Influence of Organo-Clay's Carbon Number on the Adsorption of Humic Acid

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Abstract : In order to alter the clay surface from hydrophilic to organophilic nature, the clay was modified by replacing its natural inorganic exchangeable cations with Quaternary Ammonium Cations (QACs). In this work, we studied the effect of QACs carbon chain length used for modifying Montmorillonite clay to examine its adsorption properties towards humic acid utilizing a batch equilibration technique. A comparative study was performed using Montmorillonite modified with 3 different QACs, which include Tetramethylammonium (TMA), Hexadecyltrimethylammonium (HDTMA) and Benzyldimethylhexadecylammonium (BDHDMA). The Batch adsorption results demonstrated that HDTMA-Montmorillonite and BDHDMA-Montmorillonite are better adsorbent than the precursor and TMA-Montmorillonite. The adsorption affinity of Montmorillonite towards humic acid increased with an increase

of the QACs Carbon atoms in the organo-clays. These organo-clays were also characterized for their interlayer spacing and BET surface area by X-ray diffraction and N_2 adsorption technique, respectively. Some relationships between these physical properties and the adsorption capacities of the modified Montmorillonite were observed.

Keywords: Montmorillonite, Organo-clay, Surfactant, Humic acid, Adsorption.

Introduction

Adsorption of humic acid on clay minerals has been of interest to many researchers [1-4]. Uptake of humic acid by hydrotalcites, Montmorillonite and several of their modified mineral forms were previously investigated [5, 6] and indicated that surfactant-modified Montmorillonite is the best adsorbent for humic acid compared to the other modified forms of Montmorillonite, such as alumina-based pillared clays, and also hydrotalcites. The surfactant used for the modification of Montmorillonite in several of these studies was HDTMA, which is in the form of QACs.

Humic acid, a common organic colloidal matter found in surface and groundwater is derived from the decomposition of plant and animal products [6]. Humic acids have no homogeneous, exactly specified, chemical composition. The presence of humic acids has been a problem to the water industry and

environmental purification due to its yellow-brown colour and its resistance to microbial degradation.

The present work discusses the use of three different QACs, TMA, HDTMA and BDHDMA, for preparing 3 types of organo-clays. The objective of this task was to determine the effect of the number of carbon atoms in QACs used in the preparation of organo-clays and determined their adsorption affinity towards humic acids in aqueous systems. The physical characterization of the clays, which may help to explain the adsorption mechanism, was also evaluated.

Materials and Methods

1. Starting Materials

The starting clay used was Montmorillonite, kindly supplied by Thai Nippon Chemical Industrial Co., Ltd. The chemical composition of this Montmorillonite is shown in Table 1. The cation exchange capacity (CEC), data from the supplier, is 80 meq per 100 grams of Montmorillonite.

Table 1. Chemical compositions of Montmorillonite (in weight %).

SiO_2	56-60	MgO	1.5-2
Al_2O_3	16-18	CaO	1.9-2.1
Fe_2O_3	5-7	K_2O	0.3-0.5
Na_2O	2.4-3	TiO_2	1.2-1.5

The QACs and humic acid materials were purchased from Fluka Chemie AG. They were of analytical grade and were used as received without further purification. The names and chemical formulae of the QACs used are in Table 2.

Table 2. List of the QACs used in this Study.

QACs	Abbreviation	Molecular Weight	Chemical Formulae
Tetramethylammonium	TMA$^+$	74	$(CH_3)_4N^+$
Hexadecyltrimethylammonium	HDTMA$^+$	284	$[CH_3(CH_2)_{15}](CH_3)_3N^+$
Benzyldimethylhexadecylammonuim	BDHDMA$^+$	361	$[CH_3(CH_2)_{15}]N^+ (CH_3)_2CH_2C_6H_6$

2. Preparation of Organo-clays

Solution of TMA, HDTMA and BDHDMA were used separately as the modifying agent in the preparation of organo-clays. The synthesis was carried out in a batch reactor with 0.5 litres of each QAC solution. Twenty grams of Montmorillonite were added to the reactor and shaken for 24 hours to guarantee equilibrium. The adsorption of HDTMA on Montmorillonite has been reported to reach equilibrium in 4-6 hours [7]. The suspension was allowed to settle under gravity and washed with distilled water several times until the water conductivity was less than 1.5 μS. The final suspension was separated by vacuum filtration and air-drying overnight at room temperature to avoid the destruction of the compound at higher temperatures. It has been reported that if the clays are air dried, the layers settle down very slowly and are oriented in the same parallel direction [8]. It should also be mentioned that, for every batch experiment and

organo-clay preparation, borosilicate first-class glassware was used. The three different types of organo-clays produced were named HDTMA-clays BDHDMA-clays and TMA-clays and TMA-clays, respectively. The amount of QACs in the organo-clays was approximately equivalent to 100% and 200% of the Montmorillonite CEC.

3. Characterization Techniques

The adsorbent behavior and ability of each organo-clay depend on physical properties such as the structure, particle size and surface area. The following methods were used to characterize these properties. BET surface area of the organo-clay samples was measured using N_2 physical adsorption using a Micrometritics ASAP2010. X-Ray diffraction (XRD) was used to determine the interlayer *d001*-spacing, which is the distance between the clay sheets of the QACs-treated clays and, for comparison, the starting Montmorillonite clay. XRD analysis was carried out using Bruker D5005 system with CuKα radiation. Particle size of the clay was also found using the Mastersizer.

4. Adsorption Experiments

The adsorption isotherms were conducted using a batch equilibration technique in a 0.5 litre conical flask by varying the initial humic acid concentration while maintaining the amount of adsorbent clay. A control sample with no adsorbent was also

prepared. In addition, comparative adsorption experiments were conducted with the untreated Montmorillonite as a reference material. The flasks were closed and shaken overnight to allow equilibrium to be achieved. The following day, the samples were centrifuged at 3500 rpm for 30 minutes to separate the adsorbent clays from the slurry. The supernatant was analyzed for humic acid concentrations using a UV spectrophotometer at a wavelength of 400 nm. [4]. Several adsorption parameters, such as temperature, time and pH, were varied throughout the experiments in order to see their effect on the adsorption behavior of Montmorillonite and the organo-clays.

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Results and Discussion

1. Physical Characterization

Nitrogen adsorption desorption isotherms of the precursor and modified clays are presented in Figure 1. It is noticed that the desorption branches of all samples exhibited hysteresis loop, indicating the presence of mesopores, HDTMA-clays and BDHDMA-clays had lower BET surface area than the original Montmorillonite, as seen in Table 3, because most of the exchange sites of the organo-clays were satisfied by QACs species with large molecular size. These results were attributed to the inaccessibility of the internal surface to nitrogen gas. The large differences in surface area between the original and organo-clays are attributed to the nearly total blocking of the micropores in the surfactant-loaded materials. On the other side, TMA-clays had the higher BET surface area than those of the original, HDTMA and BDHDMA-clays. Previous research has indicated the higher degree of hydration of TMA cations causes shrinkage of the interlayer pore space [9].

The basal spacing determined by X-ray powder diffraction indicated that the QACs adsorbed between the interlaminar gaps of the organo-clays because the *d001* spacing of the precursor Montmorillonite were lower than that of the QACs-modified forms.
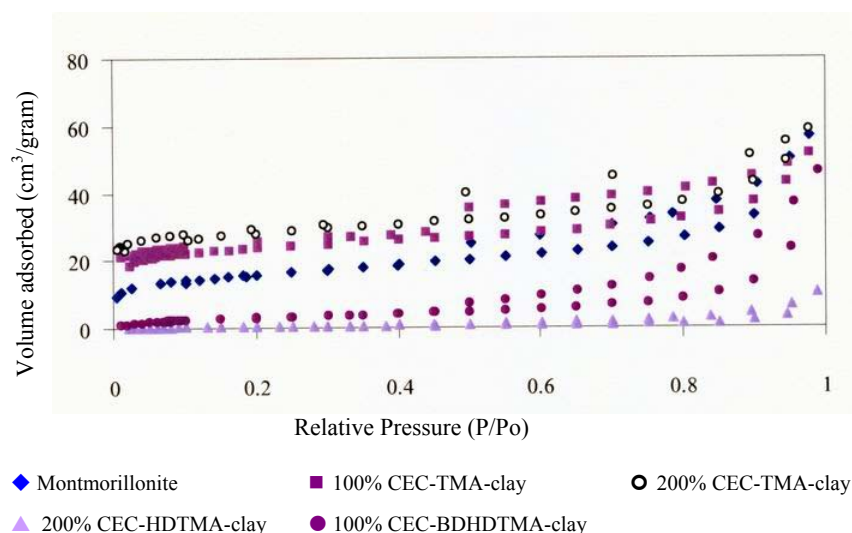
◆ Montmorillonite   ■ 100% CEC-TMA-clay   ○ 200% CEC-TMA-clay

▲ 200% CEC-HDTMA-clay   ● 100% CEC-BDHDTMA-clay

Figure 1. Nitrogen adsorption-desorption isotherm of the precursor and Modified clays.

Table 3. Physical properties of Montmorillonite and its modified forms.

Adsorbent clays	BET Surface area (m^2/g)	$d001$ spacing (Å)	2θ	Particle size (μm)
Montmorillonite	49.5	13.143	6.72	9.7
100% CEC-TMA clay	82.6	14.718	6.00	9.22
200% CEC-TMA clay	97.7	14.623	6.04	12.72
50% CEC-HDTMA clay	11.6	17.381	5.08	27.1
100% CEC-HDTMA clay	11.2	21.325	4.14	57.2
200% CEC-HDTMA clay	2.0	22.872	3.86	49.1
100% CEC-BDHDMA clay	11.3	24.253	3.64	72.34

It corresponds to the shifting of *d001* peak of most of the modified samples to lower diffraction angle, lower 2θ value, than that of the precursor Montmorillonite. This suggests that binding of organic cations to the clay generates a hydrophobic

environment in the interlayer space of the clays. The amount and the alkyl chain length of QACs affected the interlayer spacing in the order TMA-clay < HDTMA-clay < BDHDMA-clay, which is consistent with the larger size HDTMA and BDHDMA ion compared to TMA ions. The values of *d001* spacings shown in Table 3 include the thickness of the clay sheet (9.4 Å), giving an interlayer separation (Δ) of about 5.2 Å for 200% CEC-TMA clays. This observation is in general agreement with the diameter of the TMA ion, which is 4.9 Å [10]. As expected, the *d001* spacing of the 100% CEC-QACs modified clays are also significantly higher than those of the 50% CEC-QACs modified ones but the difference in basal spacing between the 100% CEC and the 200% CEC-QACs modified clays is much smaller. Therefore, the cation exchange mechanism is probably dominant for the intercalation of the QACs between the interlayer of the clays.

The surfactant-modified clays exhibit a larger particle size than the precursor Montmorillonite. The particle size of the modified clays increased as a function of the amount and the molecular size of QACs added.

2. Time course

The time course of the humic acid adsorption on Montmorillonite at different initial concentration is demonstrated in Figure 2. It is obvious that the concentration of humic acid decreased as the time was prolonged; that means, humic acid

can be removed from the aqueous system by Montmorillonite. The figure indicates there is an initial rapid decrease, followed by slower drop of humic acid concentration over time. It took about 20 minutes to attain equilibrium. The curves, then, tend to a horizontal plateau. The first part of the kinetics (0-20 mins in case of humic acid adsorption on the precursor Montmorillonite) seems to be a first-order reaction because a linear relation was found from the graph [11]. The second part (>20 minutes) of the curve exhibits, which might not be related to a reaction order. Thus it may be assumed that the adsorption consists of a fast reaction at the beginning followed by a second slower step. It is noticed in Figure 1 that the difference in the starting concentration of humic acid has no effect on the time of equilibrium.
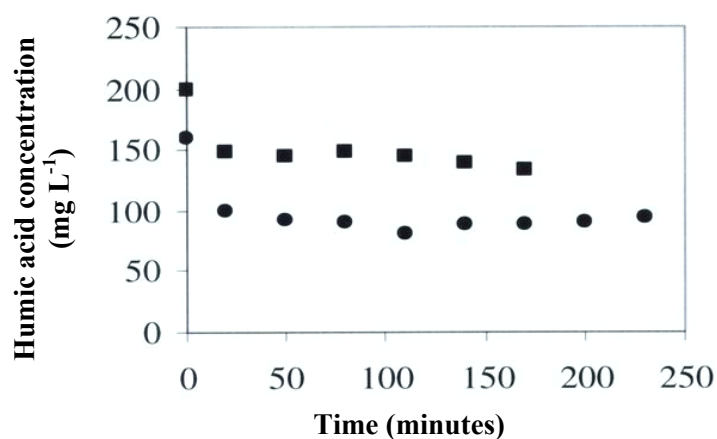

Figure 2. Time course of humic acid adsorption on the precursor Montmorillonite.

3. Adsorption Isotherms

The concentration of adsorbed species on the organo-clays could be calculated from a simple mass balance equation assuming that the decrease from the initial concentration was due to sorption. A plot of adsorbate quantity on the adsorbent against the equilibrium concentration in the solution at a constant temperature is commonly referred to as an isotherm. It can be said that the adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particle at a given temperature [12].

The adsorption isotherms for humic acid retention by various types of clay are show in Figure 3. Most of the organo-clays adsorbed greater amounts of humic acid than Montmorillonite clay. Only the TMA-clay indicates no greater uptake of humic acid, although 200% of the Montmorillonite's exchange capacities were saturated by the TMA cation. The TMA-clays, due to the small size of TMA cations [13] formed an effective partition medium, cannot be organophilic and do not behave as such in the adsorption of humic acid. In addition, much like Ca^{2+} and Na^{+}, the high degree of hydration of TMA cations has been previously addressed [9]. TMA-clays, thus, tend to be hydrophilic rather than organophilic. Consequently, the adsorption of humic acid is prohibited because of both the hydration effect and the absence of an organic moiety in the TMA cations. In contrast, the BDHDNMA-clays and HDTMA-clays uptake considerable amounts of humic acid. It should be noted

than both of these organo-clays have a lower surface area than the precursor Montmorillonite and the TMA-clays as in Table 3. Hence, the humic acid adsorption efficiency of the clays in aqueous systems is not dependent on the surface area. The more the BDHDMA or HDTMA loading on Montmorillonite is, the higher the amount of humic acid uptake. This may be because of the hydrophobic adsorption of uncharged humic substances [14] onto hydrophobic parts of organo-clays. The adsorption isotherms of humic acid onto the organo-clays were non-linear. Adsorption, rather than partitioning, was the suggested uptake mechanism [7]. It is apparent that the difference in QACs alky1 chain length of modified Montmorilonite affects the magnitude of humic acid adsorption. The ability of the organo-clays to remove humic acid decreased in order BDHDMA-clay>HDTMA-clay> the precursor Montmorillonite. This is consistent with the alkyl chain length of the QACs used in the clay modification.
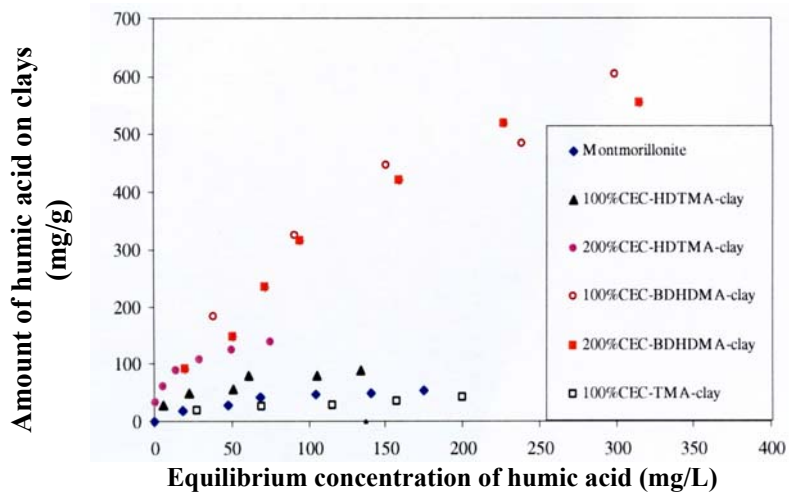

Figure 3. Adsorption isotherm of humic acid on precursor and modified clays.

Since the amount of humic acid adsorbed seems to have a limiting value when the amount of humic acid in solution tended to infinity, as seen in Figure 2, Langmuir model was used to analyze the adsorption behavior and to determine the humic acid adsorption capacity of each clay. For a single solute system, Langmuir isotherm may be expressed as:

$$y = \frac{ax}{1+bx}$$

where a and b = Langmuir constants.

The above equation can be modified to give:

$$\frac{x}{y} = \frac{1}{a} + \frac{bx}{a}$$

A plot x/y against x will give a straight line for the isotherm if the Langmuir relationship can be applied. It is common to describe the fit of linear regression in terms of $R^2=1$, which is the square of correlation co efficient. If the $R^2=1$, then the fit is perfect. As shown in Table 4, the straight line fits to the transformed data with R^2 approach to one. It is clear from this data that a Langmuir isotherm does satisfactorily describe the humic acid adsorption behaviour on Montmorillonite and its modified forms. The humic acid adsorption capacity of various clays is shown in Table 4.

4. Influence of pH on Humic Acid Adsorption

The effect of pH was evaluated by conducting an adsorption experiment for humic acid onto the original Montmorillonite clay at pH values ranging from 2 to 12. Figure 4

Table 4. Humic Acid Adsorption Capacities of Precursor and Modified Clays by means of Langmuir Isotherm.

Type of adsorbent	Correlation Coefficient, R^2	Adsorption capacity (mg humic acid/g clay)
Montmorillonite	0.9907	68.49
100% CEC-TMA clay	0.9249	52.97
50% CEC-HDTMA clay	0.9131	129.87
100% CEC-HDTMA clay	0.9665	99.01
200% CEC-HDTMA clay	0.9886	144.93
100% CEC-BDHDMA clay	0.9593	833.33
100% CEC-BDHDMA clay	0.9581	909.09

indicates that adsorption of humic substances was very sensitive to pH. The lower the pH, the greater the humic acid removed. This finding was consistent with that reported in the literature [2, 15-16]. The results in this section might be explained by the following reasons. Firstly, the interplanar spacing of Montmorillonite is pH-dependent and decreases with increasing pH. Secondly, humic acid is negatively charged in polyanion form and there is repulsion between humic acid and the natural negatively charged layer of the clays at high pH level. Conversely, at low pH level relatively few of the humic acid molecules are ionized and behave like uncharged molecules that can penetrate interlamellar spaces and displace water molecules between the alumino-silicate layers of the Montmorillonite.
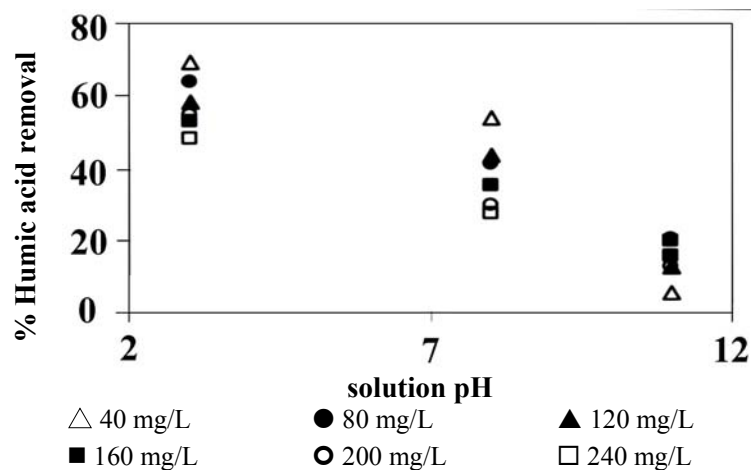
Figure 4 legend:
△ 40 mg/L   ● 80 mg/L   ▲ 120 mg/L
■ 160 mg/L   O 200 mg/L   □ 240 mg/L

Figure 4. Effect of pH on humic acid adsorption by the precursor Montmorillonite.

5. Effect of Temperature on the Uptake of Humic Acid

The influence of temperature was evaluated by conducting adsorption experiment for humic acid onto the original Montmorillonite at temperatures ranging between 20 and 40 ºC. Adsorption temperature had some affect on the uptake of humic acid by Montmorillonite as shown in Figure 5. The removal of humic acid by the Montmorillonite decreased with an increase of temperature with in the range studied. This result indicates exothermic reaction. The humic acid adsorption capacities of Montmorillonite at various temperatures by means of Langmuir isotherm is shown in Table 5.
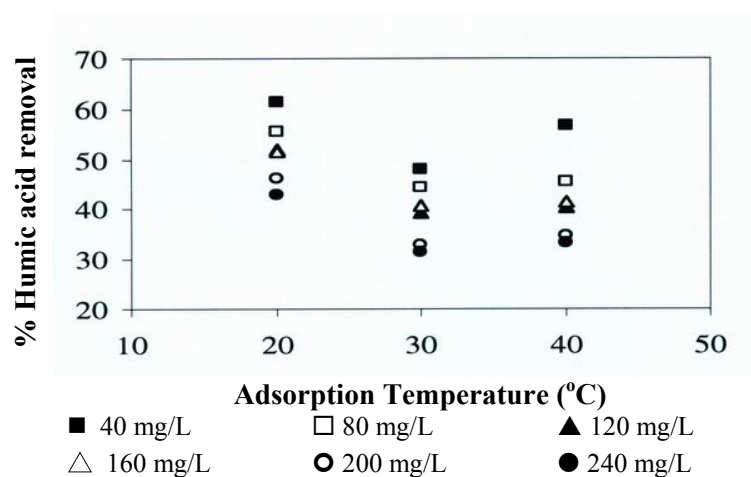
Figure 5. Influence of temperature on the uptake of humic acid by Montmorillonite.

Table 5. Humic Acid Adsorption Capacities of Montmorillonite at various temperatures by means of Langmuir isotherm.

Temperature (K)	Adsorption Capacity (mg of humic acid/g of clay)	R^2
293	151.51	0.9797
303	106.38	0.948
313	102.04	0.939

Conclusion

Montmorillonite clay can be modified in a manner that considerably improves its capacity to remove humic acid from water. The modified clays are called organo-clay because the exchangeable inorganic cations in the precursor Montmorillonite are replaced by organic cations in the form of QACs like TMA,

HDTMA and BDHDMA. The large organic QACs may also act as pillars, increasing the spacing between the tetrahedral sheet *(d001)* of Montmorillonite, as shown by XRD results in Table 3. Therefore, the organophilic sorption zone is created between the layers of the clay mineral. The batch adsorption results clearly demonstrate the ability of the sorbent clays to remove humic acid from water, especially the HDTMA-clays and the BDHDMA-clays. The type and amount of QACs used for the modification of Montmorillonite do effect its adsorption properties. Both HDTMA and BDHDMA molecules are able to change the hydrophilic surface property of Montmorillonite into organophilic surfaces. This enhances the adsorption affinity of the organo-clay towards humic acids. In general, the more hydrophobic the cation retained Montmorillonite, the greater the uptake of humic acid via hydrophobic interaction between alkyl groups of the organic cations and the humic acid. The shape of the isotherms, which is related to the uptake mechanism, varies with the carbon content of the QACs used in the modification of Montmorillonite. The isotherms indicate an increase in adsorption as a function of organic cation content in the organo-clays. This emphasizes the predominant role of hydrophobic interactions between the hydrocarbon tails in causing adsorption of humic acid. Since Montmorillonite modified by long alkyl chain length QACs, like BDHDMA and HDTMA, exhibit the capability to sorb humic acid, they may be used as effective sorbents for humic acids in engineered barriers of waste repositories.

Acknowledgement

Nomenclature

y	=	Concentration of humic acid on adsorbent clay (mg g^{-1} adsorbent)
a, b	=	Langmuir constant
x	=	Concentration of humic acid in solution (mg L^{-1})
$QACs$	=	Quaternary Ammonium Cations
$d001$	=	the perpendicular distance between pairs of adjacent planes (the interplanar spacing of the crystal)
θ	=	the Bragg angle (the glancing angle of incidence)

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