispersed in the micropores of Cr-pillared clay as efficient heterogeneous catalyst for the solvent free synthesis of 1,4-dihydropyridines *Chemical Engineering Journal* **223** 647-56

[23] Tan K H and Goenadi D H 1991 *Dasar-Dasar Kimia Tanah*: Gadjah Mada University Press)

[24] Misaelides P, Macásek F, Pinnavaia T and Colella C 2012 *Natural microporous materials in environmental technology* vol 362: Springer Science & Business Media)

[25] Brunauer S, Deming L S, Deming W E and Teller E 1940 On a Theory of the van der Waals Adsorption of Gases *Journal of the American Chemical Society* **62** 7 1723-32

[26] Gregg S and Sing K 1982 *Adsorption, Surface Area and Porosity* (New York: Academic Press)

[27] Auerbach S M, Carrado K A and Dutta P K 2004 *Handbook of layered materials*: CRC Press)

[28] Sing K, Everett D, Haul R, Moscou L, Pierotti R, Rouquerol J and Siemieniewska T 1985 Physical and biophysical chemistry division commission on colloid and surface chemistry including catalysis *Pure and Applied Chemistry* **57** 4 603-19

[29] Satyanarayana K G and Wypych F 2004 *Clay surfaces: fundamentals and applications* vol 1: Academic Press)

[30]   Auta M and Hameed B H 2012 Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue *Chemical Engineering Journal* **198–199** 219-27

[31]   Khraisheh M A M, Al-Ghouti M A, Allen S, Ahmad M, Khraisheh M A M, Al-Ghouti M A, Allen S and Ahmad M 2005 Effect of OH and Silanol groups in the removal of dyes from aqueous solution using diatomite *Water Research* **39** 5 922-32

[32]   Rafatullah M, Sulaiman O, Hashim R and Ahmad A 2010 Adsorption of methylene blue on low-cost adsorbents: A review *Journal of Hazardous Materials* **177** 1–3 70-80

[33]   Hoffmann A A, Dias S L P, Rodrigues J R, Pavan F A, Benvenutti E V and Lima E C 2008 Methylene blue immobilized on cellulose acetate with titanium dioxide: an application as sensor for ascorbic acid *Journal of the Brazilian Chemical Society* **19** 943-9

[34]   Attia A A, Girgis B S and Fathy N A 2008 Removal of methylene blue by carbons derived from peach stones by H3PO4 activation: Batch and column studies *Dyes and Pigments* **76** 1 282-9

[35]   Li L, Quinlivan P A and Knappe D R 2002 Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution *Carbon* **40** 12 2085-100