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Utilization of Modified Indonesia Natural Bentonite for Dye Removal

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Bentonite is clay mineral with many applications such as adsorbent, ion exchanger or catalyst support. Indonesia possesses high quantity of natural bentonite reserves, however, due to the limited knowledge about its properties and potential applications, the utilization is still not yet fully maximized. To address this problem, this research aimed to characterize the properties of Indonesian natural bentonite and study its capability in removing dye pollutants as an alternative application of Indonesian natural bentonite. Characterization of Indonesian natural bentonite was successfully conducted and the result showed that it had adequate properties to be utilized. Further modification with pillaring treatments using Al, Cu, Mn, and Ti were also successfully done to intercalate the metal pillaring agent into the bentonite bulk. Dye pollutants removal test showed that Indonesian natural bentonite and its modified forms were able to remove some dye pollutants from aqueous water system. The removal of the dyes was mainly influenced by the charge of the dyes as well as the pore size of the bentonites samples. Study on the influence of pH showed that cationic dye removal was promoted at high pH, while the removal of anionic dyes were promoted at low pH.

Keywords: Bentonite, Pillaring treatment, Adsorbent, Ion exchange, Wastewater, Dye removal

INTRODUCTION

Bentonite is clay mineral with many applications in the field of sorption and catalysis, due to its properties such as swelling, ion exchange, and existence of catalytic sites on its surface (Inglethorpe et al. 1993). It exists naturally in area within the volcanic region, and is very abundant in Indonesia, because the country is situated on the ring of fire. The current confirmed reserves of bentonite in Indonesia is estimated at the total number of 380 million tons (Indonesia Mine and Coal Research and Development Center 2017). Despite the availability of this resource, the potentiality of Indonesian natural bentonite is still not fully utilized yet. This is shown by the data by Panjaitan et al. that showed Indonesia still imports 20% of its bentonite requirements (Panjaitan, R. R. 2010), which indicates that there is a problem in the utilization of Indonesian natural bentonite. This condition occurred mainly due to two reasons: from the demand side and from the supply side. From the demand side, consumers avoid the use of local bentonite due to its unknown characteristics which often lead to substandard performance. On the other hand, from the supply side, there are only limited ways of application known for local bentonite, with almost all consumption comes from palm oil purification process (Panjaitan, R. R. 2010). Therefore, efforts to overcome these challenges in order to improve Indonesian natural bentonite utilization, such as characterization of materials and proposal of other usage of Indonesia natural bentonite, need to be conducted.

As a natural clay, bentonite is still possible to be modified, thus improving its properties for application. Many researches have been conducted to improve bentonite properties using methods such as acid treatment (Steudel, A. et al. 2009), thermal treatment (Al-Asheh, S. et al. 2003), organic functional group modification (Shen, D. et al. 2009), and pillaring modification (Jeenpadiphat, S. et al. 2013). Acid treatment, thermal treatment, and organic functional group modification were already established as robust treatments due to their clear mechanisms, and thus their influence on bentonite properties. On the other hand, the mechanism for pillaring treatment is still not fully understood yet, despite many studies had reported its ability to improve many of bentonite's capability. In order to be able to effectively improve bentonite properties through pillaring modification, investigation on the mechanism is necessary.

Based on the description above, the objectives of this study are as follow: to characterize the properties of Indonesian natural bentonite; to conduct pillaring treatments as efforts to improve the properties of bentonite as well as to elucidate the effects of the pillaring treatment itself; and to evaluate the capability of bentonite and its modified form in removing dye pollutants as an alternative application of Indonesian natural bentonite.

MATERIAL AND METHODS

Material

The material used as the representative of Indonesian natural bentonite is natural bentonite (NB) taken from Bogor, Indonesia. The sample was ground and mixed as one batch in the industrial grinder prior the usage in the laboratory. No additional treatment conducted before experiment.

Characterization

Characterization of NB was conducted using the following methods: X-ray diffraction spectrophotometry (XRD, MultiFlex X-Ray Diffractometer, Rigaku Corporation) to analyze the crystalline structure of NB; thermogravimetry and differential thermal analysis (TG-DTA, Thermoplus TG8120, Rigaku Corporation) to investigate the thermal behaviour of NB; Fourier transform infrared spectroscopy (FTIR, FT/IR-6100FV, Jasco Corporation) to investigate the functional groups in NB; nitrogen adsorption desorption analysis to measure the specific surface area and pore

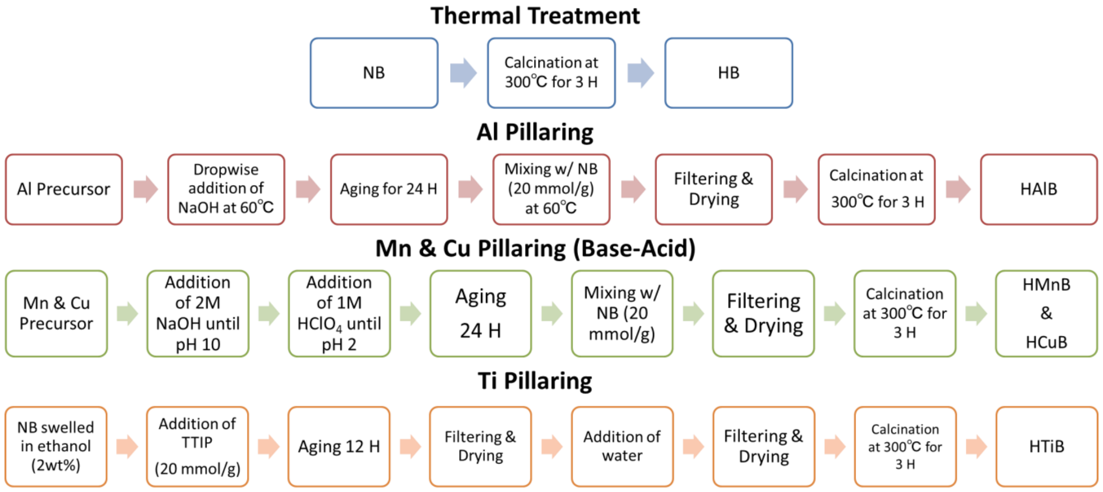

Fig. 1: Details of Procedures

size (BELSORP-max, MicrotracBEL Corporation); cation exchange capacity (CEC) analysis using Chapman method (Chapman, H.D. 1965); and chemical composition analysis measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPS7800, Seiko Instrument Inc.). For ICP-AES analysis, the sample was digested using hydrofluoric acid prior the analysis.

Pillaring Treatment

Pillaring treatments were conducted using Al, Cu, Mn, and Ti metal precursors. The technique used in the Mn and Cu pillaring treatment refers to the method used in Drljalca et al. (1997) which is also known as the Base-Acid method. Al pillaring treatment method used in this research is the widely used method for Al referring to the experiment conducted by Bertella et al. (2015). Ti pillaring treatment method was done using originally developed method by intercalating and pillaring bentonite with Ti precursor in ethanol. Thermal treated sample was also prepared for comparison. All the details of the procedure used in this research are shown in Figure 1. The bentonite treated using Mn, Cu, Ti, Al, and thermal treatment were named HMnB, HCuB, HTiB, HAlB, and HB, respectively.

All the modified bentonites were also characterized using the same analysis methods used for the NB characterization. In addition, experiment to determine the exchangeable cation amount of each sample was conducted using the following procedure: 0.1 g of sample was put into 12 mL of sodium acetate (1.0 M) and stirred for 5 minutes, followed by separation using centrifuge (this procedure was repeated for three times). The collected supernatant were analyzed using ICP-AES for the existence of cations used for pillaring treatment.

Dye Removal Experiment

In this study, the effect of time, initial dye concentration and pH on the dye removal capability of bentonite and its modified forms were investigated. Methylene blue (MB), methyl orange (MO) and naphthol green b (NG) were used as

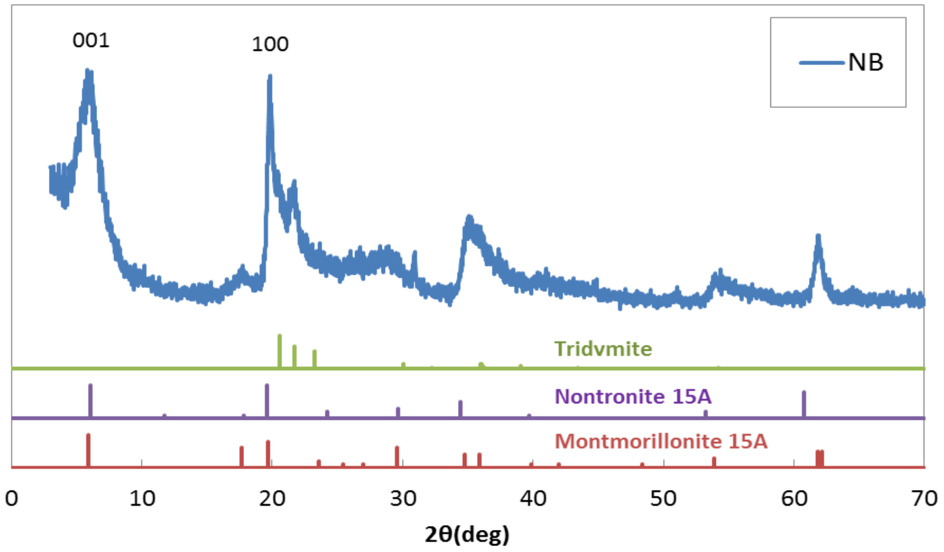

Fig. 2: XRD Spectra of NB

the target dyes. MB was used as the representative of the basic cationic dye, MO was used as the representative of anionic dye, and NG was used as the representative of nitro dye.

The effect of time was investigated by mixing 0.05 g of bentonite in 50 mL of dye solution with known concentration (Table 1). Samples were taken at regular intervals and analyzed using ultraviolet–visible spectrometer (UV-VIS, UV-1800, Shimadzu Corporation). The wavelength used in the UV-VIS adsorption measurement of MB, MO, and NG concentration were 663 nm, 464 nm and 714 nm, respectively.

The study of the effect of initial dye concentration on the dye removal performance was conducted by mixing constant amount of bentonite (0.05 g) in 50 mL of dye solutions with various concentrations. The concentration range for MB, MO, and NG were 50-500 mg/L, 25-300 mg/L and 25-300 mg/L, respectively. The mixing was conducted at room temperature in natural pH of each dye.

The effect of pH was studied by mixing 0.05 g of bentonite in 50 mL of dye solutions with known concentration, which pH already adjusted to 3, 5, 7, 9, or 11. The pH of the solutions were adjusted using HNO3 and NaOH. The dye concentration and bentonite used in this experiment were the same as the experiment on the effect of time as shown in Table 1.

Table 1. Experiment Condition

Dye	Concentration	Bentonite
MB	300 mg/L	NB
MO	200 mg/L	NB
NG	200 mg/L	HMnB

RESULTS AND DISCUSSION

Characterization

XRD pattern of NB shows that it contains smectite mineral structure, which could be a mixture of montmorillonite and nontronite with the interlayer spacing around 1.5 nm (See Figure 2). This result was in good agreement with the data from

Table 2. Basal Spacing and Relative Intensity of d001 of Samples

	Before Calcination		After Calcination	
	d_{001}(nm)	I^* (%)	d_{001}(nm)	I^* (%)
NB	1.57	102	1.00	41
AlB	1.81	100	1.60	67
MnB	1.57	110	0.98	49
CuB	1.48	78	0.99	60
TiB	1.51	112	1.01	48

Table 3. CEC, SSA and Average Pore Size

	CEC (meq/100g)	SSA (m^2/g)	AVG. Pore Size (nm)
NB	98	70.7	8.25
HB	83.2	69.8	8.32
HAlB	107.5	151.3	5.18
HMnB	107.4	92.4	7.08
HCuB	91.2	82.8	6.35
HTiB	125.3	113.9	4.96

chemical composition analysis that shows there are significant percentage of Mg and Fe exist as the structural cation in the clay. The existence of tridymite impurity was also detected through the XRD analysis.

Pillaring Treatment Result

The intercalation of pillaring agent that is shown by the increase of basal spacing was observed in the sample treated using Al, while other samples showed basal spacing equal or lower than NB. Furthermore, only Al treated sample could maintain the basal spacing due to the newly created structural bonds after heating. Details of the basal spacing data and peak intensities are shown in Table 2. Despite the inability to maintain the basal spacing, the intercalation of metal was confirmed by the chemical composition analysis. Moreover, the addition of 5.61 wt% of Al, 1.57 wt% of Mn, 2.01 wt% of Cu and 13.33 wt% of Ti were found to have remained in bentonite bulk, not as exchangeable cation. Therefore, it can be concluded that the decrease in basal spacing in pillaring treatments for samples other than AlB after calcination was caused by the loss of coordinated water inside the basal spacing.

All the conducted pillaring treatment also successfully increased the CEC and SSA of NB. However, each pillaring agent caused a decrease in the average pore size of the bentonite bulk. The result of CEC, SSA values and average pore size values of the samples are shown in Table 3.

Dye Removal Evaluation

Equilibrium Time Study

In the equilibrium time study, almost 48% of the total amount removal was achieved for all 3 target dyes in the first 5 minutes. Equilibrium was achieved in around 2 hours after mixing. This equilibrium time was used to determine the period for the study of initial dye concentration effect.

Effect of Concentration

All of NB and its modified forms showed capability of MB and MO removal. However, in NG removal test, only HMnB showed the removal capability. The removal increased as the initial dye concentration increased until the adsorbent maximum capacity was reached. This means that the removal occurred due to the existence of limited removal sites in the bentonite.

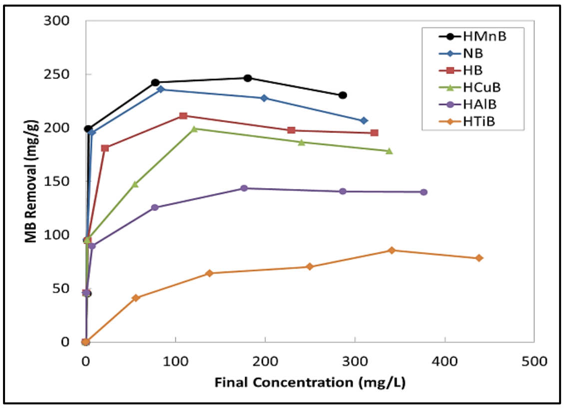

Fig. 3: MB Removal Test Result

In MB removal test, HMnB showed the highest removal capability, followed by NB, HB, HCuB, HAlB and HTiB, respectively. The removal process is suggested to be highly influenced by the synergistic effect of the overall negative charge of bentonite structure shown by CEC values and the average pore size which determines the likelihood of MB to enter the bentonite bulk. MB is classified as a cationic dye, thus the more negative charge exist in the structure of bentonite, the higher its capacity to attract and adsorb MB. In addition, the pore size played a role to limit the molecule that can enter bentonite pores, thus, the smaller the pore size, the lower the removal capacity. HMnB has one of the highest CEC values and a sufficiently large average pore size which enable a high amount of MB removal. On the other hand, despite HAlB possesses high CEC, the average pore size of the sample limited the amount of MB uptake, thus the removal result for this sample was relatively low.

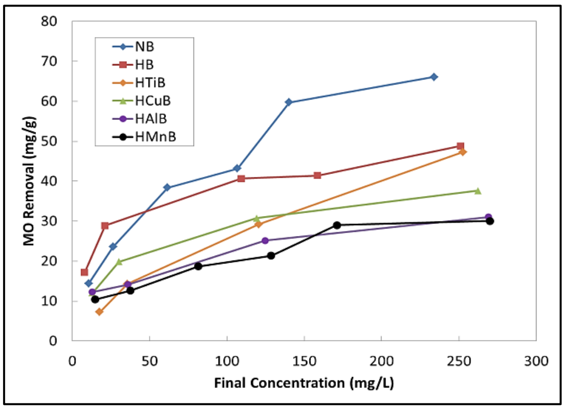

Fig. 4: MO Removal Test Result

In MO removal test the order of the removal capacity changed. This time, NB shows the highest removal capability, followed by HTiB, HCuB, HAlB and HMnB. Different from MB, MO is a dye that has anionic character, thus the positive charge will attract it more. Therefore, it is thought that MO removal phenomenon occurs at the locally positive charge in the platelet edge of small unit of layered bentonite due to the deficit of oxide anion that balancing the Si, Al, Mg or Fe metal structure (Cetco 2013, Kunimine Industries Co. Ltd 2017). This limited number of positive charged edges made the removal amount of MO is much lower than MB removal. This MO removal may depend on the number of edges of bentonite's platelet and charge of the overall structure. However, all the conducted treatments have the tendency to diminish the number of platelet due to the thermal treatment which may fully oxidize the positive charge or facilitating the bonding of several platelets on the edge. Especially in the pillaring treatment of Mn, Cu, and Al, there are a lot of free cations which has oxidation number above one that could become bridge and bond several platelets and deplete the positively charged edges. HTiB may still has more positively charged edges because the pillaring was done using TTIP instead of Ti ion, but the small pore restrict the transfer of dyes into the bulk of bentonite and decrease its removal. Therefore, NB and minimally treated NB showed the best capability for MO removal.

For NG removal test, only HMnB showed capability in removing NG from the solution. This result was probably occurred due to the principle behind the removal of NG, which is not just an ordinary physisorption or ion exchange, but rather a chemical reaction that include Mn as one of the reactants. Mn, especially the exchangeable one in the HMnB, was attracted by NG and may substitute the dye's Fe that lead to precipitation of NG, which lead to the removal of the dye.

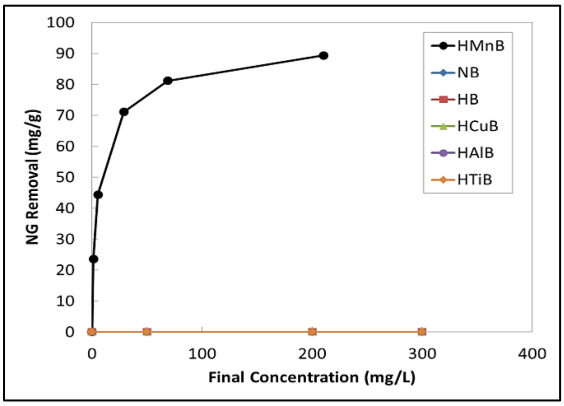

Fig. 5: NG Removal Test Result

Effect of pH

From the study of pH, it was observed that the process of dye removal by bentonite was significantly affected by pH of the solution and the characteristic were different for each dye pollutant.

For MB which is a cationic dye, the removal process competes with positive charge from proton, thus the amount of removal is reduced at lower pH and increase at higher pH. Reversely, for anionic MO and NG dyes, the removal shows higher value at lower pH than at higher pH due to the competition with hydroxide ion in the solution.

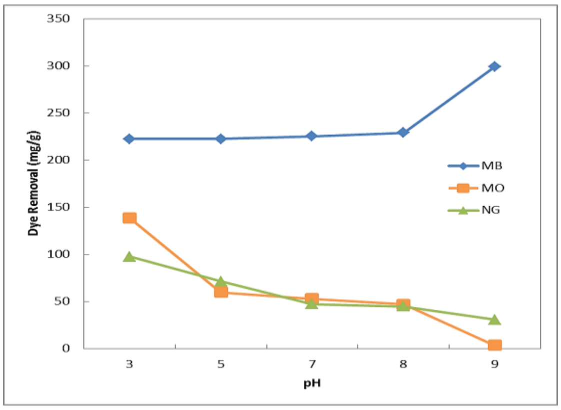

Fig. 6: Effect of pH on Dyes Removal by Bentonite Samples

CONCLUSION

Natural bentonite taken from Bogor, Indonesia was confirmed to contain smectite minerals which are Montmorillonite and Nontronite with some impurities of Trimydite. The natural bentonite also shows a relatively high CEC of 98 meq/100 g and SSA of 70.7 m^2/g compared to bentonite taken from other regions.

The pillaring treatment using Al, Cu, Mn, and Ti were able to put the metal precursor into the bulk of bentonite clay, which is confirmed by the chemical composition analysis. Treatment using Al was able to increase the basal spacing of the sample, while other precursor maintained or reduced the basal spacing of the samples. These pillaring treatments successfully improve the CEC and SSA value of the natural bentonite while decreasing the average pore size of the bulk.

The dye removal experiments show that all the material used in this study, including the untreated NB were able to remove MB and MO from the solution. However, only HMnB showed the capability of NG removal. The removal capacity of the MB and MO was influenced by the charge of the dyes, as well as the pore size of the samples.

The study on the effect of pH shows that removal of MB was promoted at high pH, while removal of MO and NG were facilitated at low pH due to the cationic character of MB and anionic character of MO and organic part of NG.

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