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รายงานวิจัยฉบับสมบูรณ์

โครงการ
การกำจัดสารอินทรีย์ในน้ำเสียโดยใช้ Montmorillonite Clay

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กรกฎาคม 2544

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ผู้วิจัย

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

Abstract

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Project Tittle : การกำจัดสารอินทร์ในน้ำเสีย โดยใช้ Montmorillonite Clay

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The aims of this study is to investigate the feasibility of utilising Montmorillonite and various type of its modified forms as an adsorbent for the removal of organic compounds from aqueous solution. Montmorillonite is a smectite clay based on alumino-silicate structures and for this reason it, like zeolite, has been proposed as an adsorbent in water treatment application. In order to improve the organic adsorption ability of Montmorillonite, the clay was modified by replacing its natural exchangeable inorganic cations with four different quarternary ammonium compounds (QACs). The QACs, sometimes named as cationic surfactant, used in preparation of organo-clays were were TMA, BDHDMA, HDTMA and TDMA. These QACs are different in their alkyl chain length and size. Adsorption of six different organic compounds by these modified clays were studied; humic acid, two types of dyes (methylene blue and methyl orange), naphthalene and two phenolic substances (phenol and 3-monochlorophenol). Most of them are classified as polluting elements, which cause problem to the environment. A series of adsorption experiments have been carried out in batch techniques. Comparative experiments were carried out using Montmorillonite, which is the starting clay, as a reference material. The batch adsorption tests show an interesting capacity of modified Montmorillonite in separating organic contaminants from water. These modified Montmorillonite samples, TMA-clays, HDTMA-clays, BDHDMA-clays and TDMA-clays, were also characterized for their interlayer spacing and BET surface area by X-ray Diffraction and N_2 adsorption technique respectively. Relations between those physical properties and the adsorption capacities of the modified Montmorillonite were noticed.

Keywords : Montmorillonite, Organo-clay, Quaternary Ammonium Compounds (QACs), Water Treatment, Adsorption

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จุดมุ่งหมายของการศึกษางานชุดนี้เพื่อจะศึกษาความเป็นไปได้ในการนำมอนต์มอริลโลไนต์ (Montmorillonite) ธรรมชาติ และมอนต์มอริลโลไนต์ที่ผ่านการปรับปรุงคุณสมบัติพื้นผิวมาดูดซับสารอินทรีย์ที่ละลายอยู่ในน้ำ มอนต์มอริลโลไนต์เป็นแร่ดินในกลุ่มซีแมกไทต์ (Smectite) ที่มี อลูมินา-ซิลิกาเป็นส่วนประกอบในลักษณะโครงสร้างซ้อนกันเป็นชั้นๆ ด้วยเหตุนี้จึงทำให้มอนต์มอริลโลไนต์มีคุณลักษณะเหมือนกับซีโอไลต์กล่าวคือมีพื้นที่ผิวสูง จากคุณสมบัตินี้จึงมีความเป็นไปได้ที่จะนำไปใช้เป็นตัวดูดซับในกระบวนการบำบัดน้ำเสีย การปรับปรุงคุณสมบัติพื้นผิวมอนต์มอริลโลไนต์เพื่อให้เหมาะกับการดูดซับสารอินทรีย์สามารถทำได้โดยการแลกเปลี่ยนประจุบวกของสารอนินทรีย์ที่มีอยู่ในโครงสร้างตามธรรมชาติของมอนต์มอริลโลไนต์ด้วยสารอินทรีย์ประเภท Quaternary Ammonium Compounds (QACs) ซึ่งบางครั้งจะเรียกสารประเภทนี้ว่า สารลดแรงตึงผิวที่มีประจุบวก สารที่ใช้ได้ tetramethylammonium chloride ($C_4H_{12}ClN$), hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$), tetradecyltrimethylammonium bromide ($C_{17}H_{38}NBr$) และ benzyldimethylhexadecylammonium chloride ($C_{25}H_{46}ClN$) ซึ่งสารเหล่านี้จะมีความยาวของหมู่อัลคิลและขนาดโมเลกุลต่างกัน

ในการศึกษาครั้งนี้ได้ทำการศึกษาความสามารถของมอนต์มอริลโลไนต์ธรรมชาติ และมอนต์มอริลโลไนต์ที่ผ่านการปรับปรุงคุณสมบัติพื้นผิวแล้วในการดูดซับสารอินทรีย์ 6 ชนิด คือ humic acid, methylene blue, methyl orange, naphthalene, phenol และ 3-monochlorophenol โดยทำการทดลองเป็นแบบกะ จากการทดลองพบว่าการดูดซับสารอินทรีย์จากน้ำโดยใช้มอนต์มอริลโลไนต์ที่ปรับปรุงคุณสมบัติพื้นผิวแล้วได้แก่ TMA-clays, BDHDMA-clays, HDTMA-clays และ TDMA-clays จะมีประสิทธิภาพดีกว่ามอนต์มอริลโลไนต์ธรรมชาติ และมีความเป็นไปได้ที่จะนำไปใช้งานจริง นอกจากนี้จากการศึกษาสมบัติทางกายภาพ (เช่น ระยะห่างระหว่างชั้นโครงสร้างและพื้นที่ผิว) ของมอนต์มอริลโลไนต์ธรรมชาติ และมอนต์มอริลโลไนต์ที่ผ่านการปรับปรุงคุณสมบัติพื้นผิวแล้วพบว่ามีความสัมพันธ์กันระหว่างลักษณะทางกายภาพและความสามารถในการดูดซับของมอนต์มอริลโลไนต์ชนิดต่างๆ

กิตติกรรมประกาศ

โครงการวิจัยหลังปริญญาเอก เรื่อง **การกำจัดสารอินทรีย์ในน้ำโดยใช้ Montmorillnite Clays** ครั้งนี้เสร็จสมบูรณ์ได้ด้วยดีจากความร่วมมือและการสนับสนุนของหลายฝ่ายดังนี้

1. เจ้าหน้าที่ศูนย์เครื่องมือ มหาวิทยาลัยเทคโนโลยีสุรนารี ที่ให้ความช่วยเหลือในการนำตัวอย่างไปวิเคราะห์ด้วยเครื่องมือ เป็นอย่างดี
2. รศ.ดร.ชัยยศ ตั้งสถิตย์กุลชัย หัวหน้าสาขาวิช่วิศวกรรมเคมี มหาวิทยาลัยเทคโนโลยีสุรนารี ที่กรุณาให้คำแนะนำทางวิชาการที่เป็นประโยชน์
3. บริษัท ไทยนิปปอนเคมีภัณฑ์อุตสาหกรรม จำกัด ที่ได้อนุเคราะห์ Montmorillonite Clays มาใช้ในโครงการ
4. สำนักงานกองทุนสนับสนุนการวิจัย สนับสนุนทุนวิจัยหลังปริญญาเอก

ผู้วิจัยรู้สึกซาบซึ้งน้ำใจเป็นอย่างยิ่ง จึงใคร่ขอขอบพระคุณอย่างสูงไว้ ณ โอกาสนี้

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(a) Paper manuscript

CHAPTER 1 INTRODUCTION

1.1 Research aims

The goal of this study is to investigate the feasibility of utilising Montmorillonite and its modified forms as an adsorbent for organic waste in water. Firstly Montmorillonite were modified by four of the quaternary ammonium compounds (QACs), which were TMA, BDHDMA, HDTMA and TDMA. Secondly the ability of the starting and modified clays to remove six various organic contaminants, which were humic acid, methylene blue, methyl orange, phenol, chlorophenol and naphthalene, were found by batch adsorption experiments.

1.2 Using natural and modified clays as an adsorbent for water treatment

Clay minerals are aluminosilicates with a bidimensional lamellar structure leading to a high area/volume ratio [Arbeloa F.L. *et al.* 1995]. The guest molecules can be imbibed between their siliceous layers causing their crystals to swell. Clays can be classified according to their layered structure. Each layer is formed by condensate sheets of linked $Si(O,OH)_4$ tetrahedral with sheets of linked $M_{2\text{-}3}(OH)_6$ octahedra, where M is a trivalent or divalent cation, usually Al or Mg. Different clays are formed depending on the way that these sheets condense [Gessner F. *et al.* 1994] resulting a variety of amorphous chain and layered structure [Kaviratna P.D. *et al.* 1996]. Clays can be synthesized or taken from natural deposits since they are some of the most profuse components of soil [Cione A.P.P. *et al.* 1998]. Research in clay minerals, especially swelling clays, is becoming more and more important because of their extensive applications. Fields such as industry, environment studies, catalysis, new material technology and agriculture are interested in these materials [Estevez M.J. *et al.* 1995].

1.2.1 Montmorillonite

Montmorillonite is a member of the smectite group of minerals. It is the most intensely studied mineral due to its broad range of chemical composition, intercalation properties and the ability to swell and undergo pillaring [Kaviratna P.D. *et al.* 1996]. It is composed of two tetrahedral silica sheets and sandwiched between them is an octahedral aluminium sheet. The tetrahedral and octahedral sheets are so arranged that the top of each silica tetrahedral and the hydroxy group is replaced by an oxygen atom.

The layers are continuous in *a* and *b* directions, and are stacked in the *c* direction. The stacking is such that the base oxygens of the silica sheets face each other. There is no covalent bonding between sheets and so they are only held together by weak electrostatic forces. This means that there is excellent cleavage of the sheets and that polar molecules can enter and alter the *c* spacing. Thus there is no fixed separation, but typically the spacing has a lower range of around 9.5 Å, and can increase to such a value that the layers are effectively separated. Data from X-ray powder investigations show two distinctive reflections. Firstly, an integer order of reflections in the *c* direction. Secondly, general reflections from the *hk*-band system (in the *a* and *b* directions) that are used to characterise this class of mineral. The first point indicates that interlayer swelling is by single, double or multiple layers of water and that each degree of swelling has a characteristic spacing. The control of humidity is thus very important when measurements of the *c* spacing are made. Reflections in the *a* and *b* directions can be used for identifying the main constituent of the sample and any other substances present.

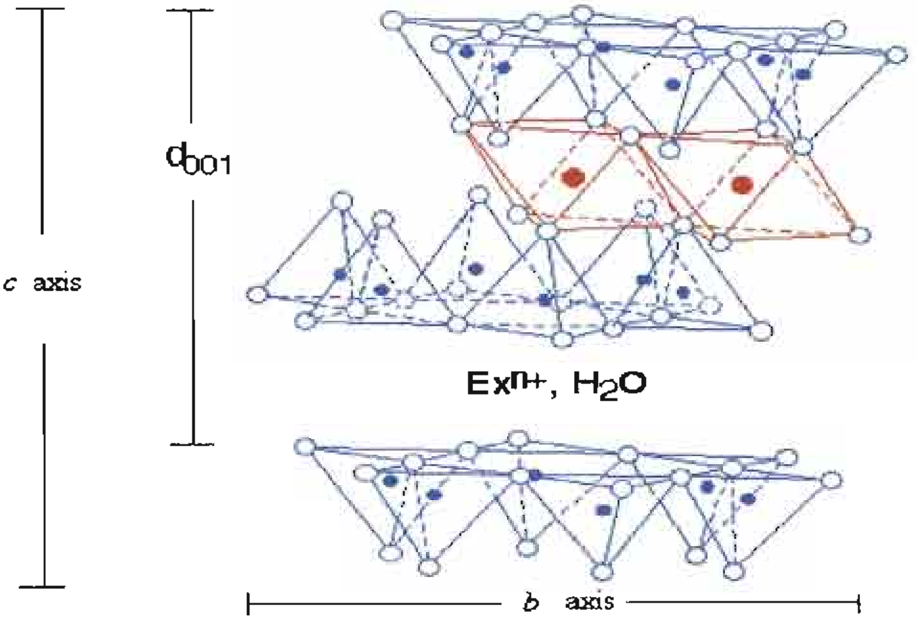

Figure 1.1: Idealised structure of Montmorillonite. Small blue circles are Si^{4+}, red circles are Al^{3+} or Mg^{2+}, open circles oxygen atoms. Exchange cations and water occupies the interlayer region.

There are many hundreds of analyses of Montmorillonite samples in the literature. This indicates how variable its composition can be. A general formula can be given which takes account of this variation.

$$M_y^+ (Al_{2-y} Mg_y) (Si_4 O_{10} (OH_2)).nH_2O$$

The variable y indicates the degree of imperfection in the sample. The substitution of magnesium for aluminium would give the clay a net negative charge. This is because aluminium is in its 3+ oxidation state, and magnesium in its 2+. This imbalance is rectified by the ion M^+, which is referred to as the exchangeable cation. These ions are located in the space between layers. Analyses have also indicated that aluminium as Al^{3+} can be substituted for silica, which will again cause a net negative charge. It could be said that Montmorillonite particles carry two kinds of electrical charges: one is from the cation exchange sites and the other is the structural negative charge resulting from isomorphous substitutions within the clay structure. A study reports that for Montmorillonite the point of zero charge (PZC), which is the pH where the net charge of the clay surface is zero, is between 8.70 – 8.94 [Avena M.J. and De Pauli C.P. 1998].

When in suspension the physical arrangement of the silicate layers depends greatly upon the exchangeable ions. Individual platelets normally exist as structures consisting of a number of platelets formed as a result of electrostatic attractive forces. These structures are sometimes referred to as tactoids and consist of lattice platelets stacked together face to face forming a sandwich type structure. The magnitude of the forces holding the tactoids together enlarges with the charge density of the exchangeable ion. The predominant exchangeable ions found naturally occurring in Montmorillonite samples are sodium and calcium. The exchange ions in the clays are normally hydrated. If a sample with only sodium exchangeable cations is put into suspension on average each tactoid will consist of 1.4 platelets. This value increases to 3.9 when a pure calcium form is made.

As mentioned previously, when there is water present, the clay will swell due to the attraction of water molecules to the exchange cations. The amount of swelling depends on how much water is available and which exchange ion is present. If the ion is sodium and there is a large amount of water present it is possible for the layers to swell to several times their dry volume [Kaviratna P.D. *et al.* 1996] so that they separate. A study shows that the interplanar spacing of Montmorillonite is pH-dependent and decreases with increase in pH, the steepest decrease occurring between pH 4 and 5 as shown in Figure 1.2 [Schnitzer M. and Khan S.U. 1972].

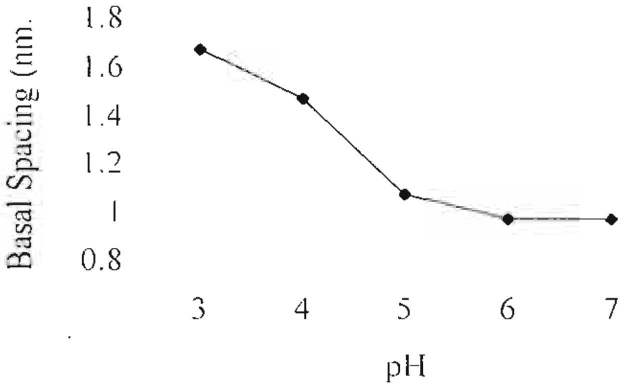

Figure 1.2: Effect of pH on the interlayer spacing of Na-Montmorillonite [Schnitzer M. and Khan S.U. 1972]

Due to the unusual intercalation properties of Montmorillonite as mentioned above, it has recently been widely investigated as an adsorbent, cation exchanger and heterogeneous catalyst and also catalyst support [Huai-Te Shu *et al.* 1997].

1.2.2 Organo-clays

Since the inorganic exchangeable cations (e.g., Na^+ and Ca^{2+}) between the layers of Montmorillonite are strongly hydrated in the presence of water, a hydrophilic nature to the mineral surface is created. Consequently the adsorption of nonionic organic compounds (NOCs), such as benzene, alkylbenzenes and chlorinated phenols [Kukkadapu R.K. and Boyd S.A. 1995], by clays is reduced in the presence of water because relatively NOCs cannot effectively compete with highly polar water molecules for adsorption sites on the clay surface. The sorbent property of Montmorillonite for NOCs can be greatly improved by replacing the inorganic interlayer cations with organic cations like Quaternary Ammonium Cations (QACs) of the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NR_2]^+$ [Lawrence M.A. *et al.* 1998]. The molecular structure of QACs includes a central nitrogen atom joined to four organic groups along with an acid radical [Gitipour

S. *et al.* 1997]. QACs sometimes are classified as surface-active agents (surfactants) because each molecule has a nonpolar hydrocarbon group and ionic polar component. Unlike NOCs, QACs can effectively displace inorganic cations such as Ca^{2+} and Na^{+} in the negatively charged surface clays by ion-exchange [Lagaly G. 1994; Smith J.A. *et al.* 1990].

During the exchange reaction, QACs are not only intercalated between the layers but also accumulated at the external surfaces of the clays [Lagaly G. 1994]. It could be said that QACs create the adsorption sites both on the external surfaces and in the interlayer of the clays [Michot L.J. and Pinnavaia T.J. 1991]. The amount of QACs adsorption is generally not beyond the Cation-Exchange Capacity (CEC) of Montmorillonite in the case of short-chain quarternary amines such as TMA (tetramethylammonium cation). However longer chain alkylamines, such as HDTMA (hexadecyltrimethylammonium cation), are adsorbed above the CEC. It has been reported that HDTMA was initially adsorbed by cation exchange. Afterward with higher loading, HDTMA was adsorbed by both cation exchange and hydrophobic bonding [Zhao H. and Vance G.F. 1998]. Considering that Van der Waals forces are stronger with longer alkyl chains, the extent of hydrophobicity increases with increasing chain length. An increase in the length of the hydrocarbon chain increases the adsorption of QACs on the solid surface. The basal spacing of Montmorillonite modified at 100 % CEC by three different kinds of QACs were measured, showing that 13.5 Å for TMA (trimethylammonium)-Montmorillonite, 19.9 Å for HDTMA (hexadecyltrimethyl ammonium)-Montmorillonite and 19.5 Å for DDDMA(dioctecyldimethylammonium)-Montmorillonite [Dentel S.K. *et al.* 1996]. The larger organic cations may act as pillars [Dentel S.K. *et al.* 1998] which result in an increase in the inter-lamellar spacing [Nzengung V.A. *et al.* 1996] and a more organophilic clay compared to the natural clay precursor. These modified clays are commonly named as 'Organo-clays'.

It has been reported that the adsorption of QACs on clays in the CEC range is irreversible in the presence of other ions [Kim Y.S. *et al.* 1996]. Charge reversal typically occurs when organic-cation sorption exceeds the CEC of the clay [Zhao H. and Vance G.F. 1998]. The organophilic properties of the organo-clays result in part from the reduced degree of hydration of the organic cations compared to the natural inorganic exchangeable cations. Thus it may have utility for the treatment of contaminated water and for the immobilization of organic contaminant plumes on the surface.

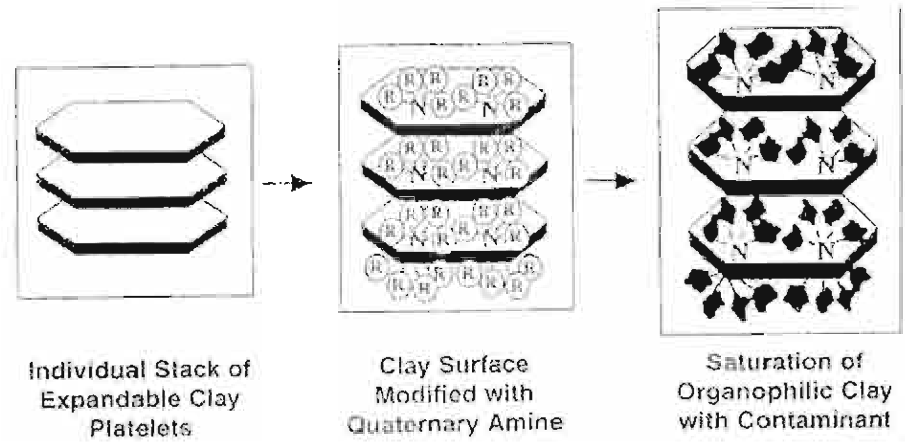

Figure 1.3 : The principle of the preparation of organo-clays [Gitipour S. *et al.* 1997]

1.3 Description of organic adsorbates studied

The choice of organic molecules studied was justified by their properties.

1.3.1 Humic substances

Humic substances are the major fraction of organic matter in natural water and effluents. They are the naturally occurring compounds arising from decomposition of natural plant and animal matter that give the water their characteristic yellowish to brownish colour due to the presence of 'humic' and 'fulvic' acids. Typically, humic and fulvic acids account for 40% to 90% of the carbon content of the dissolved organic matter of natural water. Humic and fulvic acids are structurally similar, but differ in molecular weight, ultimate analysis, and functional group content [Schnitzer M. and Kodama H. 1977]. Fulvic acid has lower molecular weight than humic acid and dissolve at all pHs. Fulvic acid may be oxidized fragment of larger humic substances, or perhaps humic acid precursors [Davies G. and Ghabbour E.A. 1999]. Humic acid is a long-chain polyanion of varying molecular weight range. It can exist in several size fractions with some fraction of colloidal dimensions 60 - 100 Å [Fitch A. and Du J. 1996]. Humic acid are substances of considerable chemical heterogeneity [Rothe J. *et al.* 2000] The latest work has found the humic acid empirical formula to be $C_{36}H_{30}O_{15}N_2 \cdot xH_2O$ (where x is between 0 and 15) [Davies G. and Ghabbour E.A. 1999]. The composition and structures of humic substances in different aquatic systems can vary appreciably because of environmental factors such as water pH, biological processes and the presence of other chemical species that affect the concentration of humic substances. Commonly, humic substances consists of an organic component R onto which carboxylic (-COOH) and amide (-N(OH)H) groups are attached. Therefore, it can be said that humic substances are composed of hydrophobic and hydrophilic sites. The hydrophobic sites can form a complex with NOCs, while the hydrophilic sites can form a complex with positive-charged mineral surfaces. In acidic media the amide group takes in a proton and become (-N(OH)H^{+}_{2}) and this makes the humic substances cationic. In neutral and alkaline solution the carboxylic groups lose a proton to become (-COO^{-}). De-protonised carboxylic acids are well known as complexing agent for trivalent ions such as Fe^{3+} and Al^{3+}. To a lesser extent they will also form complexes with Mn. Some of the most important characteristics exhibited by all humic fractions are their resistance to microbial degradation [Amin S. and Jayson G.G. 1996]. A simple model of humic substances can be used to explain many of their properties describing them as having both amino and carboxyl groups and as such they exhibit amphoteric characteristics being cationic at low pH and anionic at high pH.

$$H^{+}_{2}(OH)N\text{-}R\text{-}COOH \xleftarrow{+H^{+}} H(OH)N\text{-}R\text{-}COOH \xrightarrow{+OH^{-}} H(OH)N\text{-}R\text{-}COO^{-} + H_2O$$

Figure 1.4: A simple model of humic substances

The removal of humic substances from water is desirable not only for aesthetical reasons but also for minimising possible health risks [Hodge I.G. 1996]. If humic substances are in high concentrations, it can react with chlorine used for disinfecting in wastewater treatment unit. The result is the production of trihalomethanes (THMs) which are suspected carcinogens. Moreover, owing to their prevalence and relative stability in natural water, humic substances are the most significant organic components that affect the removal of Synthetic Organic Chemicals (SOCs) by adsorption process. When both humic acid and SOCs are present and adsorbing simultaneously, humic substances can compete with the SOCs for available adsorption sites. SOCs have also been shown to bind to humic substances dispersed in the solution, and thus effectively enhance the solubility of target compounds and reduce the affinities for adsorption from solution. For example, a 50% reduction in adsorption capacity of activated carbon for trichlorophenol in the presence of humic substances has been reported in the literature [Dentel S.K. *et al.* 1996]. It is normal practice to reduce the level of the humic substances before chlorination and adsorption to minimise the risk.

1.3.2 Dye

Soluble dyes are organic electrolytes that dissociate to give coloured anions and/or cations [Correia V. and Judd S.J. 1997]. Dyes are mainly found in waste water from the textile industry [Sawyer C.N. *et al.* 1994]. Dyes, because they are intensely coloured, present special problems in effluent discharge; even a very small amount is noticeable. However, the effect is more aesthetically displeasing than hazardous [Anonymous 1997]. One azo anionic and one cationic dye were selected to study their adsorption phenomena on Montmorillonite and its modified forms in this project. The selection of representative dyes was based principally on molecular structure considerations, not on current dyeing practices.

Methylene blue

Methylene blue ($C_{16}H_{18}ClN_3S$) is a monovalent cationic or protonated form of dye in dye classification as C.I. Basic Blue 9; C.I. Solvent Blue 8; C.I. 52015 with molecular weight 373.9. It is principally used for dyeing silk, wood, paper, office stationary, cosmetic and in printing silk [Rhy P. and Zollinger H. 1972]. Therefore methylene blue might be found in the effluents of those industries. The formula of methylene blue is given in Figure 1.5.

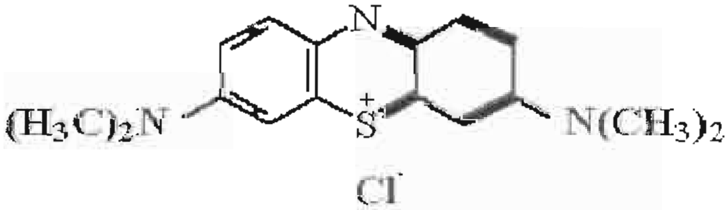

Figure 1.5: Molecular structure of methylene blue

A great deal of work has been done on the interaction of methylene blue with clays. The adsorption, by cation exchange mechanism, of methylene blue on clays in aqueous suspension leads to a concentration of the dyes in a small volume around the clay particles. The effective concentration of the dyes in this surface region is much higher than in solution and the dye molecules aggregate. Dimer, trimers and higher aggregates are formed [Schonheydt R.A. and Heughebaert L. 1992]. Methylene blue has been found to adsorb strongly to clays.

Methyl Orange

A large fraction of all the clothing manufactured today is coloured by the use of azo dyes. Methyl orange is an example of an azo anionic dye [Maeda Y. and Kitano H. 1995]. It is an intensely colored compound used in dyeing of synthetic fibers as well as the formulation of many industrial pigments and printing textiles, though it is not commercially useful for colouring clothing because it does not bind to most varieties of cloth strongly enough to prevent washing it out when the clothing is laundered. It is also known as C.I. Acid Orange 52; C.I. 13025; Helianthine B; Orange III; Gold Orange; Tropaeolin with molecular weight 327.34. Methyl orange is not biodegradable and also harmful if swallowed. It may cause eye, skin, respiratory and digestive tract irritation. The formula of methyl orange is given in Figure 1.6.

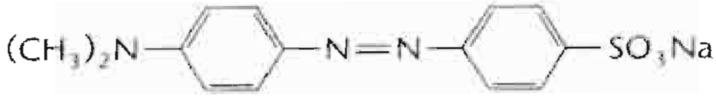

Figure 1.6: Molecular structure of methyl orange [Dutta R.K.and Bhat S.N. 1996]

1.3.3 Phenol

Phenolic compounds, the hydroxy derivative of benzene, require special mention because of their possible effects on the taste and odor quality of potable water, their potential toxicity to aquatic life in natural waters and their possible human health effects [Faust S.D. and Aly O.M. 1998]. The presence of phenolic compounds in water and wasterwater has been of great public concern [Srivastava S.K. *et al.* 1997]. Phenolic compounds are toxic to soil microorganisms at parts-per-million level. The fate of phenolic compounds in the environment and their removal from aqueous media is complicated by their low solubility, ability to ionize, low vapour pressure and tendency to undergo oxidation and oxidative polymerization with humic and fulvic acid-type products [Vansant E.F.1997]. The monohydroxy derivative of benzene is known as phenol (C_6H_5OH). The formula of phenol is given in Figure 1.7.

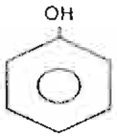

Figure 1.7: Molecular structure of phenol

Phenol is known to the layperson as carbolic acid. It ionizes to yield H^- to a limited extent ($K_a = 1.2 * 10^{-10}$). Phenol occurs as a natural component in industrial wastes from the coal-gas, coal-coking, and petroleum industries as well as in a wide variety of industrial wastes from processes involving the use of phenol as a raw material [Sawyer C.N. *et al.* 1994]. It is one of the most frequent contaminants at hazardous-waste sites. As the World Health Organization regulation, 0.002 mg L^{-1} is the permissible limit for phenol concentration in potable water [Srivastava S.K. *et al.* 1997].

1.3.4 Naphthalene

Naphthalene is an ideal hydrophobic component without polar functional groups. It is one of a large number of non-ionic contaminants found in soils, surface sediments and ground water [Magdaliniuk S. *et al.* 1995]. It is the smallest of the polyaromatics hydrocarbons (PAHs) which are found naturally in crude oil, creosote, coal tar and coal. Moreover it has been shown to be carcinogenic in experimental animals and thus pose a potential human health risk [Malakul P. *et al.* 1998]. The entry of naphthalene into soil and water compartments arises mainly due to discharges and spills during the storage, transportation and disposal of fuel oil and coal tar. The formula of naphthalene is given in Figure 1.8.

Figure 1.8: Molecular structure of naphthalene

Naphthalene has the strong aromatic odor that is associated with mothballs. Synonyms for naphthalene include mothballs, white tar, tar camphor and albo carbon.

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CHAPTER 2 MATERIALS AND METHODS

This chapter discusses the use of four different quaternary ammonium compounds (QACs), TMA, HDTMA, TDMA and TMA, for preparing 4 types of organo-clays. The objective of this task is to determine the effect of the number of carbon atoms in QACs used for the preparation of organo-clays on their physical properties and also on the adsorption affinity of each clay towards specific organic pollutants in aqueous systems. The choice of these organic molecules was mentioned in Chapter 1 and most of them are classified as the polluting elements.

2.1 Starting materials

2.1.1 Precursor clay

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

Table 2.1: Chemical composition (in weight%) of Montmorillonite

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

2.1.2 Hexadecyltrimethylammonium (HDTMA) solution

HDTMA, of molecular weight 364.46, was the Quaternary Ammonium Cation (QACs) selected for this study because it can be adsorbed on a negatively charged clay surface resulting the higher basal spacing of the clays and HDTMA ionization is not influenced by solution pH [Dental S.K. 1996]. The formula of HDTMA is $[CH_3(CH_2)_{15}](CH_3)_3N$ and was used without further purification The Critical Micelle Concentrations (CMCs) of HDTMA is 0.9 meq/L [Sullivan E.J. *et al* 1998].

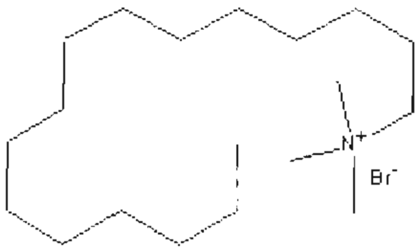

Figure 2.1: Molecular structure of HDTMA

2.1.3 Tetradecyltrimethylammonium (TDMA) solution

TDMA is another QACs used in the preparation of organo-clay in this work. The formula of TDMA is $[CH_3(CH_2)_{13}](CH_3)_3N$, supplied by Sigma Chemicals Ltd, was used without further purification. The Critical Micelle Concentrations (CMCs) of TDMA is 1.2 mol/m^3 [Huang L. *et al.* 1996].

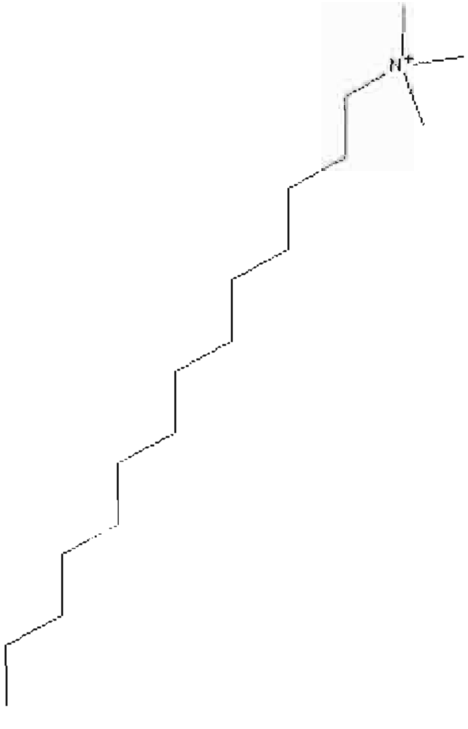

Figure 2.2: Molecular structure of TDMA

2.1.4 Tetramethylammonium (TMA) solution

TMA, of molecular weight 109.6, is the smallest QACs used in the preparation of organo-clay. The formula of TMA is $(CH_3)_4N$, supplied by Sigma Chemicals Ltd, was used without further purification.

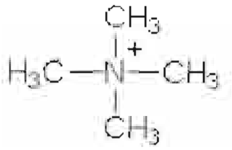

Figure 2.3: Molecular structure of TMA

2.1.5 Benzyldimethylhexadecylammonium (BDHDMA) solution

The formula of BDHDMA, of molecular weight 396, is $CH_3(CH_2)_{15}NCl(CH_3)_2$ $CH_2C_6H_6$ supplied by Fluka, was used without further purification.

Figure 2.4: Molecular structure of HDBDMA

2.2 Preparation of organo-clays

The solution of HDTMA, TDMA, HDBDMA and TMA were used separately as the modifying agent in the preparation of organo-clay. The synthesis was carried out in a batch reactor with 500 mL of each QACs solution. Twenty grams of Montmorillonite were added to this reactor and shaken for 24 hours to guarantee equilibrium. It has been reported that the adsorption of HDTMA on Montmorillonite usually reached equilibrium in 4-6 hours [Dentel *et al.* 1998]. Then the suspension was allowed to settle under gravity and washed with distilled water several times until the water conductivity was under 1.5 μS. The final suspension was separated from water by vacuum filtration and air-dried overnight at room temperature to avoid the destruction of that compound at higher temperature. It has been reported previously that if the clays are air dried, the layers settle down very slowly and all of them are oriented in the same parallel direction [Molinard A. and Vansant E.F. 1995]. It should also be mentioned that, for every experiment and preparation, the borosilicate first-class glassware was used.

Four different types of organo-clays produced were named after the QAC's used in the clay preparation as BDHDMA-clays, HDTMA-clays, TDMA-clays and TMA-clays respectively. The load QACs on clay was varied equivalent to 0.50, 1 and 2 times the CEC of Montmorillonite. It is to be noted that these QAC's loads are all beyond their CMC so they are in the forms of micelle. It has been previously reported that sorption of monomers QACs produced a lower sorption plateau that their equivalent micelle sorption [Sullivan E.J. *et al* 1998].

Since the adsorbent behaviour and ability are dependent on its physical properties such as its particle size, structure, and also surface area. The following methods were used to characterize the aforementioned physical properties. Surface area of adsorbent clays was measured using N_2 physical adsorption by Micromeritics ASAP 2000. XRD, using CuKα radiation, was used to determine the interlayer *d001* spacing of the clays. Particle size of the clays was also found using the Mastersizer. The results were summarized in Table 2.2.

Table 2.2: 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	*	22.872	3.86	49.1
50%CEC-TDMA clay	17.6	18.019	4.90	41.5
100%CEC-TDMA clay	10.4	21.325	4.14	50.6
200%CEC-TDMA clay	7.10	21.639	4.08	65.2
100%CEC-BDHDMA clay	*	24.253	3.64	72.34

Note

The BET surface area of 200%CEC-HDTMA clay and 100%CEC-BDHDMA clay are not found yet due to the technical problem.

HDTMA clays and TDMA-clays had lower BET surface area than Montmorillonite because most of the exchange sites of the organo-clays were satisfied by QACs species with large molecular size. These were attributed to the inaccessibility of the internal surface to nitrogen gas. The large differences in surface area between the raw and organo-clays are attributed to the nearly total blocking of the micropores in the surfactant-loaded material. On the other side, TMA-clays have the higher BET surface area than those of the raw clays and the organo-clays. The previous research indicated the higher degree of hydration of TMA cations causes shrinkage of the interlayer pores [Kukkadapu R.K. and Boyd S.A 1995].

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. The effect of particle size in surface area has been previously reported [Carrado K.A. 2000] that smaller sizes yield larger surface area, which is also true in this work.

The basal spacing determined by X-ray powder diffraction indicates that the QACs adsorbed between the interlaminar gaps of the clay since the *d001* spacing of the precursor Montmorillonite is lower than those of the QACs-modified forms. 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 Montmorillonite. This may support the notion 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 the QACs affect the interlayer spacing following the order TMA-clays < TDMA-clays < HDTMA-clays < BDHDTMA-clays which is consistent with the larger size of BDHDTMA ions compared to TMA ions. The value of *d001* spacings in Table 2.2 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 almost in agreement with the diameter of the TMA ion, which is 4.9 Å [Nzengung V.A. *et al* 1996]. 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 are not much. Therefore, the cation exchange mechanism might be dominant for the intercalation of the QACs between the interlayer of the clays.

2.3 Adsorption Experiments

The adsorption isotherms were carried out using a batch equilibration technique in a 500 mL conical flask. Each flask was filled with a specific type and a fixed amount of adsorbent and adsorbate, at a known concentration, depending on each experiment. A control sample with no adsorbent was also prepared. Besides, comparative adsorption experiments were conducted with the untreated Montmorillonite as a reference material. The flask was then closed and continuously shaken overnight to allow equilibrium to be achieved. The following day, the sample was centrifuged at 3500 rpm for 30 minutes to separate the adsorbent clays from the slurry. The supernatant was analysed for adsorbate concentration using the UV spectrophotometer. Several adsorption parameters, such as temperature, time and pH, were varied throughout the experiments in order to see their effects on the adsorption behavior of Montmorillonite. Moreover, in order to ensure the quality of the data, "blank" sample was prepared and handled in parallel for each adsorption test. A blank sample consisted of the adsorbent clay and water combined in a conical flask without any sorbate.

Table 2.3: UV maximum wavelength (λ_{max}) of adsorbate studied

Adsorbate	λ_{max} (nm.)
Humic Acid	400
Methylene blue	698
Methyl Orange	463
Chlorophenol	274
Phenol	269
Naphthalene	275

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