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# PREPARATION AND CHARACTERIZATION OF ORGANOCLAYS SYNTHESIZED FROM THANH HOA BENTONITE AND DIMETHYL DIOCTADECYL AMMONIUM CHLORIDE

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ABSTRACT

*In this study, organoclays were synthesized by placing dimethyl dioctadecyl ammonium (DMDODA) cation onto bentonites. The structure of modified bentonites was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), chemical analysis, thermal analysis and FT-IR spectra. The intercalation of the DMDODA cation increased the interlamellar distances from 15.6Å (Na-bentonites) to 40.57Å. The effect of temperature, pH, time and amount of quaternary ammonium salt on the distance layer of organoclays was addressed.*

## I - INTRODUCTION

In recent decades, researches on preparation and application of materials from Bentonite have been an interesting area for both national and international scientists. Bentonite has been widely used in petroleum, paint industry, heavy metals treatment, dyes treatment in wastewater [1, 2].

Our country is rich in amount of clays. But up to now, clays are only applied in small scale, mostly for pottery materials, constructing materials and so on. There are not many researches using clays as a material to treat pollutants. Thank for ion exchange capacity, Bentonite is usually modified by cations such as: $H^+$, polyoxocations, amines ... and is used to adsorb organic pollutants. In Wolf et al. research, they use primary amines as the exchange cations [3]. However, the cationic nature as well as the adsorption of cations on the clay is very much a function of pH [4]. For that reason, we have used quaternary ammonium ions whose cationic nature was not affected by pH and thus remained on the cation exchange sites of the mineral by coulombic forces, regardless of pH. Therefore, adsoptive property of organoclay prepared from quaternary ammonium salt is not affected by pH [3].

In our research, quaternary ammonium cation, dioctadecyl dimethylammonium, was used to modify bentonite, resulting material is called organoclay. Once hydrocarbon chains are immobilized on bentonite, hydrophobic ability increases, therefore increases tendency toward organic substances. Because of this property, organoclay can be used as adsorptive materials to adsorb organic substances in wastewater [3, 5]. Object of this work is to prepare organoclay to adsorb big organic pollutants.

## II - EXPERIMENT

### 1. Materials

Thanh Hoa bentonite (CEC = 71 meq/100g dried clay) is provided by Truong Thinh company. Dimethyl dioctadecyl ammonium chloride, isopropylic alcohol is from Aldrich.

### 2. Bentonite – DMDODA preparation

Organoclay was prepared from Bentonite and dioctadecyldimethyl- ammoniumchloride by wet method. Four conditions were investigated: amount of quaternary ammonium, pH, temperature, and preparation time to find out the optimum conditions.

Quaternary ammonium salt was dissolved in isopropylic alcohol, then added gradually into 2% enriched clay suspension (temperature, pH, time and amount of ammonium salt were varied to find ideal conditions for organoclay preparation) in continuous stirring. Suspension mixture was aged overnight at room temperature, filtered and washed by deionized water at 50-60$^oC$ until free of chloride (test with $AgNO_3$) and dried at 70$^oC$. The obtained material is organoclay.

### 3. Analytical methods

Adsorptive characterization was investigated by X-ray diffraction method using D8 ADVANCE instrument (Bruker – Germany), SEM (JEOS JSM - 5410 LV, Japan), IR spectra (Nicolet Magna-IR 760 Spectrometer), thermal analysis (Shimadzu DTA-50H thermal analyzer, Japan). Cation exchange capacity of clay was measured by methylene blue adsorption method according to American Petroleum Institute.

## III - RESULTS AND DISCUSSION

### 1. Effects of different conditions on organoclay synthesis

Data in table 1 shows that increasing amount of DMDODA leads to the increase in $d_{001}$ value. However, when the amount of DMDODA increases to 100% CEC, there is little change in interlayer distance. This can be explained that when the amount of quaternary ammonium chloride reaches 100% CEC, the cation exchange process reaches equilibrium. As the consequence, $d_{001}$ varies little.

From data in Table 1, it can be seen that when pH changes from 6 to 9, $d_{001}$ does not change much. We even carried out experiment at pH 3 and received organoclay with $d_{001}$ = 39.59 Å (data not shown in Table 1). This totally agrees with previous study [4]. Because cation nature of quaternary ammonium ion is not a function of pH, it remains in the cation exchange site by columbic force, not hydrophobic force. Therefore, organoclays can be used to treat toxic organic pollutants in a wide range of pH. Clay modified with $Na_2CO_3$ has pH 9, hence this pH is chosen to prepare organoclay.

It also can be seen from data that $d_{001}$ varies insignificantly when the temperature changes from 35$^oC$ (room temperature) to 85$^oC$. However, low temperature can limit the movement of particles. To ensure the cation exchange rate fast enough, optimum temperature to prepare organoclays from Thanh Hoa bentonite is set at 55$^oC$.

Time of reaction is also an important factor on preparation of organoclay. If reaction is carried out in a short period of time, exchange reaction between quaternary ammonium cations and interlayer cations of clay cannot reach equilibrium; if reaction time is too long, time and energy are wasted. From Table 1, layer distances are approximately equal when reaction time is 1, 2, 3, 4, and 5 hours. In order to achieve equilibrium completely, we choose 2h to be the optimum.

*Table 1*: Effects of different conditions on interlayer distance ($d_{001}$) of organoclay synthesis

| **Conditions: pH 9; Temperature 55°C; Time 4h** | | | | | |
|---|---|---|---|---|---|
| Amount of DMDODA (% CEC) | 0 | 75 | 100 | 125 | 150 |
| $d_{001}$(Å) | 15.61 | 37.51 | 40.57 | 40.86 | 41.52 |
| **Conditions: 100% CEC Quaternary ammonium; Temperature 55°C; Time 4 h** | | | | | |
| pH | 6 | 7 | 8 | 9 | 10 |
| $d_{001}$ (Å) | 38.89 | 39.53 | 38.82 | 40.57 | 38.55 |
| **Conditions: 100% CEC Quaternary ammonium; pH 9;Time 4 h** | | | | | |
| Temperature (°C) | 35 | 55 | 65 | 75 | 85 |
| $d_{001}$(Å) | 39.39 | 40.57 | 39.76 | 38.97 | 38.26 |
| **Conditions: 100% CEC Quaternary ammonium; pH 9; Temperature 55 °C** | | | | | |
| Time (h) | 1 | 2 | 3 | 4 | 5 |
| $d_{001}$(Å) | 38.65 | 39.22 | 39.52 | 39.39 | 39.36 |

## 2. Material characterization

*a) Bentonite*

*Table 2*: Mineral compositions of enriched Thanh Hoa clay

| Mineral concentration | Concentration, wt% |
|---|---|
| Montmorillonite | 59-61 |
| Illite | 3-5 |
| Zeolite (Heulandit +Chabazit) | 3-5 |
| Kaolinite + Clorite | 12-14 |
| Quartz | 4-6 |
| Felspat | 4-6 |
| Gotit | 6-8 |
| Lepidocrocit | Small |
| Gipxit | Small |

*Table 3*: Chemical composition of original Thanh Hoa clay

| Substances | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | $TiO_2$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|
| (wt%) | 44.8 | 15.7 | 13.7 | 1.27 | 2.79 | 0.14 | 2.44 | 1.11 | 0.48 |

*Table 4*: Chemical composition of enriched Thanh Hoa clay

| Component | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ |
|---|---|---|---|
| (wt %) | 48.95 | 29.33 | 2.86 |

*b) Organoclay*

Below is character of organoclay prepared at optimum conditions: amount of quaternary ammonium chloride equals to 100% CEC, pH is at 9, temperature is at 55$^{o}$C and reaction is carried out in 2 hours.

XRD patterns (Fig 1) show original bentonite has interlayer distance equals to 15Å at 2θ = 6$^{o}$. When modified by DMDODA, interlayer distance increases to 40.57Å and peak shifts to smaller diffraction angle 2θ = 2.5$^{o}$. This proves that alkyl chains are intercalated between clay layers, resulting in an increase interlayer distance.

From SEM patterns, there is difference between organoclay and original bentonite. This results from the intercalation of ammonium salt into bentonite.

(a)

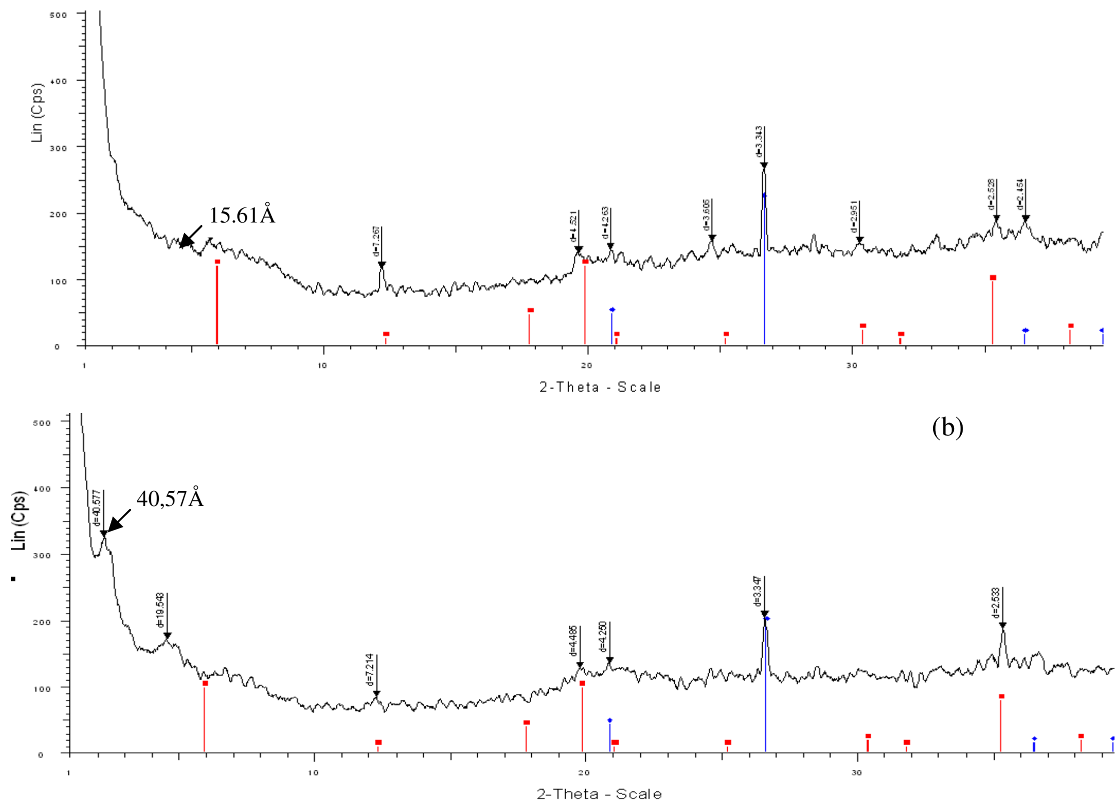


*Figure 1*: XRD pattern of (a) original bentonite and (b) organoclay

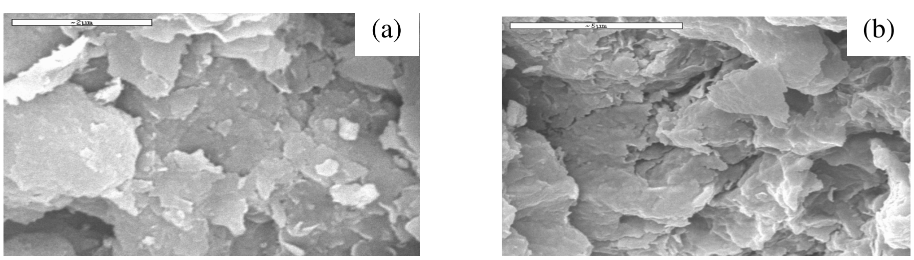


*Figure 2:* SEM pattern of (a) original bentonite and (b) organoclay

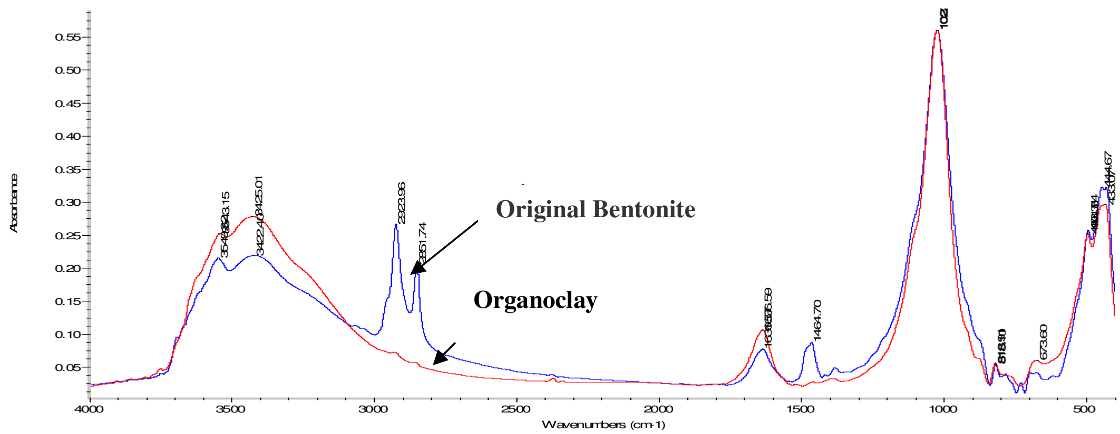


*Figure 3*: IR pattern of original bentonite and organoclay

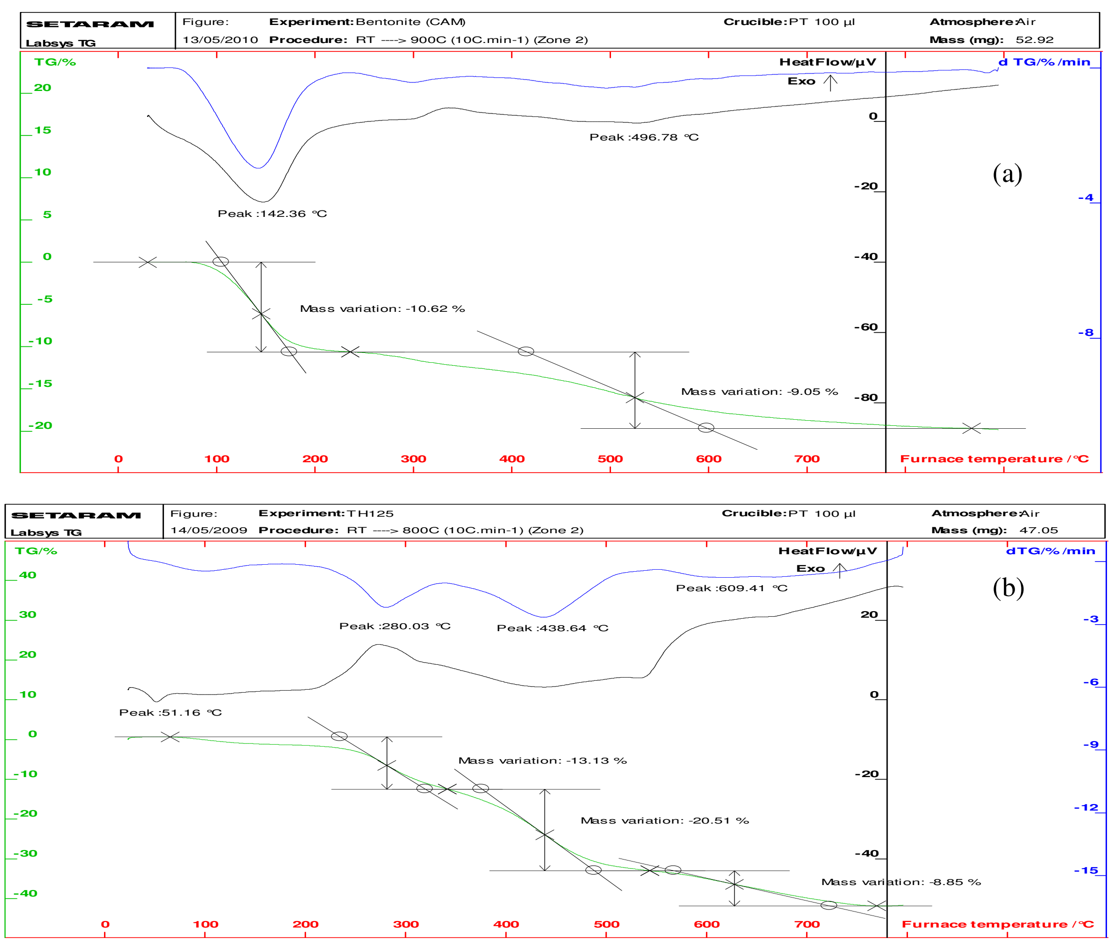


*Figure 4*: Thermal analysis pattern of (a) original Bentonite and (b) organoclay

In the IR pattern (Fig 3), there is a peak at 1464.7 $cm^{-1}$ from C-N stretching band of quaternary ammonium salts. Peaks at 2851.74 $cm^{-1}$ and 2923.96 $cm^{-1}$ are characterized for $–CH_3$ and $–CH_2$ vibrations in ankyl chains, respectively. There are other peaks characterizing bentonite such as deformation modes of Si-O in $SiO_4$ tetrahedral from 433 to 470 $cm^{-1}$; peaks characterized for Al – O stretching vibrations are about 818 $cm^{-1}$ ; $OH^-$ in material structure is characterized by vibrations at 3549 $cm^{-1}$.

These results agree with data from XRD pattern. Again, quaternary ammonium salts are proved to be immobilized onto Bentonite.

In thermal analysis pattern of Bentonite (Fig 4), there is an endothermic effect at 142$^o$C for physical dehydration (loss 10.62 wt%). But in that of organoclay, there is no peak at 142$^o$C. It proves that once quaternary ammonium cations are intercalated into clay layers, hydrophilic property changes to hydrophobic property. In addition, there is an exothermic effect at 280$^o$C from burning of organic substances in Bentonites.

## IV – CONCLUSION

Organoclay from Bentonite and dioctadecyl dimethyl ammonium chloride was successfully prepared. Organoclay obtained has higher interlayer distances than those in other studies [6]. Results prove that interlayer distance depends strongly on amount of quaternary ammonium chloride, although when increasing to a certain amount (100% CEC), this dependence is lost because equilibrium is reached. Interlayer distance is independent of pH, hence choosing pH 9, at pH of clay, is more convenient to prepare. Optimum temperature is 55$^o$C and the reaction is carried out in 2 hours. Above results open a new door to apply this material in practice to treat organic pollutants, especially ones with big size.

In the future, we will continue to investigate adsorption ability of organoclays on other big organic pollutants.

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## REFERENCES

1. Barbara Witthuhn, Peter Klauth, Erwin Klumpp, Hans-Dieter Narres, Holger Martinius. Applied Clay Science, 28, 55 - 66 (2005).
2. Ji-Hoon Kim, Won Sik Shin, Young- Hun Kim, Sang-June Choi, Wan-Keun Jo and Dong-Ik Song. Korean J. Chem. Eng., 22(6), 857 - 864 (2005).
3. T. A. Wolf, T. Demirel, and R. E. Bauman. J. Water Pollution Control Fed., Vol. 58, 68 - 76 (1986).
4. Stephen A. Boy**,** Sun Shaobai, Jiunn – Fwu Lee and max M. Mortland. Clays and Clay Minerals, Vol. 36(2), 125 - 130 (1988).
5. Lucilene Betega de Paiva, Ana Rita Morales, Francisco R. Valenzuela Díaz. Applied Clay Science 42, 8 - 24 (2008).
6. A. Khenifi · Z. Bouberka · F. Sekrane · M. Kameche · Z. Derriche. Adsorption, 13, 149 - 158 (2007).
7. Maosheng Xia, Yinshan Jiang, Fangfei Li, Mengmeng Sun, Bing Xue, Xi chen. Colloids and Surfaces A: Physicochem. Eng. Aspects 338, 1 - 6 (2009).
8. Mehmet Akçay. Journal of Colloid and Interface Science, Vol. 296, 16 - 21 (2006).

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