PHENOL ADSORPTION BY CTAB MODIFIED MONTMORILLONITE

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Abstract

This research involved the preparation of modified montmorillonite with cetyltrimetylammonium bromide (CTAB-MMT) by cation-exchange reaction. The CTAB – MMT contained about 27.2 %wt of CTAB. The CTAB could enlarge the gaps between layers of clay, therefore, the d_{001} was increased from 1.25 to 2.26 nm. The CTAB-MMT provided non-polar surface to adsorb phenol from water. The CTAB-MMT was used to adsorb phenol under batch adsorption, i.e. shaking and stirring, and column adsorption experiments. For the batch system, the effects of initial phenol concentration and adsorption time on the adsorption capacities were studied. The adsorption capacity of CTAB-MMT increased with increasing of initial phenol concentration and adsorption time. The mechanical stirring system showed higher adsorption capacity than the shaking system due to the effect of high phenol-adsorbent contact area. In the column system, the longer phenol-adsorbent contact time was obtained when low feed rate and high amount of CTAB – MMT were used, resulting in the higher %removal of phenol was obtained.

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Chapter 1
Introduction

1.1 Introduction

Nowadays water pollutants releasing from various industries such as pharmaceutical, petrochemical, and other chemical manufacturing processes are increased gradually. So industries need effective methods to remove those pollutants.

Among various pollutants, phenol is one of organic pollutant found in many industries which need to be removed before liberate to public water resources. So, various methods and materials are researched and developed to solve this problem including sorption, biological degradation, chemical oxidation, solvent extraction, activated carbons, polymeric resins, and organo clays. The adsorption of these pollutants by modified clay is a cheap, commonly applied and effective method which can minimize their harmful effects by reducing phenol concentration in water.

Clay is the popular adsorbent, however, clay is organophobic which is not suitable for adsorption organic compound. According to this reason modification of clay by organic surfactant is required. In modification, raw clay is swelled and treated with surfactant in order to change the surface of the soil material from organophobic to organophilic.

The adsorption capacity of organic surfactant modified clay will be studied under various conditions, i.e. pH and phenol concentrations in simulated wastewater and adsorption time, in comparison with other adsorbent.

1.2 Objective

1. To study the preparation of cetylmethylammoniumbromide modified montmorillonite (CTAB – MMT)
2. To study adsorption capacity of CTAB – MMT under various conditions, i.e., initial phenol concentrations, adsorption times and adsorption systems

1.3 Scopes of study

1. The CTAB – MMT was prepared and characterized by XRD and TGA.
2. The adsorption capacity was evaluate under various conditions as follow:
    - Phenol concentrations i.e. 100-1000 mg/L
    - Adsorption times i.e. 30, 60, 90 and 120 min
    - Adsorption system i.e. stirring, shaking and column
3. In the column system, the phenol absorption capacity was evaluated under various factors;
    - Feed flow rate
    - Amount of CTAB-MMT

1.4 Expected results

1. The effective adsorbent for phenol removal was prepared
2. Suitable condition for phenol adsorption was determined.

Chapter 2

Theory and Literature Reviews

2.1 Clay

Clay is one of the three principal types of soil, the other two being sand and loam. A certain amount of clay is a desirable constituent of soil, since it binds other kinds of particles together and makes the whole retentive of water. Excessively clayey soils, however, are exceedingly difficult to cultivate. Their stiffness presents resistance to implements, impedes the growth of the plants, and prevents free circulation of air around the roots. They are cold and sticky in wet weather, while in dry weather they bake hard and crack. Clods form very often in clayey soils. Clays can be improved by the addition of lime, chalk, or organic matter; sodium nitrate, however, intensifies the injurious effects. In spite of their disadvantages, the richness of clay soils makes them favorable to the growth of crops that have been started in other soil.

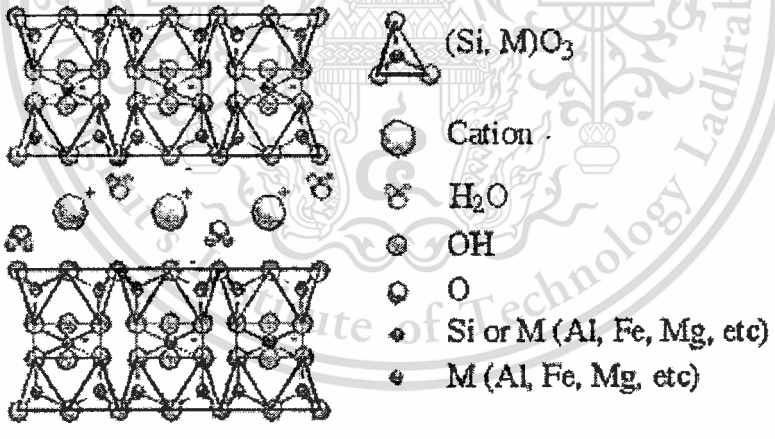

Figure 2.1: Basic layer structure of a natural clay mineral

Clays are distinguished from other fine-grained soils by various differences in composition. Silts, which are fine-grained soils which do not include clay minerals, tend to have larger particle sizes than clays, but there is some overlap in both particle size and other physical properties, and there are many naturally occurring deposits which include both silts and clays. The distinction between silt and clay varies by

discipline. Particles which have size between 1 – 4 μm in diameter will be considered as clay.

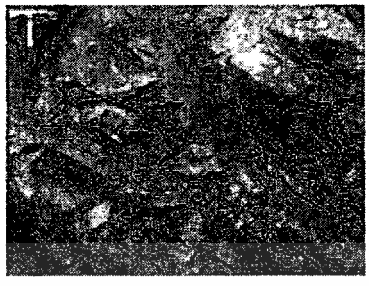

Figure 2.2: Quaternary clay in Estonia

Clay consists of a sheet of interconnected silicates combined with a second sheetlike grouping of metallic atoms, oxygen, and hydroxyl, forming a two-layer mineral such as kaolinite. Sometimes the latter sheetlike structure is found sandwiched between two silica sheets, forming a three-layer mineral such as vermiculite. In the lithification process, compacted clay layers can be transformed into shale. Under the intense heat and pressure that may develop in the layers, the shale can be metamorphosed into slate.

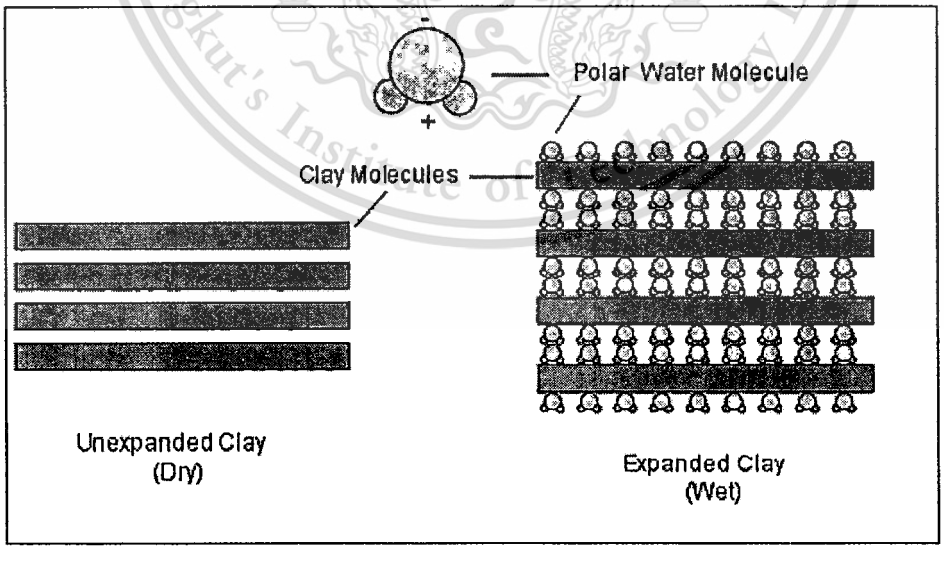

Figure 2.3: Sheets of clay

Clay is a naturally occurring material composed primarily of fine-grained minerals, which show plasticity through a variable range of water content, and which can be hardened when dried and/or fired. Clay deposits are mostly composed of clay minerals (phyllosilicate minerals), minerals which impart plasticity and harden when fired and/or dried, and variable amounts of water trapped in the mineral structure by polar attraction. Organic materials which do not impart plasticity may also be a part of clay deposits.

Clay minerals are typically formed over long periods of time by the gradual chemical weathering of rocks (usually silicate-bearing) by low concentrations of carbonic acid and other diluted solvents. In addition to the weathering process, some clay minerals are formed by hydrothermal activity. Clay deposits may be formed in place as residual deposits, but thick deposits usually are formed as the result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation. Clay deposits are typically associated with very low energy depositional environments such as large lake and marine deposits. This following equation show weathering of rock by carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 + CaCO_3 \xrightarrow{\text{carbonation}} Ca^{2+} + 2HCO_3^-$$

Figure 2.4: Equation of weathering rock with carbonic acid

Properties of the clays include plasticity, shrinkage under firing and under air drying, fineness of grain, color after firing, hardness, cohesion, and capacity of the surface to take decoration. On the basis of such qualities clays are variously divided into classes or groups; products are generally made from mixtures of clays and other substances. The purest clays are the china clays and kaolins. "Ball clay" is a name for a group of plastic, refractory (high-temperature) clays used with other clays to improve their plasticity and to increase their strength. Bentonites are clays composed of very fine particles derived usually from volcanic ash. They are composed chiefly of

the hydrous magnesium-calcium-aluminum silicate called montmorillonite. See also fuller's earth.

Individual clay particles are always smaller than 0.004 mm. Clays often form colloidal suspensions when immersed in water, but the clay particles flocculate (clump) and settle quickly in saline water. Clays are easily molded into a form that they retain when dry, and they become hard and lose their plasticity when subjected to heat.

2.1.1 Groups of clay

Depending upon academic source, there are three or four main groups of clays: kaolinite, montmorillonite-smectite, illite, and chlorite. Chlorites are not always considered a clay, sometimes being classified as a separate group within the phyllosilicates. There are approximately thirty different types of "pure" clays in these, but most "natural" clays are mixtures of these different types, along with other weathered minerals.

2.1.1.1 Montmorillonite

Montmorillonite is a member of the general mineral groups the clays. It typically forms microscopic or at least very small flat sheets consist of crystals. The water content is variable, and in fact when water is absorbed by the crystals they tend to swell to several times of their original volume. This makes montmorillonite a useful mineral for several purposes. It is the main component in a volcanic ash called bentonite. The bentonite gives the water greater viscosity("thickness" of flow), which is very important in keeping a drill head cool during drilling and facilitating removal of rock and dirt from within a drill hole. Another important use of montmorillonite is as an additive to soils and rocks. The effect of the montmorillonite is to slow the motion of water through the soil or rocks. This is important to farmers with extended dry periods, engineers of earthen dams or levees or perhaps to plug up old drill holes to prevent leakage of toxic fluids from bottom levels to higher aquifers used for drinking water.

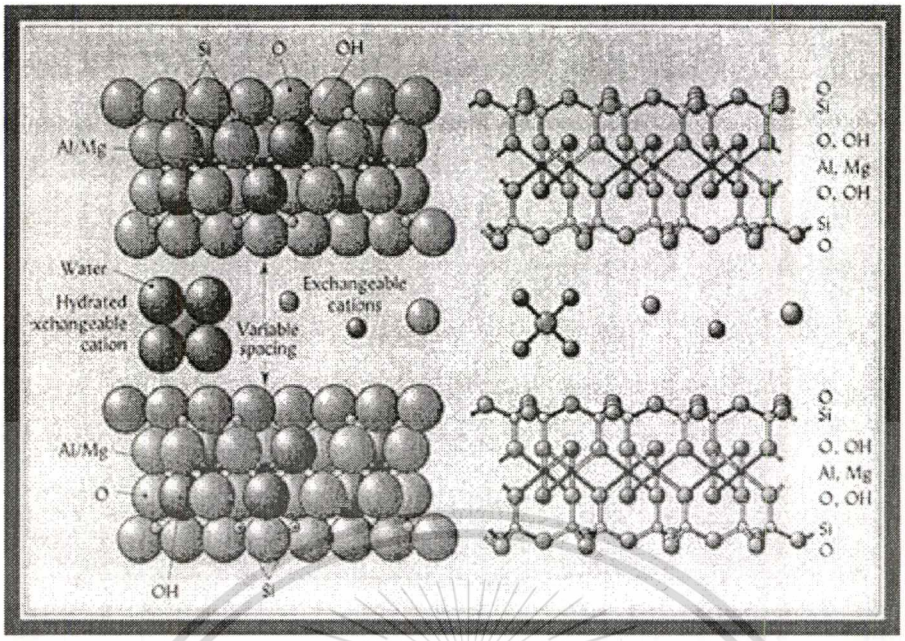

Figure 2.5: Layer structure of Montmorillonite

Montmorillonite clays also have wide commercial use. The high colloidal, plastic, and binding properties make them especially in demand for bonding molding sands and for oil-well drilling muds. They are also widely used to decolorize oils and as a source of petroleum cracking catalysts.

Similar to other clays, montmorillonite swells with the addition of water. However, some montmorillonites expand considerably more than other clays due to water penetrating the interlayer molecular spaces and concomitant adsorption. The amount of expansion is due largely to the type of exchangeable cation contained in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume. Hence, sodium montmorillonite has come to be used as the major constituent in non-explosive agents for splitting rock in natural stone quarries in order to limit the amount of waste, or for the demolition of concrete structures where the use of explosive charges is unacceptable.

This swelling property makes montmorillonite-containing bentonite useful also as an annular seal or plug for water wells and as a protective liner for landfills.

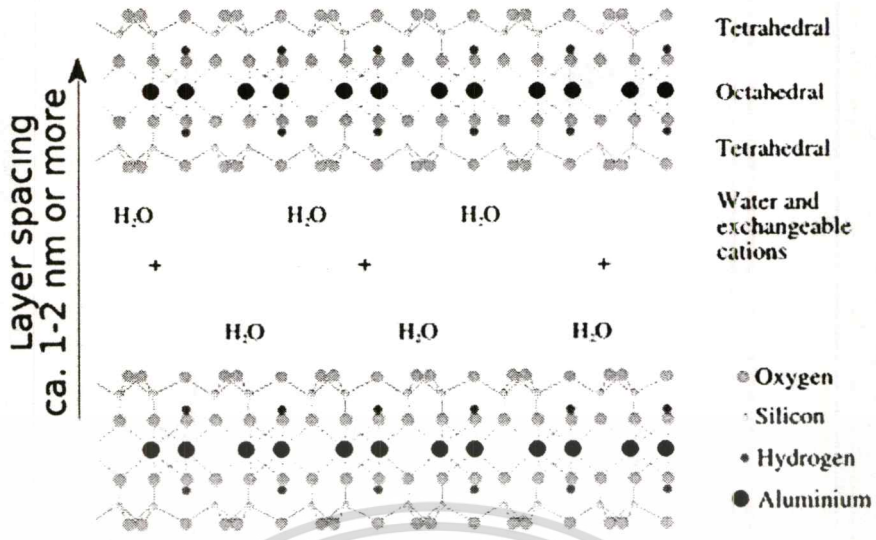

Figure 2.6: Layer structure of wetting Montmorillonite

As a mineral specimen, montmorillonite does not get much consideration. Usually, pure samples of montmorillonite are heavy, dull and not very attractive. However, as with all minerals, there are those exceptional specimens that defy the norm. Montmorillonite has been found as attractive pink inclusions in quartz crystals, and these make for interesting specimens.

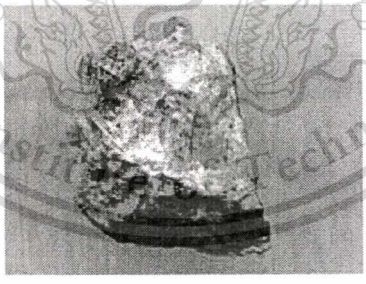

Figure 2.7: Montmorillonite

PHYSICAL CHARACTERISTICS:

- Color is usually white, gray or pink with tints of yellow or green.
- Luster is dull.
- Transparency crystals are translucent and masses are opaque.
- Crystal System is monoclinic; 2/m.
- Crystal Habits: never in large individual crystals, usually found in compact or lamellar masses. Also seen as inclusions in quartz as fibers and powder-like masses.
- Cleavage is perfect in one direction, basal; not seen in massive specimens.
- Fracture is uneven to lamellar.
- Hardness is 1- 2 (can sometimes leave marks on paper)
- Specific Gravity is variable from 2.3 - 3 (average)
- Streak is white.
- Other Characteristics: crystals expand to many times their original volume when added to water.
- Associated Minerals include other clays, garnets, biotite and quartz.
- Notable Occurances: include sources in France, Italy, USA and many other locallities world wide.
- Best Field Indicators softness, color, soapy feel, luster and expandability when added to water.

2.1.1.2 Kaolinite

Kaolinite, which is named for its type locality, Kao-Ling, Jianxi, China; is a common phyllosilicate mineral. Kaolinite's structure is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsite layers. The silicate and gibbsite layers are tightly bonded together with only weak bonding existing between these silicate/gibbsite paired layers (called s-g layers). The weak bonds between these s-g layers causes the cleavage and softness of this mineral.

Kaolinite shares the same chemistry as the minerals halloysite, dickite and nacrite. The four minerals are polymorphs; meaning they have the same chemistry, but different structures. All four minerals form from the alteration (mostly weathering) of aluminum rich silicate minerals such as feldspars.

Kaolinite is important to the production of ceramics and porcelain. It is also used as a filler for paint, rubber and plastics since it is relatively inert and is long lasting. But the greatest demand for kaolinite is in the paper industry to produce a glossy paper such as is used in most magazines.

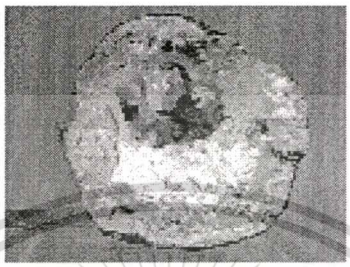

Figure 2.8: Kaolinite

PHYSICAL CHARACTERISTICS:

- Color is usually white, colorless, greenish or yellow.
- Luster is earthy.
- Transparency: Crystals are translucent.
- Crystal System is triclinic; 1.
- Crystal Habits include foliated and earthy masses. Crystals of any size are quite rare, usually microscopic.
- Cleavage is perfect in one direction, basal.
- Fracture is earthy.
- Hardness is 1.5 - 2 (can leave marks on paper).
- Specific Gravity is 2.6 (average).
- Streak is white.
- Best Field Indicators are habit, softness, color, luster and clay like properties.

2.1.1.3 Illite

Illite is essentially a group name for non-expanding, clay-sized, dioctahedral, consisting of minerals. It is structurally similar to muscovite in that its basic unit is a layer composed of two inward-pointing silica tetragonal sheets with a central octahedral sheet. However, illite has on average slightly more Si, Mg, Fe, and water and slightly less tetrahedral Al and interlayer K than muscovite (Bailey, 1980). The weaker interlayer forces caused by fewer interlayer cations in illite also allow for more variability in the manner of stacking (Grim, 1962). Glauconite is the green iron-rich member of this group.

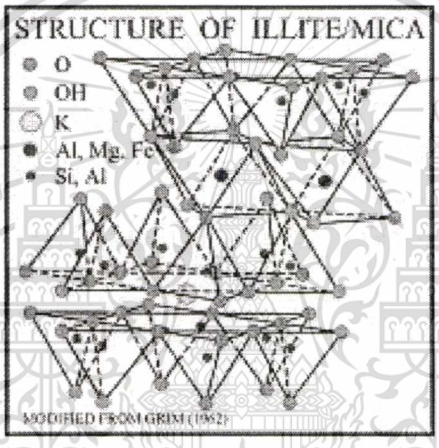

Figure 2.9: Structure of Illite

Illites, which are the dominant clay minerals in argillaceous rocks, form by the weathering of silicates (primarily feldspar), through the alteration of other clay minerals, and during the degradation of muscovite (Deer and others, 1975). Formation of illite is generally favored by alkaline conditions and by high concentrations of Al and K. Glauconite forms authigenically in marine environments and occurs primarily in pelletal form.

Members of the illite group are characterized by intense 10-angstrom 001 and a 3.3-angstrom 003 peaks that remain unaltered by ethylene glycol or glycerol solvation, potassium saturation, and heating to 550 degrees C (Fanning and others, 1989). Glauconite can be differentiated from illite by a 1.5- to 1.52-angstrom 060 peak (illite's 060 peak occurs at 1.50 angstroms), and by the presence of only a very weak 5-angstrom 002 peak.

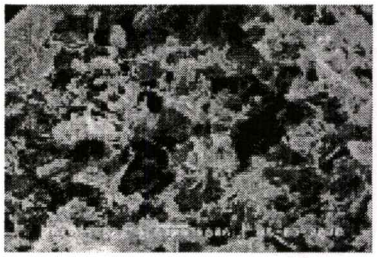

Figure 2.10: Illite

PHYSICAL CHARACTERISTICS:

- Color is usually white or colorless.
- Luster is earthy (Dull).
- Transparency: Crystals are translucent.
- Crystal System is triclinic; 1.
- Crystal Habit is Aggregates (Made of numerous individual crystals or clusters).
- Cleavage is perfect in one direction, basal.
- Hardness is 1 – 2 (Between Talc and Gypsum).
- Specific Gravity is 2.75 (average).
- Streak is white.
- Best Field Indicators are habit, softness, color, luster and clay like properties.

2.2.1.4 Cholrite

Chlorite is a general name for several minerals that are difficult to distinguish by ordinary methods. These minerals are all apart of the Chlorite Group of minerals. The chlorites are often, but not always considered a subset of the larger silicate group, The clays.

The general formula for chlorite is (Fe, Mg, Al)6(Si, Al)4O10(OH)8. However there are several different minerals that are apart of the chlorite group of minerals. The above formula is only a generalization of the more common members of this group.

For practical reasons most of the chlorites will be considered here as a single mineral, chlorite. Chlorites are generally green and crystallize in the monoclinic symmetry system. They all have a basal cleavage due to their stacked structure. Chlorites typically form flaky microscopic crystals and it is this reason that they are sometimes included in the clay group of minerals. However chlorites also form large individual tabular to platy crystals that are unlike most of the other clay minerals.

Chlorites are most often known to mineral collectors as inclusions in or coatings on quartz, danburite, topaz, calcite and many other minerals. The inclusions are usually a very strong green color despite the small amount of material that actually constitutes the inclusion. These inclusions and coatings can be an enhancement but are more often a bane to what might have been a really valuable mineral specimen.

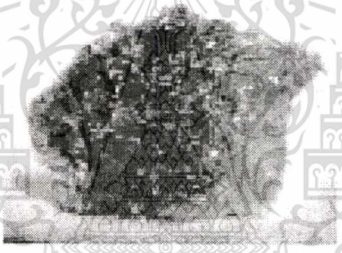

Figure 2.11: Chlorite

THE PHYSICAL CHARACTERISTICS OF CHLORITE:

- Color is usually green but can also be white, yellow, red, lavender and black.
- Luster is vitreous, dull or pearly.
- Transparency: Crystals are translucent transparent.
- Crystal System is monoclinic; 2/m.
- Crystal Habits: Rarely in large individual barrel or tabular crystals with an hexagonal outline. Usually found as alteration products of iron-magnesium minerals and as inclusions in other minerals. Aggregates can be scaly, compact, platy and as crusts.
- Cleavage is perfect in one direction, basal; not seen in massive specimens.
- Fracture is lamellar.
- Hardness is 2 - 3
- Specific Gravity is variable from 2.6 - 3.4 (average to slightly above average)
- Streak is pal green to gray or brown.
- Best Field Indicators color, cleavage, associations and crystal habits.

2.2 Organoclay

Organoclays are manufactured by modifying bentonite with quaternary amines, a type of surfactant that contains a nitrogen ion. The nitrogen end of the quaternary amine, the hydrophilic end, is positively charged, and ion exchanges onto the clay platelet for sodium or calcium, the most common cations that balance the charges of a montmorillonite clay platelet. The amines used are of the long chain type with 12-18 carbon atoms. After some 30 per cent of the clay surface is coated with these amines it becomes hydrophobic and, with certain amines, organophilic.

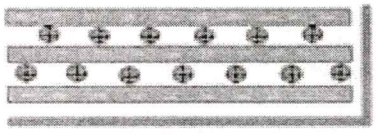

Figure 2.12: Layer structure of clay before modifying

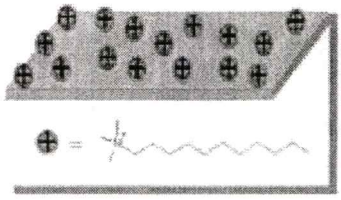

Figure 2.13: Cation of clay are exchanged with organic compound.

The main component of organoclay is bentonite, a chemically altered volcanic ash that consists primarily of the clay mineral montmorillonite. The bentonite in its natural state can absorb up to seven times its weight in water, after treatment can absorb only 5 to 10 per cent of its weight in water, but 40 to 70 per cent in oil, grease, and other sparingly-soluble, hydrophobic chlorinated hydrocarbons.

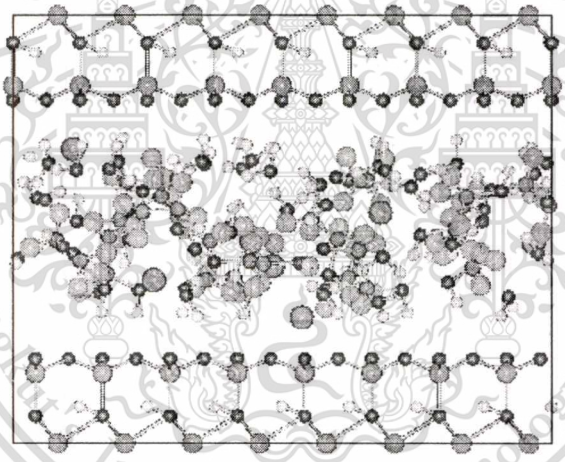

Figure 2.14: Organic compound in clay

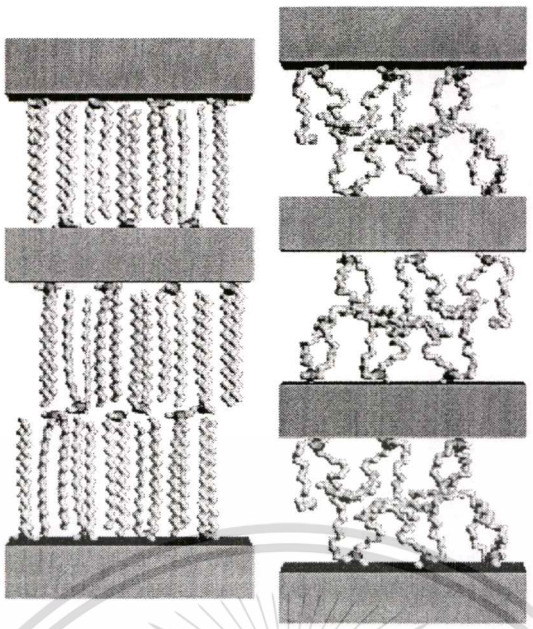

Figure 2.15: Surfactant in clay

As the organoclay is introduced into water, the quaternary amine is activated and extends perpendicularly off the clay platelets into the water. A chlorine or bromine ion is loosely attached to the carbon chain. Since the sodium ions that were replaced by the nitrogen are positively charged, they bond with the chlorine ion, resulting in sodium salt that is washed away. The result is a neutral surfactant with a solid base, which is the organoclay. The hydrophilic end of the amine dissolves into the oil droplet because "like dissolves like," thus removing that droplet from water. Because the partition reaction takes place "outside" of the clay particle (in contrast to adsorption of oil by carbon, which takes place inside its pores), the organoclay does not foul quickly.

Organophilic clay can function is as a prepolisher to activated carbon, ion exchange resins, and membranes (to prevent fouling), and as a post polisher to oil/water separators, dissolved air flotation (DAF) units, evaporators, membranes, and skimmers. Organophilic clay powder can be a component or the main staple of a flocculent clay powder. They are excellent adsorbers for the removal of oil, surfactants, and solvents, including methyl ethyl ketone, t-butyl alcohol (TBA), and others.

Application

- By removing oil and greases at an extremely high volume/wieght ratio, organophilic clays can save an end user fifty per cent or more of operations costs. Organophilic clay may be disposed of through landfilling, fuel blending, asphalt plants, or stabilization. As long as the clay passes the liquid paint filtration test, it can be disposed of in the dumpster of a facility whose contents are landfilled.
- Environmental applications of organophilic clays include groundwater cleanup at old disposal sites and underground storage tank sites as well as the treatment of landfill leachates. Industrial applications include air compressors, cooling water, deburring and metal finishing, gas compressors, boiler blow-down, boiler feed water, metal casting, general manufacturing process water, water produced at oil well drilling sites, and stormwater.
- Most applications to date have been in groundwater remediation at US Superfund sites, underground storage tank sites, landfill leachate cleanup, and de-watering of contaminated sites during construction.
- Industrial applications for organoclay use include air compressors, cooling water, deburring and metal plating process water, boiler blowdown, boiler feed water, refinery waste water, steel mill waste water, etc.

2.3 Surfactant

A member of the class of materials that, in small quantity, markedly affect the surface characteristics of a system; also known as surface-active agent. In a two-phase system, for example, liquid-liquid or solid-liquid, a surfactant tends to locate at the interface of the two phases, where it introduces a degree of continuity between the two different materials. Soaps and detergents are classic examples of surfactants due to their dual (amphipathic) character, meaning they contain both hydrophobic groups (their "tails") which like to dissolve is water and usually a long – chain hydrocarbon and hydrophilic groups (their "heads")which dislike to dissolve in water and often ionic. Therefore, It tends to dissolve in both aqueous and oil phase and to locate at the oil-water interface.

Surfactants are employed to increase the contact of two materials, sometimes known as wettability or wetting agents, which lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. Surfactants and surface activity are controlling features in many important systems, including emulsification, detergency, foaming, wetting, lubrication, water repellance, waterproofing, spreading and dispersion, and colloid stability.

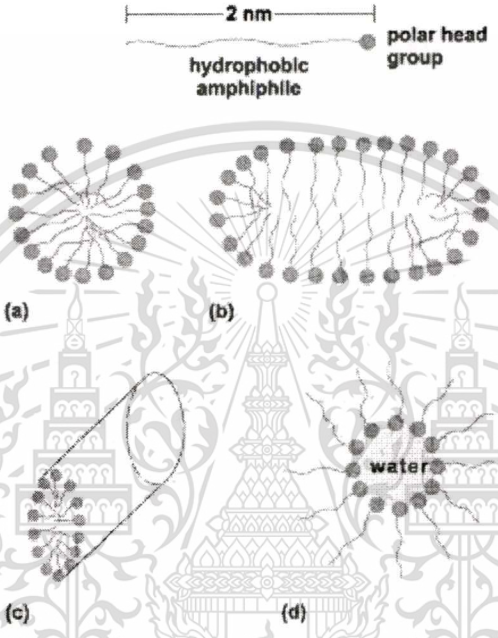

Figure 2.16: Surfactant and micelle

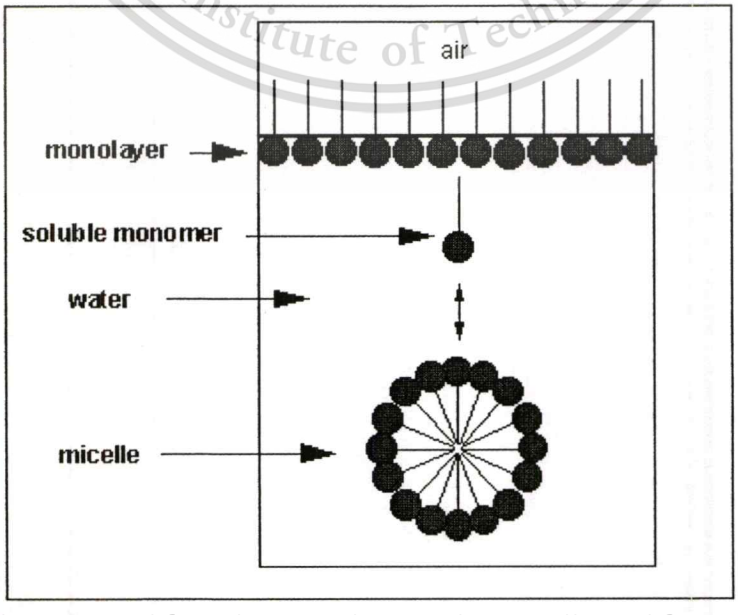

Figure 2.17: Micelle formation

A colloidal aggregate of a unique number (50→100) of amphipathic molecules, which occurs at a well-defined concentration called the critical micelle concentration. In polar media such as water, the hydrophobic part of the amphiphiles forming the micelle tends to locate away from the polar phase while the polar parts of the molecule (head groups) tend to locate at the polar micelle solvent interface. A micelle may take several forms, depending on the conditions and composition of the system, such as distorted spheres, disks, or rods (see illustration). Micelles are formed in nonpolar media such as benzene, where the amphiphiles cluster around small water droplets in the system, forming an assembly known as a reversed micelle.

Quite different materials, such as polymers and clays, can also exhibit surface activity; many polymeric materials, for example, polyvinyl alcohol and polyacrylamide, are excellent stabilizers for a variety of colloid systems. These entities adsorb at the colloid interface and, by means of steric effects, prevent colloid-colloid adhesion and flocculation. Clays readily adsorb other materials or adsorb onto large particles suspended in solution, so that the particle interface consists of charged clay particles, which increase colloid stability by electrostatic and steric effects.

2.3.1 Types of surfactant

A surfactant can be classified by the presence of formally charged groups in its head. A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Some commonly encountered surfactants of each type include:

Ionic

1. Anionic (based on sulfate, sulfonate or carboxylate anions)
    - Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts
    - Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES)
    - Alkyl benzene sulfonate

- Soaps, or fatty acid salts

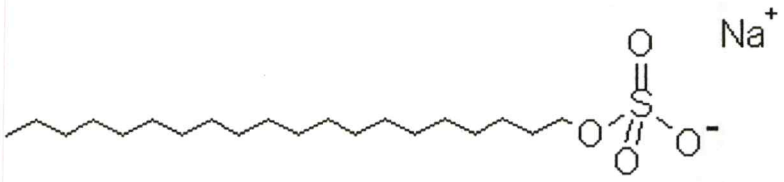

Figure 2.18: Example of anionic surfactant

2. Cationic (based on quaternary ammonium cations)
   - trimethylammonium bromide (CTAB) a.k.a. hexadecyl trimethyl ammonium bromide, and other alkyltrimethylammonium salts
   - Cetylpyridinium chloride (CPC)
   - Polyethoxylated tallow amine (POEA)
   - Benzalkonium chloride (BAC)
   - Benzethonium chloride (BZT)

Figure 2.19: Example of cationic surfactant

3. Zwitterionic (amphoteric)
   - Dodecyl betaine
   - Dodecyl dimethylamine oxide
   - Cocamidopropyl betaine
   - Coco ampho glycinate

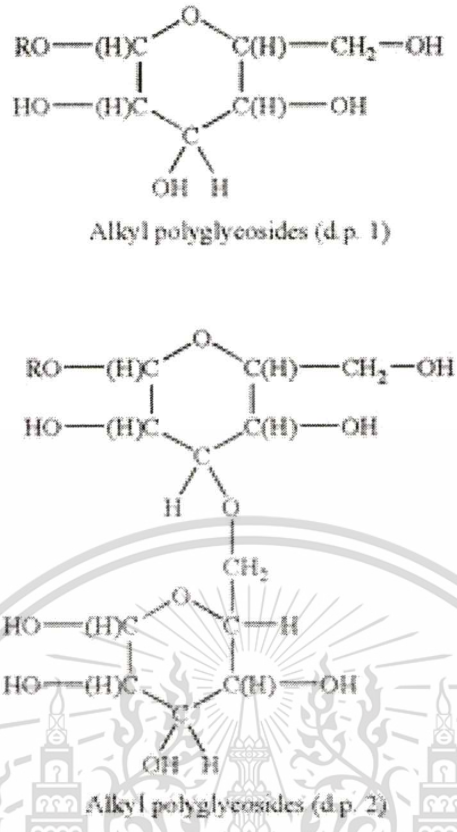

Figure 2.20: Example of amphoteric surfactant

4. Nonionic
   - Alkyl poly(ethylene oxide)
   - Copolymers of poly(ethylene oxide) and poly(propylene oxide) (commercially called Poloxamers or Poloxamines)
   - Alkyl polyglucosides, including:
   - Octyl glucoside
   - Decyl maltoside
   - Fatty alcohols
   - Cetyl alcohol
   - Oleyl alcohol
   - Cocamide MEA, cocamide DEA

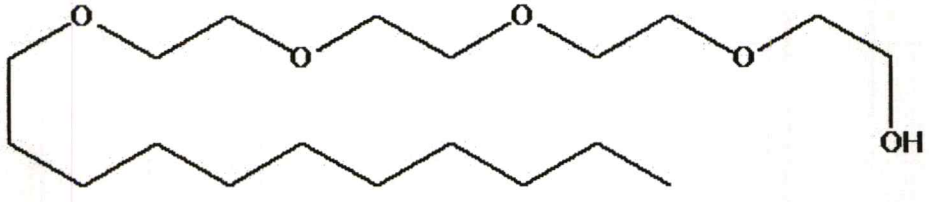

Figure 2.21: Example of nonionic surfactant

2.3.2 Operation and effects

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

2.4 Phenol

Phenol is also used to refer to any compound that contains a six-membered aromatic ring, bonded directly to a hydroxyl group (-OH). Chemical formula can be written as C6H5OH. In effect, phenols are a class of organic compounds. Phenol is a toxic, colourless or white crystalline solid with a sweet tarry odor. It evaporates more slowly than water and dissolves fairly well in water. Phenol can catch on fire. It has to be handled with great care because it causes immediate white blistering to the skin.

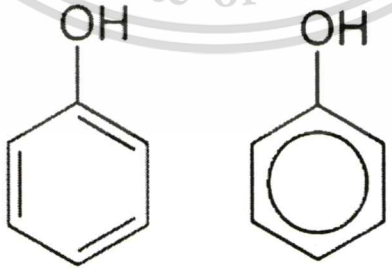

Figure 2.22: Structure of phanol

2.4.1 Acidity of phenol

Phenol has a limited solubility in water (8.3 g/100 ml). It is slightly acidic: The phenol molecule has weak tendencies to lose the H+ ion from the hydroxyl group, resulting in the highly water-soluble phenoxide anion $C6H5O^-$. Compared to aliphatic alcohols, phenol shows much higher acidity; it even reacts with aqueous NaOH to lose H^+, whereas aliphatic alcohols do not. One explanation for the increased acidity is resonance stabilization of the phenoxide anion by the aromatic ring. In this way, the negative charge on oxygen is shared by the ortho and para carbon atoms. In another explanation, increased acidity is the result of orbital overlap between the oxygen's lone pairs and the aromatic system. In a third, the dominant effect is the induction from the sp^2 hybridised carbons ; the comparatively more powerful inductive withdrawal of electron density that is provided by the sp^2 system compared to an sp^3 system allows for great stabilization of the oxyanion.

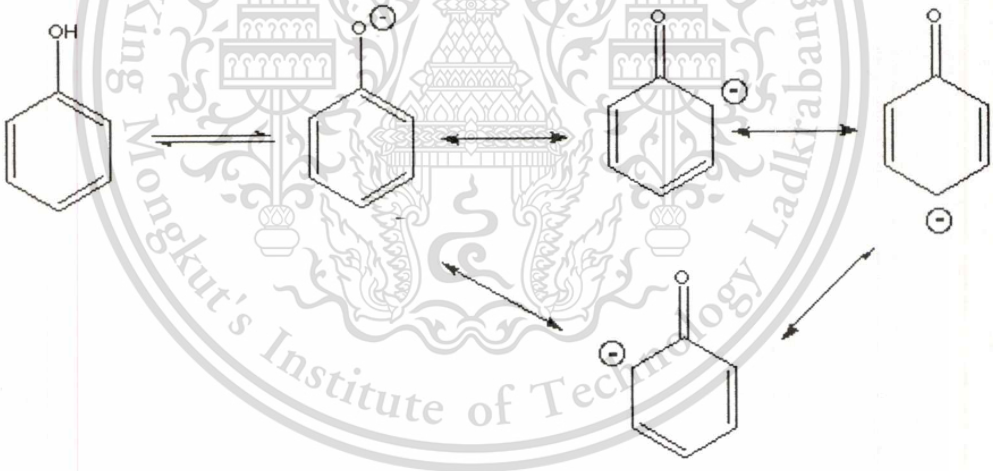

Figure 2.23 Delocarization of phenol

2.4.2 Solubility in water

Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water. If you try to dissolve more than this, you get two layers of *liquid*. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol. The solubility behavior of phenol and water is complicated, and beyond UK A level. Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

Phenol is mainly a man-made chemical, although it is found in nature in animal wastes and organic material. The largest single use of phenol is to make plastics, but it also is used to make caprolactam (used to make nylon 6 and other man-made fibers) and bisphenol A (used to make epoxy and other resins). It also is used as a slimicide (a chemical that kills bacteria and fungi found in watery slimes), as a disinfectant, and in medical products.

Small, single releases of phenol do not stay long in the air (usually half is removed in less than 1 day), and usually do not stay in the soil for long periods (usually completely gone in 2-5 days), but can stay in water for longer than 9 days. Phenol will stay in the air, soil, and water for much longer times if a large amount of it is released at one time, or if a steady amount is released over a long time. More phenol than is usually found in the environment has been found in surface waters and surrounding air that were contaminated when phenol was released from industries and commercial products that contain phenol. Phenol has been found in materials released from landfills and hazardous waste sites, and it has been found in the groundwater near these sites. Phenol is usually found in the environment below 100 parts per billion (ppb), although much higher levels have been reported. One ppb or less of phenol has been found in relatively unpolluted surface and ground waters.

Health Effects

- The serious effects of a harmful substance usually increase as both the level and length of exposure increase. Repeated exposure to low levels of phenol in drinking water has been linked with diarrhea and mouth sores in humans; eating very large amounts of phenol has resulted in death. Laboratory animals that drank very large amounts of phenol in water had muscle tremors and loss of coordination.
- The effects on humans of breathing phenol in air are unknown. Exposure of animals to high levels of phenol in air for a few minutes is irritating to the lungs, and repeated exposure for several days causes muscle tremors and loss of coordination. Exposure to high levels of phenol for several weeks results in paralysis and severe injury to the heart, kidneys, liver, and lungs, followed by death in some cases.

- When exposures involve the skin surface, the size of the total exposed skin can influence the severity of the toxic effects. Small amounts of phenol put on the skin of animals for short times can cause blisters and burns on the exposed area, and spilling weak phenol solutions on large parts of the body (more than 25% of the body surface) can result in death.
- The effects of exposure to phenol on human reproduction and the developing fetus are unknown. Pregnant animals that drank water containing high amounts of phenol gave birth to offspring that had low birth weights and birth defects. We do not know whether phenol causes cancer in humans, but cancer occurs in mice when phenol is put on the skin. When phenol is combined with other chemicals that cause cancer and put on the skin, more cancer may occur than when the other chemicals are put on alone.

2.5 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process.

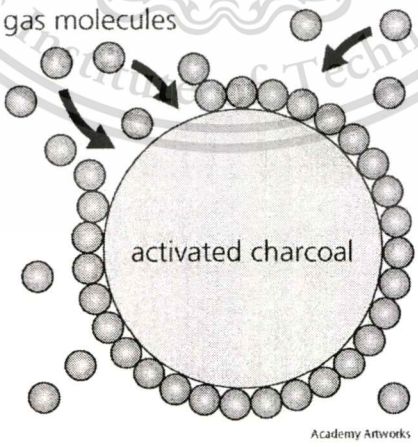

Figure 2.23: Adsorption of gas on activated charcoal

Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. Sorption is a more general term that includes both adsorption and absorption. Desorption refers to the reverse of adsorption, and is a process in which molecules adsorbed on a surface are transferred back into a bulk phase. The term adsorption is most often used in the context of solid surfaces in contact with liquids and gases. Molecules that have been adsorbed onto solid surfaces are referred to generically as adsorbates, and the surface to which they are adsorbed as the substrate or adsorbent.

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding) which describe in following article.

2.5.1 Mechanical of the adsorption.

Mechanical of the adsorption can divide to 2 types.

1. Physisorption: happen because of Wan Der Vaal force and the reversible process when the efficiency of the inventory has absorbed to is ruined go to already must do new recovery (Regeneration). For the inventory absorbs to have the ability in absorbing well such as originally which often use high heat in the restoration. In this step is will have losing inventory absorbs to go to about 5% of inventory quantity absorbs. And if the force between solute and

adsorbent more than the solvent and the absorbent will be absorbing quite right stripes give stick where the surface of the absorbent.

Characteristic of physisorption

- Low ambient temperature, always under the critical temperature of the adsorbate;
- Type of interaction: Intermolecular forces (van der Waals forces);
- Low enthalpy: $\Delta H < 20$ kJ/mol;
- Adsorption takes place in multilayers;
- Low activation energy.
- The energy state of adsorbate is not altered.
- Reversible.

2. Chemisorption: happen because of the chemical reaction between solid and the absorbent and the procedure is irreversible. When the efficiency of the absorbent is ruined go to already. It can not do new recovery (Regeneration) of the absorbent like the Physisorption.

Characteristic of chemisorption

- High temperatures.
- Type of interaction: strong; covalent bond between adsorbate and surface.
- High enthalpy: 50 kJ/mol $<\Delta H<$ 800 kJ/mol
- Adsorption takes place only in a monolayer.
- High activation energy
- Increase in electron density in the adsorbent-adsorbate interface.
- Reversible only at high temperature.

2.6 Related literature reviews

L. Yan et.al [31] Studied on the effect of lead on the sorption of phenol onto montmorillonites and organo-montmorillonites using a batch equilibration method when phenol and Pb were sorbed simultaneously and either Pb or phenol was previously sorbed. The sorbents were Na-MMT, Ca2-MMT, hexadecyl trimethylammonium (HDTMA)-Na-MMT, and HDTMA-Ca-MMT. Pb diminished the sorption of phenol largely onto Na-MMT or Ca2-MMT, while phenol had little effect on the sorption of Pb onto all sorbents. Pb had no effect on the sorption of phenol onto HDTMA-Na-MMT or HDTMA- Ca2-MMT either. The sorption capacity of phenol followed the order HDTMA-Na-MMT > HDTMA- Ca2-MMT > Na-MMT > Ca2-MMT. The pseudo-second-order equation described the kinetics of phenol sorption well. Sorption isotherms of phenol followed the Freundlich equation. Phenol sorption on HDTMA-Na-MMT and HDTMA- Ca2-MMT was linear, while that on Na-MMT and Ca2-MMT was nonlinear.

T. Okada et.al [32] Studied about the effect of the molecular structure of cationic azo dye on the photoinduced intercalation of phenol in a montmorillonite. Two types of cationic azo dyes were used; one has (2-hydroxyethyl) dimethylammonium group (AZ(OH)+), and the other has trimethylammonium group (AZ(CH3)+). Phenol was intercalated into both cation exchanged azo dye-montmorillonites (Kunipia F) by mechanical mixing without solvent. By the UV irradiation, the basal spacings increased further, and subsequent visible light irradiation led to decrease the basal spacings, indicating the intercalation and the deintercalation of phenol by the UV and visible light, respectively. The amounts of the phenol intercalated both chemically and photochemically varied depending on the azobenzene cations, showing the interactions between the cationic head group and phenol.

R. Juang et.al [33] Studied about sorption of phenol from water in column systems using surfactant-modified montmorillonite. The sorption isotherms were fitted by the Langmuir equation. Column experiments were performed at 25 °C to determine the breakthrough curves at different flow rates, feed sorbate concentrations, and bed lengths. It was shown that the proposed constant-pattern wave approach with the Langmuir model could well describe the breakthrough curves. The time required when the effluent concentration reached half of the feed concentration (t1/2) decreased with increasing feed flow rate, but the mass transfer coefficient (KLa)

increased. In addition, an increase in feed sorbate concentration led to a decrease of both values of t1/2and KLa. The effect of axial dispersion on breakthrough dynamics in these sorption systems was finally discussed.

Chapter 3
Experimental

The objective of this part of the study is to modify montmorillonite with a surfactant for phenol adsorption. The data was compared to the standard curve to obtain the amount of phenol adsorbed. The results were repeated at various concentrations to study the effect of concentration on adsorption.

3.1. Chemicals

1. Clay (Montmorironite, MMT), Mac Gel, Thai Nippon Chemical Industry
2. Cationic surfactant (CTAB), AR grade, Arcros organic
3. Silver nitrate solution($AgNO_3$), AR grade, CARLO ERBA

3.2. Instrument

1. Glassware
2. Oven
3. Vacuum filter
4. Filter paper, 5B, Toyo Roshi Kaisha, Ltd.
5. Magnetic Stirrer
6. Sonication machine, 14H, Ney Dental
7. X-ray Diffractometer; XRD, D8 Advance, Broker AG
8. Thermogravimetric Analyzer; TGA, Pyris 1 TGA, Perkin Elmer
9. UV-Visible spectrophotometer, Helιosα (double beam) thermo electron Corporation

3.3. Preparation of the CTAB-modified clays

1. Disperse 2 g montmorillonite into 500 ml water.
2. Prepare 10 ml of 0.2M CTAB solution, add slowly into the mixture from 1 and stir it for 3 hours.
3. Filter the modified MMT from solution by vacuum suction and washed with distillation water until the white precipitate absented. When test with 0.1% $AgNO_3$ solution.
4. Dry the precipitate in an oven at 80°C for overnight.

5. Grind and sieve with 400-mesh. Sieve
6. Characterize the modified MMT by XRD and TGA.

3.4. Characterization

3.4.1. XRD

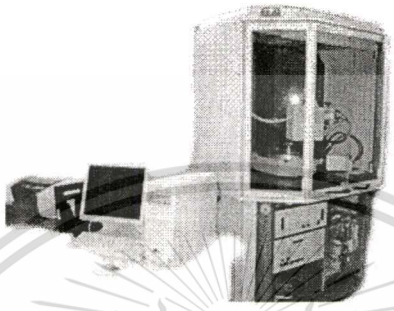

Figure 3.1: X-ray Diffractometer; XRD

X-ray powder diffraction (XRD) is analytical technique was used for phase identification of a crystalline material such as size and orientation of crystalline.

Analysis condition

2□ to analysis	1°-35°
Step size	0.04°
Step time	5 sec

3.4.2 TGA

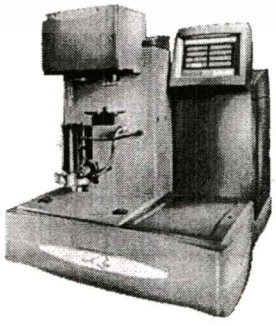

Figure 3.2: Thermogravimetric Analyzer; TGA

This technique is use to determine the CTAB content in the modified MMT by putting dry powder in a small furnace inside the heater chamber.

Analysis condition	
Temperature range	50-800 °C
Temperature rate	10 °C/min
Nitrogen flow	20 ml/min
Sample weight	5-10 mg

3.5. Batch adsorption experiments

3.5.1 Effect of initial phenol concentration

1. 2 g of air-dried CTAB modified clay was added into 30 ml of 80, 100, 300, 500 and 800 mg/L phenol solution.
2. The mixture was continuously mixed at room temperature by shaking at 150 rpm for 30 min.
3. The sample mixture was filtered with 5B filter paper.
4. Dry the precipitate at 80 °C in an oven for one night.
5. The phenol solution was measured the concentration by using UV-Vis Spectrophotometer.
6. The standard solutions of phenol (10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/L) were prepared and measured UV-absorbance by using UV-VIS spectrophotometer technique at 270 nm.

3.5.2 Effect of adsorption time

1. 2 g of air-dried CTAB modified clay was added into 30 ml of 100 mg/L phenol solution.
2. The mixture was continuously mixed at room temperature by shaking at 150 rpm.
3. Sampling the adsorbed solution at 10, 20, 30, 60, 90, 120 min
4. The sample mixture was filtered with 5B filter paper.
5. Dry the precipitate dried at 80 °C in an oven for one night.
6. Sampling adsorbed phenol solution was measured the concentration by using UV-Vis Spectrophotometer.

3.5.3 Effect of adsorption system

1. 2 g of air-dried CTAB modified clay was added into 30 ml for 2 batch of 100, 500, and 800 mg/L phenol solution.
2. First batch is continuous shake at 150 rpm for 30 min whereas second batch is continuous stirred for 30 min also.
3. The sample mixture was filtered with 5B filter paper.
4. Dry precipitate at 80 ℃ in an oven for one night.
5. Sampling adsorbed phenol solution was measured the concentration by using UV-Vis Spectrophotometer.

3.6 Column adsorption experiment

1. 7.5 g of CTAB-MMT was measured and packed into column in which it was pecked between 1 inch height of sand at the bottom and top.
2. The phenol solution was fed by using high pressure pump.
3. The effluent of phenol solution was collected every 10 ml
4. The phenol concentration of collected solution was measured by UV-Vis Spectrophotometer.
5. Repeat experiment with various conditions

Using 7.5 g of CTAB-MMT and low pressure pump.

Using 5 g of CTAB-MMT and low pressure pump.

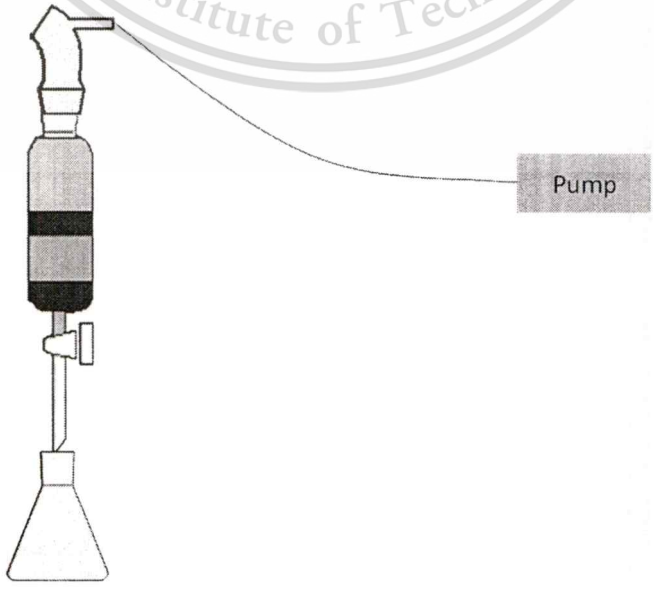

Figure 3.3: Column adsorption experiment

Chapter 4

Result and discussion

This research studied the adsorption of phenol by organoclay which was the montmorillonite (MMT) modified with cetyltrimethylammoniumbromide cation surfactant (CTAB). CTAB surfactant could exchange with sodium cation on the MMT surface to enlarge the basal spacing and provide a larger non-polar active sites for interaction with phenol.

4.1 Characterization of MMT and CTAB-MMT

4.1.1 XRD

X-ray diffraction method (XRD) is used to analyze the crystalline compounds. Figure 4.1 shows the XRD patterns of the starting montmorillonite (MMT) and the CTAB modified MMT (CTAB-MMT). Before modification, characterization of MMT with XRD technique gave peak at 2□ = 7.085° as a results according to Figure 4.1B. Corresponding to d-spacing of MMT is 1.25 nm. While the CTAB-MMT gave a peak at 2□ = 3.915 ° which is 2.26 nm. The larger gap between sheets of MMT indicated the interrelation of CTAB in MMT.

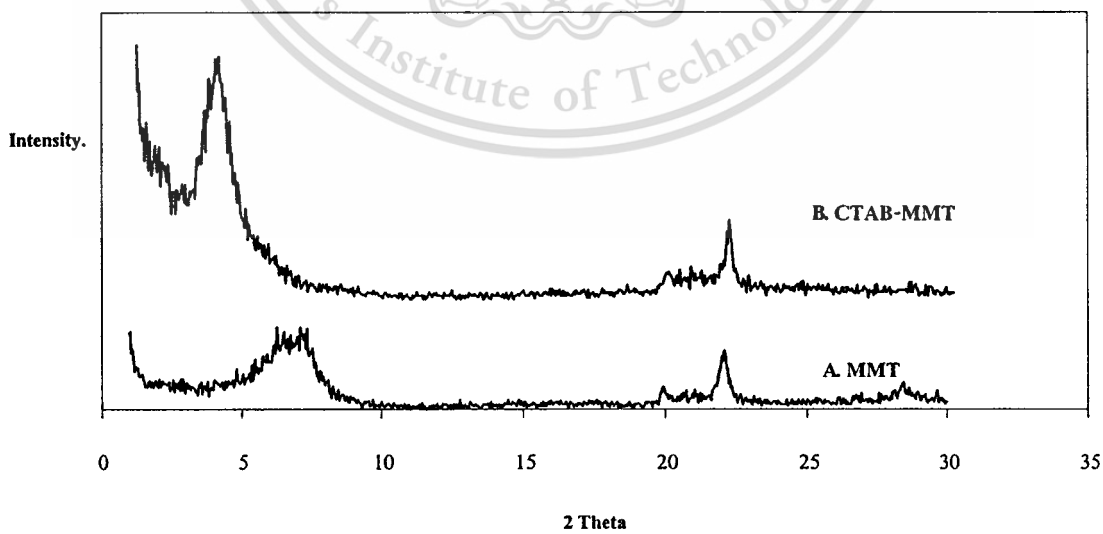

Figure 4.1: XRD patterns of MMT and CTAB-MMT

The pattern of XRD the CTAB-MMT after phenol adsorption was shown in Figure 4.2. The similar XRD pattern as the CTAB-MMT was observed. This indicates the phenol adsorption doesn't effect to size of the gap in MMT.

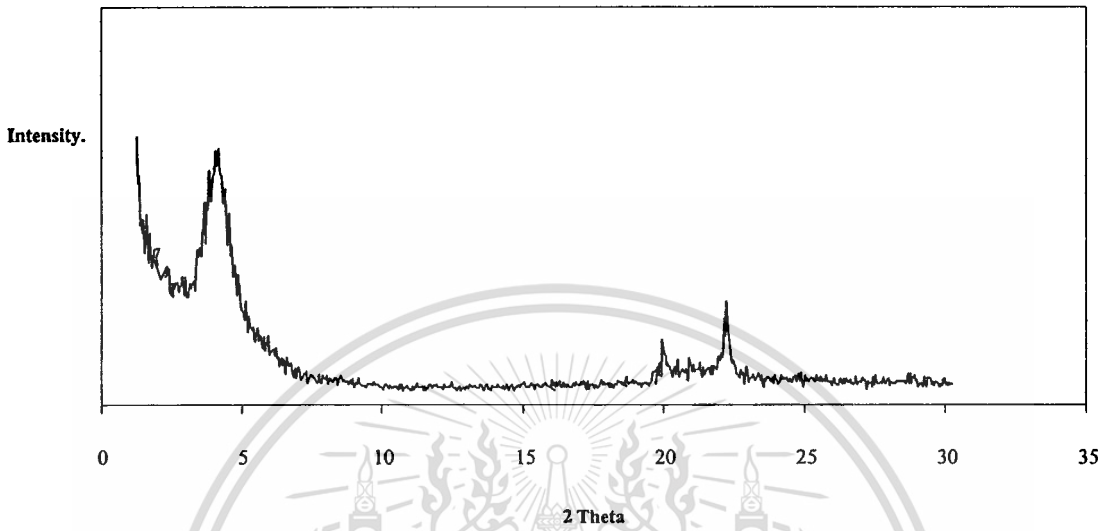

Figure 4.2: XRD pattern of CTAB-MMT after phenol adsorption

4.1.2 TGA

Another technique used to assert exchanging CTAB into MMT was TGA as shown in Figure 4.3. The TGA thermogram was used for determining changes in weight in relation to change in temperature. In the oxygen atmosphere the CTAB started to decompose at 198.87 °C. The total weight loss was 16.2754 wt% corresponding to the CTAB content in MMT.

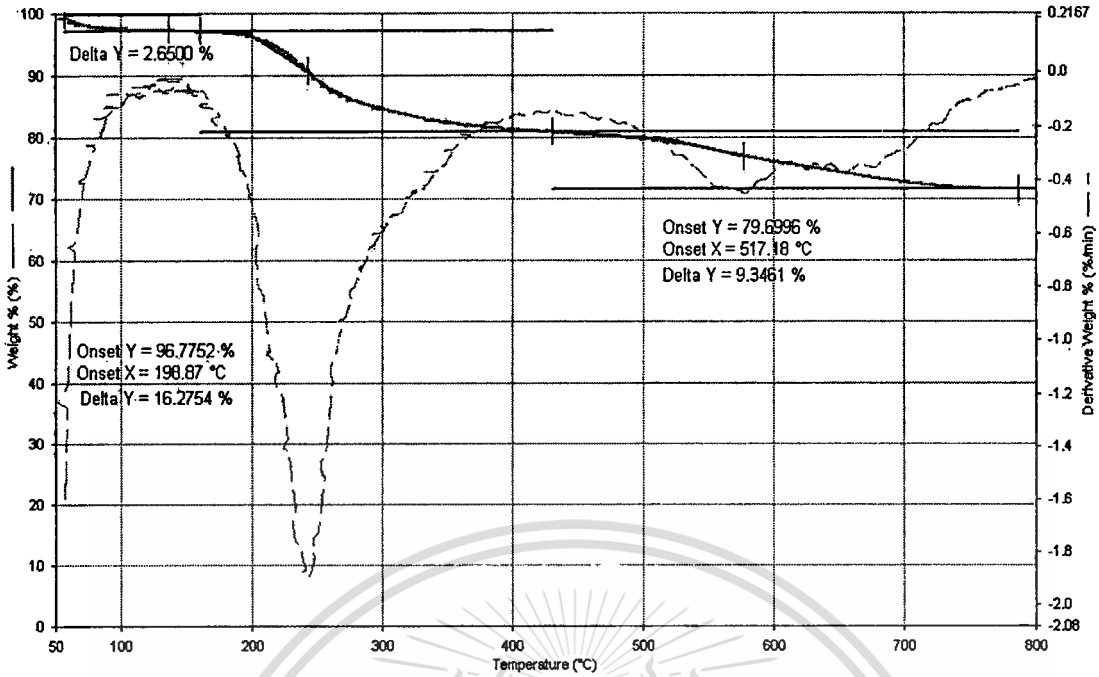

Figure 4.3: TGA thermogram of CTAB-MMT

4.2 Phenol adsorption (Batch type)

4.2.1 Effect of initial phenol concentration

Two grams of clay was used to adsorb 30 ml of phenol using various initial concentration of phenol; i.e. 80, 100, 300, 500 and 800 mg/L. The mixtures were shaked at 150 rpm for 30 minutes. The adsorption results are shown in Table 4.1 and Figure 4.4.

Table 4.1: Effect of initial concentration of phenol on the %removal and adsorption capacity of CTAB-MMT

Concentration of phenol (mg/L)	Absorbance	% remove	Adsorption capacity (mg/g clay)
80	0.325	75.0	0.9
100	0.393	75.2	1.1
300	0.827	73.7	3.7
500	1.993	70.0	5.3
800	2.723	62.5	7.5

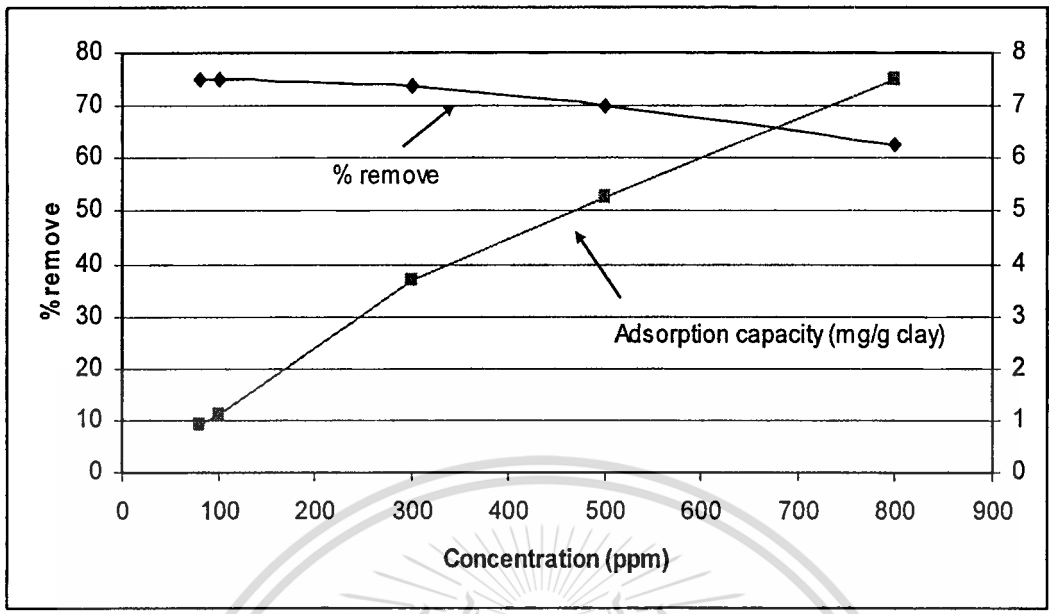

Figure 4.4: Graph for effect of initial concentration

When the initial concentration of 80 and 100 mg/L were used, the percentage of phenol removed was about 75%. When the initial concentration increased, the of phenol removed would decrease but the adsorption capacity would increase. These result indicate that the excess amount of CTAB-MMT was used in the systems with the initial concentration in the range of 80 – 100 mg/L.

When the initial concentration was adjusted to 300 – 800 mg/L, the phenol content in the adsorption system increased, so the adsorption capacity would increased, however, the %remove would decreased due to the excess content of phenol.

4.2.2 Effect of adsorption time

Two grams of clay was used to adsorb 30 ml at various adsorption time of phenol; i.e. 10, 20, 30, 60, 90 and 120 minutes. The mixtures were continuously shaked at 150 rpm. The adsorption results are shown in Table 4.2 and Figure 4.5.

Table 4.2: Effect of adsorption time of phenol on the %removal and adsorption capacity of CTAB-MMT

Adsorption time (min)	Absorbance	% remove	Adsorption capacity (mg/g clay)
10	0.497	67.4	1.0
20	0.451	70.5	1.1
30	0.393	75.2	1.1
60	0.393	75.2	1.1
90	0.393	75.2	1.1
120	0.393	75.2	1.1

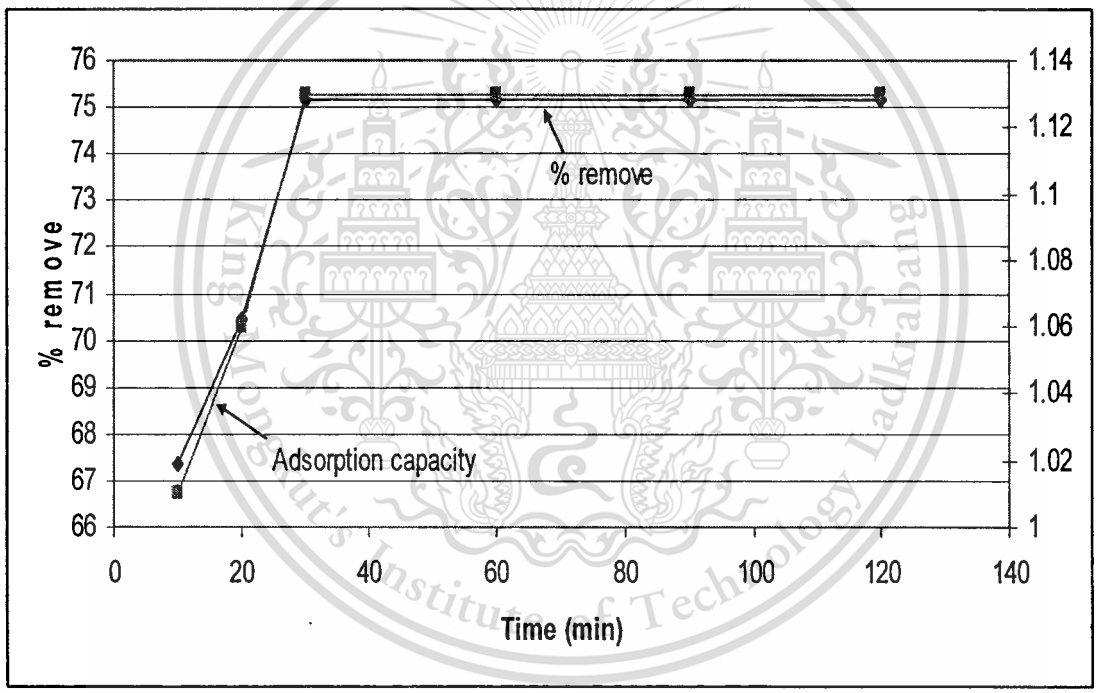

Figure 4.5: graph for effect of adsorption time

When the adsorption time increased, the %remove and adsorption capacity would increased. The %remove and adsorption capacity reached the highest value and became constant when the adsorption time was 30 minutes.

4.2.3 Effect of adsorption system

Comparing between two adsorption systems; i.e. shaking and mechanical stirring systems, two grams of clay was used to adsorb 30 ml phenol in three different concentrations; 100, 500 and 800 mg/L. The adsorption result are shown in Table 4.3 and Figure 4.6 - 4.7.

Table 4.3: Effect of adsorption system of phenol on the %removal and adsorption capacity of CTAB-MMT

Concentration of phenol (mg/L)	Shaking system		Stirring system	
	Adsorption capacity	% remove	Adsorption capacity	% remove
100	1.1	75.2	1.3	89.2
500	5.3	70.0	5.6	75.0
800	7.5	62.5	8.3	68.8

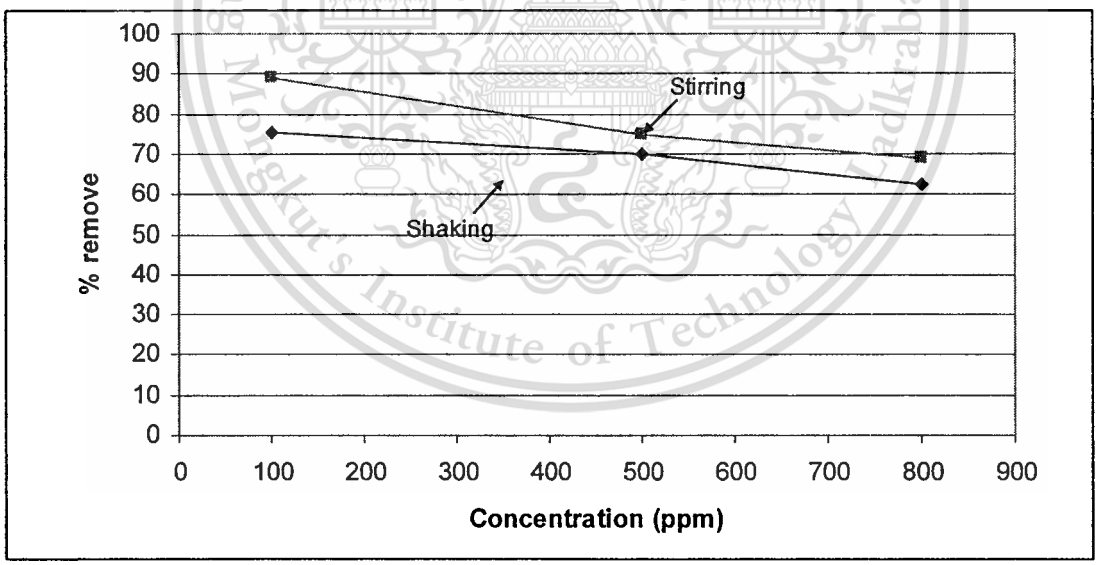

Figure 4.6: Graph for effect of adsorption system, compare %remove between shaking and stirring system

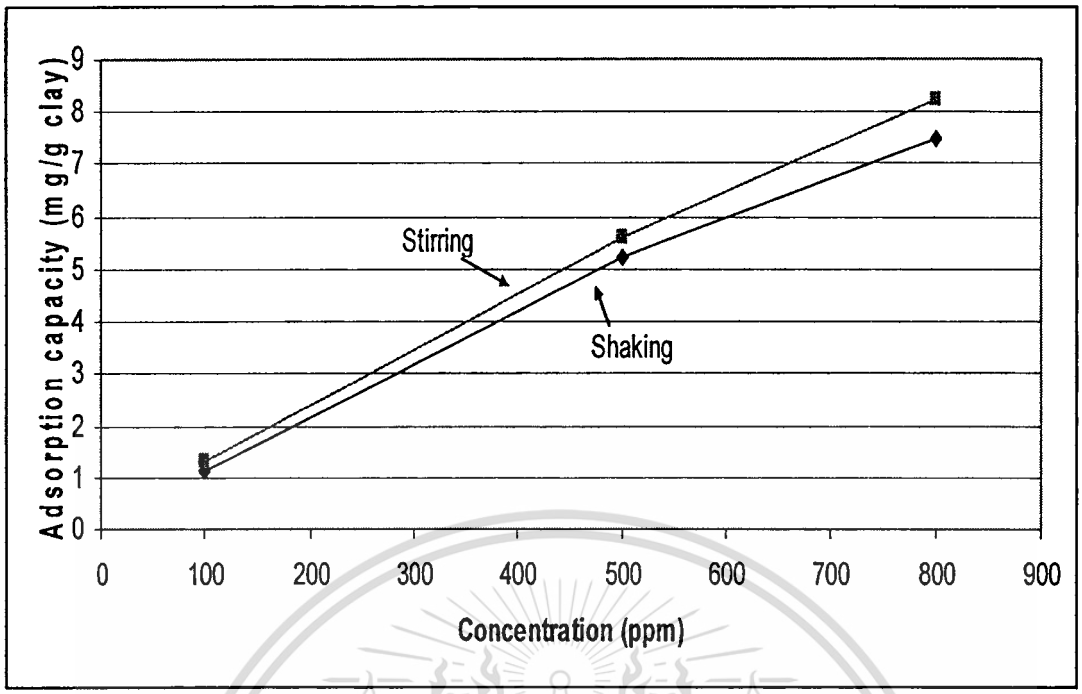

Figure 4.7: Graph for effect of adsorption system, compare adsorption capacity between shaking and stirring system

The mechanical stirring system showed higher %removal and adsorption capacity than those of shaking system. The mechanical stirring generated the vortex movement of CTAB-MMT in phenol solution, resulting in increasing of the contact area between CTAB-MMT and phenol , so the adsorption capacity would increase from the shaking.

From the previous results, the adsorption time and contact area play an important role on the adsorption capacity, so the column experiment was setup in order to increase the adsorption efficiency of CTAB-MMT.

4.3 Preliminary study on phenol adsorption by column system

4.3.1 Packing column by using 7.5 g of clay for 5 cm height to adsorb 800 mg/L phenol solution with high pressure pump.

Table 4.4: %removal of phenol by CTAB-MMT (height of CTAB-MMT was 5 cm)

No.	Time for 10 ml (min)	% remove	No.	Time for 10 ml (min)	% remove
1	5	21.6	16	8	4.7
2	5	21.3	17	9	7.7
3	7	19.3	18	10	7.8
4	5	17.8	19	9	4.3
5	6	16.8	20	9	3.7
6	6	14.2	21	9	2.6
7	7	12.8	22	10	5.8
8	7	10.8	23	9	0.0
9	7	7.6	24	9	0.0
10	8	11.5	25	9	0.0
11	8	8.2	26	10	0.0
12	8	6.2	27	10	0.0
13	6	5.2	28	10	0.0
14	8	7.3	29	10	0.0
15	8	4.7	30	10	0.0

When high pressure pump was used, %removal of phenol was very low because of short contact time of CTAB-MMT and phenol.

4.3.2 Packing column by using 7.5 g of clay for 5 cm height to adsorb 800 mg/L phenol solution with low pressure pump

Table 4.5: %removal of phenol by CTAB-MMT (height of CTAB-MMT was 5 cm)

No.	Time for 10 ml (min)	% remove	No.	Time for 10 ml (min)	% remove
1	105	94.0	11	177	100.0
2	132	98.2	12	165	100.0
3	133	99.5	13	153	100.0
4	135	99.9	14	174	100.0
5	135	100.0	15	175	100.0
6	137	100.0	16	180	100.0
7	123	100.0	17	174	100.0
8	162	100.0	18	129	100.0
9	132	100.0	19	165	100.0
10	186	100.0	20	141	100.0

The contact time was increased in order to increase the efficiency of phenol adsorption, low pressure pump was used instead of high pressure pump. Low pressure pump provided slower flow of phenol through the column CTAB-MMT and higher %removal were observed

4.3.3 Packing column by using 5 g of clay for 3.5 cm height to adsorb 800 mg/L phenol solution with low pressure pump

Table 4.6: %removal of CTAB-MMT when phenol solution passed through 3.5 cm height of CTAB-MMT column

No.	Time for 10 ml (min)	% remove	No.	Time for 10 ml (min)	% remove
1	70	78.1	21	90	99.3
2	70	99.0	22	90	99.2
3	70	99.5	23	90	99.6
4	70	99.0	24	90	99.0
5	70	99.7	25	90	99.2
6	70	99.6	26	90	98.9
7	75	99.8	27	90	98.5
8	75	99.6	28	90	98.1
9	75	99.6	29	90	96.8
10	75	99.4	30	90	96.8
11	75	99.4	31	90	96.7
12	75	99.6	32	90	95.2
13	75	100.0	33	90	93.7
14	75	100.0	34	90	91.8
15	90	99.8	35	90	90.8
16	90	99.6	36	90	90.0
17	90	100.0	37	90	87.4
18	90	100.0	38	105	85.2
19	90	100.0	39	115	81.8
20	90	99.6	40	115	79.6

In this experiment, the amount of CTAB-MMT was decreased in order to reduce the contact time. It was found that the %removal of phenol was 78.1% in the first 10 ml of effluent. Nevertheless, the %removal reached about 100% in the second 10 ml of effluent. The %removal reduced after 200 ml phenol solution pass through.

Chapter 5
Conclusion

5.1 Conclusion

Montmorillonite (MMT) was modified by cetylmethylammonium bromide (CTAB). The CTAB modified MMT contained about 27.2% of CTAB in which CTAB could enlarge the gap between sheets of clay from 1.25 nm to 2.26 nm. The CTAB modified MMT was used as adsorbent for phenol adsorption.

Various adsorption conditions were studied as follows:

- The adsorption capacity increased with increasing of adsorption time and initial concentration of phenol.
- The adsorption capacity of mechanical stirring system was higher than that of shaking system.
- The column system was the most suitable adsorption system for phenol adsorption in which the longer contact time, the higher %removal was obtained.

5.2 Suggestion for future works

5.2.1 CTAB might be replaced by other cationic surfactants such as Cetylpyridinium chloride (CPC), Polyethoxylated tallow amine (POEA), Benzalkonium chloride (BAC), Benzethonium chloride (BZT) etc.

5.2.2 Column experiment might be attempted using other conditions to give better result such as changing the height of CTAB-MMT, Feed flow rate, etc.

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APPENDIX

Appendix A:
Result of phenol adsorption by CTAB-MMT various conditions in batch adsorption

Table A.1: Effect of initial concentration of phenol on the %removal and adsorption capacity of CTAB-MMT

Concentration of phenol	Absorbance	Concentration	% remove	Adsorption capacity (mg/g clay)
80	0.325	20	75	0.9
100	0.393	25	75.15	1.13
300	0.827	79	73.67	3.67
500	1.993	150	70	5.25
800	2.723	300	62.5	7.5

Table A.2: Effect of adsorption time of phenol on the %removal and adsorption capacity of CTAB-MMT

Adsorption time (min)	Absorbance	Concentration	% remove	Adsorption capacity (mg/g clay)
10	0.497	33	67.37	1.01
20	0.451	30	70.45	1.06
30	0.393	25	75.15	1.13
60	0.393	25	75.15	1.13
90	0.393	25	75.15	1.13
120	0.393	25	75.15	1.13

Table A.3: Effect of adsorption system of phenol on the %removal and adsorption capacity of CTAB-MMT

Concentration of phenol	Shaking		Stirring	
	Absorbance	% remove	Absorbance	% remove
100	0.393	75.15	0.218	89.17
500	1.993	70	1.742	75
800	2.723	62.5	2.611	68.75

Table A.3: Effect of adsorption system of phenol on the %removal and adsorption capacity of CTAB-MMT

Concentration of phenol	Adsorption capacity (shaking)	Adsorption capacity (stiring)
100	1.13	1.34
500	5.25	5.63
800	7.5	8.25

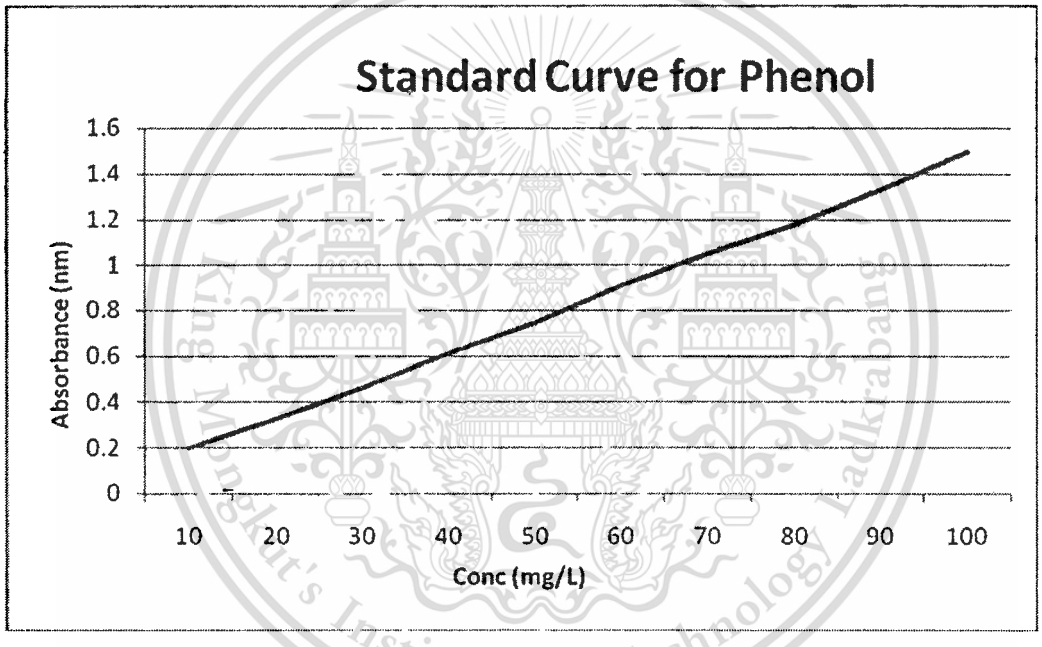

Figure A.1: standard curve

Appendix B:

Result of phenol adsorption by CTAB-MMT various conditions in column system

Table B.1: result of phenol adsorption by CTAB-MMT (high pressure pump and 5 cm height of CTAB-MMT were used)

No.	Time for 10 ml	Absorbance	Concentration	% remove	Flow rate(ml/sec)
1	5	0.941	627	21.6	2.00
2	5	0.944	629	21.3	2.00
3	7	0.968	645	19.3	1.43
4	5	0.986	657	17.8	2.00
5	6	0.999	666	16.8	1.67
6	6	1.030	687	14.2	1.67
7	7	1.047	698	12.8	1.43
8	7	1.071	714	10.8	1.43
9	7	1.109	739	7.6	1.43
10	8	1.062	708	11.5	1.25
11	8	1.102	735	8.2	1.25
12	8	1.126	750	6.2	1.25
13	6	1.138	759	5.2	1.67
14	8	1.112	741	7.3	1.25
15	8	1.144	763	4.7	1.25
16	8	1.108	763	4.7	1.25
17	9	1.106	739	7.7	1.11
18	10	1.149	737	7.8	1.00
19	9	1.156	766	4.3	1.11
20	9	1.169	771	3.7	1.11
21	9	1.131	779	2.6	1.11
22	10	1.202	754	5.8	1.00
23	9	1.200	801	0.0	1.11
24	9	1.204	800	0.0	1.11
25	9	1.203	803	0.0	1.11

Table B.2: result of phenol adsorption by CTAB-MMT (high pressure pump and 5.2 cm height of CTAB-MMT were used)

No.	Time for 10 ml	Absorbance	Concentration	%remove	Flow rate(ml/sec)
1	62	0.093	51	93.7	0.16
2	66	0.030	16	98.0	0.15
3	66	0.021	11	98.6	0.15
4	66	0.010	5	99.3	0.15
5	66	0.007	4	99.5	0.15
6	67	0.002	1	99.9	0.15
7	67	0.001	1	99.9	0.15

Table B.3: result of phenol adsorption by CTAB-MMT (high pressure pump and 4.8 cm height of CTAB-MMT were used)

No.	Time for 10 ml	Absorbance	Concentration	%remove	Flow rate(ml/sec)
1	120	0.082	35	95.7	0.08
2	123	0.028	15	98.2	0.08
3	125	0.019	8	99.0	0.08
4	124	0.011	5	99.4	0.08
5	130	0.003	2	99.7	0.08
6	133	0.002	1	99.9	0.08
7	145	0.001	0	99.9	0.07
8	147	0.002	1	99.9	0.07
9	156	0.000	0	99.9	0.06
10	178	0.000	0	99.9	0.06

Table B.4: result of phenol adsorption by CTAB-MMT (high pressure pump and 5 cm height of CTAB-MMT were used)

No.	Time for 10 ml	Absorbance	Concentration	% remove	Flow rate(ml/sec)
1	105	0.081	4	99.5	0.10
2	132	0.008	0	99.9	0.08
3	133	0.000	0	100.0	0.08
4	135	0.000	0	100.0	0.07
5	135	0.000	0	100.0	0.07
6	137	0.000	0	100.0	0.07
7	123	0.000	0	100.0	0.08
8	162	0.000	0	100.0	0.06
9	132	0.000	0	100.0	0.08
10	186	0.000	0	100.0	0.05
11	177	0.000	0	100.0	0.06
12	165	0.000	0	100.0	0.06
13	153	0.000	0	100.0	0.07
14	174	0.000	0	100.0	0.06
15	175	0.000	0	100.0	0.06
16	180	0.000	0	100.0	0.06
17	174	0.000	0	100.0	0.06
18	129	0.000	0	100.0	0.08
19	165	0.000	0	100.0	0.06
20	141	0.000	0	100.0	0.07

Table B.5: result of phenol adsorption by CTAB-MMT (high pressure pump and 3.5 cm height of CTAB-MMT were used)

No.	Time for 10 ml	Absorbance	Concentration	% remove	Flow rate(ml/sec)
1	70	0.291	17	78.1	0.14
2	70	0.016	1	99.0	0.14
3	70	0.008	0	99.5	0.14
4	70	0.015	1	99.0	0.14
5	70	0.004	0	99.7	0.14
6	70	0.007	0	99.6	0.14
7	75	0.003	0	99.8	0.13
8	75	0.007	0	99.6	0.13
9	75	0.007	0	99.6	0.13
10	75	0.010	1	99.4	0.13
11	75	0.010	1	99.4	0.13
12	75	0.006	0	99.6	0.13
13	75	0.000	0	100.0	0.13
14	75	0.000	0	100.0	0.13
15	90	0.003	0	99.8	0.11
16	90	0.007	0	99.6	0.11
17	90	0.000	0	100.0	0.11
18	90	0.000	0	100.0	0.11
19	90	0.000	0	100.0	0.11
20	90	0.007	0	99.6	0.11
21	90	0.011	1	99.3	0.11
22	90	0.013	1	99.2	0.11
23	90	0.007	0	99.6	0.11
24	90	0.016	1	99.0	0.11
25	90	0.013	1	99.2	0.11

Table B.6: result of phenol adsorption by CTAB-MMT (high pressure pump and 3.5 cm height of CTAB-MMT were used) (continue)

No.	Time for 10 ml	Absorbance	Concentration	% remove	Flow rate(ml/sec)
26	90	0.017	1	98.9	0.11
27	90	0.024	1	98.5	0.11
28	90	0.030	2	98.1	0.11
29	90	0.050	3	96.8	0.11
30	90	0.050	3	96.8	0.11
31	90	0.052	3	96.7	0.11
32	90	0.075	4	95.2	0.11
33	90	0.099	5	93.7	0.11
34	90	0.128	7	91.8	0.11
35	90	0.144	7	90.8	0.11
36	90	0.157	8	90.0	0.11
37	90	0.197	10	87.4	0.11
38	105	0.232	12	85.2	0.10
39	115	0.286	15	81.8	0.09
40	115	0.320	16	79.6	0.09

Appendix C:

XRD

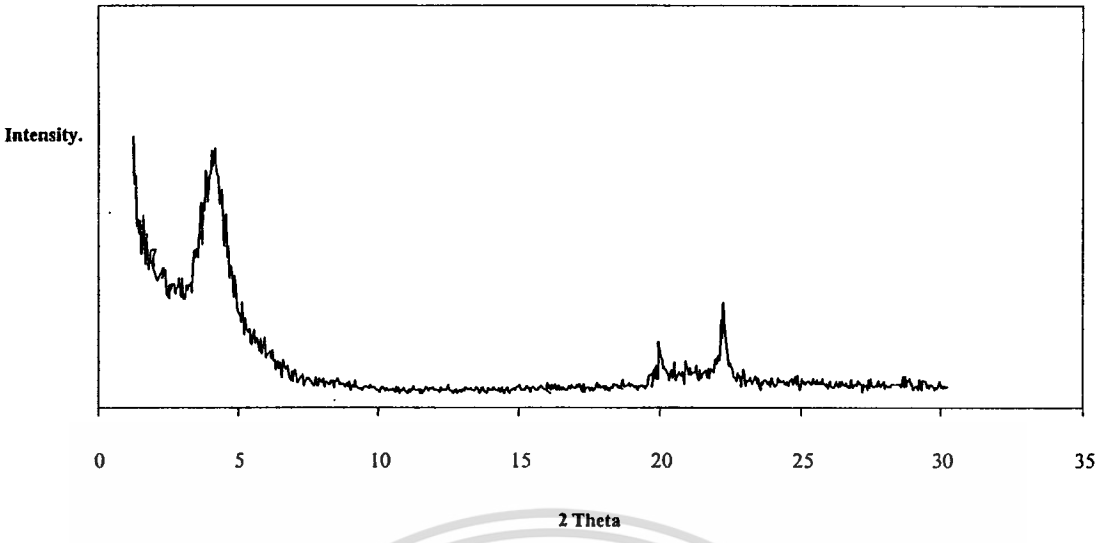

Figure C.1: XRD pattern of CTAB-MMT after phenol adsorption (concentration of phenol solution was 800 mg/L)

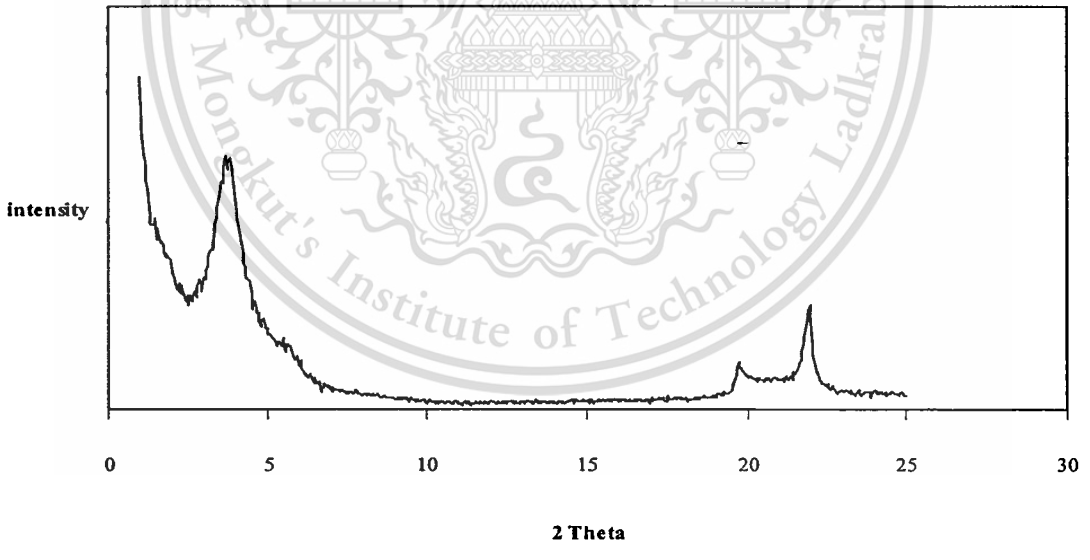

Figure C.2: XRD pattern of CTAB-MMT after phenol adsorption (concentration of phenol solution was 1000 mg/L)