# การดูดซับปรอทโดยใช้เบนโทไนต์ ไซน่าเคลย์และบอลเคลย์

นางสาว ณาฐวรา จิรันดร

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# ADSORPTION OF MERCURY USING BENTONITE, CHINA CLAY AND BALL CLAY

**Miss Nartwara Chirandorn**

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**By** Miss Nartwara Chirandorn
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**Thesis Advisor** Associate Professor Wimonrat Trakarnpruk, Ph.D.

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Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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(Professor Piamsak Menasveta, Ph.D.)

**Thesis Committee**

..………………………………..……..…..Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

……………………………………………Thesis Advisor
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

…………………………………………….Member
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

……………………………………….…….Member
(Assistant Professor Vipavee P. Hoven, Ph.D.)

………………………………………………Member
(Assistant Professor Aroonsiri Shitangkoon, Ph.D.)

ณาฐวรา จิรันดร: การดูดซับปรอทโดยใช้เบนโทไนต์ ไชน่าเคลย์และบอลเคลย์ (ADSORPTION OF MERCURY USING BENTONITE, CHINA CLAY AND BALL CLAY) อ. ที่ปรึกษา: รศ. ดร. วิมลรัตน์ ตระการพฤกษ์, 81 หน้า,

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งานวิจัยนี้ศึกษาวิธีการดูดซับปรอทด้วยดินเหนียวที่มีอยู่ในประเทศไทย ได้แก่ เบนโทไนต์ ไชน่าเคลย์ และ บอลเคลย์ โดยวิเคราะห์เปรียบเทียบปริมาณปรอทก่อนและหลังการดูดซับ ได้ปรับสภาพของสารดูดซับด้วยวิธีต่างๆ ได้แก่ การให้ความร้อน และการเติมสารเคมี ชนิดต่างๆ ได้แก่ กรด โซเดียมซัลไฟด์ ไธโอยูเรีย และ 2-เมอร์แคพโทเบนโซไธเอโซล พร้อมทั้งศึกษาปัจจัยที่มีผลต่อการดูดซับ ได้แก่ ค่าความเป็นกรด-ด่าง เวลาที่ใช้ในการดูดซับ การเติมเกลือ ความเข้มข้นของสารปรอท และอุณหภูมิที่ใช้ในการดูดซับ ผลที่ได้พบว่า ประสิทธิภาพการดูดซับของสารปรอทสูงในภาวะพีเอชเป็น 6-8 และเพิ่มขึ้นตามอุณหภูมิและปริมาณของสารดูดซับ ภาวะที่เหมาะสมคือที่ความเข้มข้นของปรอท 100 ไมโครกรัมต่อลิตร ในเวลา 30 นาที ประสิทธิภาพของสารดูดซับ 3 ชนิด มีลำดับดังนี้: เบนโทไนต์ > ไชน่าเคลย์ > บอลเคลย์ ผลการปรับสภาพของสารดูดซับด้วยสารเคมีต่างๆ เรียงลำดับประสิทธิภาพได้ดังนี้: 2-เมอร์แคพโทเบนโซไธเอโซล > ซัลไฟด์ > ไธโอยูเรีย ศึกษาเปรียบเทียบวิธีการดูดซับ 2 วิธี คือ แบบแบทซ์และแบบคอลัมน์ พบว่า แบบแบทซ์ให้การดูดซับปรอทได้ดีกว่าเล็กน้อย ปรอทที่ถูกดูดซับสามารถชะออกจากสารดูดซับได้ง่ายโดยใช้สารละลายกรดไฮโดรคลอริก นอกจากนี้ได้ใช้วิธีการดูดซับปรอทที่ได้กับตัวอย่างดินและตัวอย่างน้ำจากแหล่งขุดเจาะน้ำมันในอ่าวไทย

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต....................................................

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NARTWARA CHIRANDORN: ADSORPTION OF MERCURY USING BENTONITE, CHINA CLAY AND BALL CLAY. THESIS ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D., 81 pp.
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In this work, adsorption of mercury was studied using clays available in Thailand: bentonite, china clay and ball clay. The amounts of mercury before and after adsorption were compared. The clays were treated with various methods: heat treatment and chemical treatment. For the chemical treatment, different kinds of chemicals were used: acid, sodium sulfide, thiourea and 2-mercaptobenzothiazole. Factors affecting the adsorption were investigated: pH, ionic stregth, concentration of mercury solution and adsorption temperature. The results showed that adsorption efficiency was maximum at pH 6-8, it increased with temperature, and adsorbent dose. The optimum condition determined in this work was mercury concentration of 100 microgram/litre in 30 minutes. Adsorption efficiency of three kinds of clays is in the order: bentonite > china clay > ball clay. Chemical treatments performed demonstrate the following adsorption efficiency order: 2-mercaptobenzothiazole > sulfide > thiourea. Two different methods of adsorption were compared and it was found that batch method has little higher efficiency than column method. The mercury adsorbed can be leached out easily using hydrochloric acid solution. In addition, the method found in this work was applied to real mud and water samples from the Gulf of Thailand.

Field of study…Petrochemistry and Polymer Science…Student’s signature…………
Academic year……………………2004………………Advisor’s signature...............

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# CHAPTER I

# INTRODUCTION

## 1.1 Mercury

The understanding of the chemistry of geologic mercury has evolved due to technical advances that allow differentiation of the various chemical forms of mercury in hydrocarbon matrices. Mercury compound is found in wide range of petroleum and environmental such as natural gas, condensate, crude oil, soil and water around platform. Chemical structure and quantity of mercury depend on the source and type of petroleum feedstock. The mercury which is found in the condensate and water around platform are presented in various chemical states; elemental, ionic and organometallic. The presence of mercury in soil and water around platform can cause the environmental problems. Furthermore, mercury in petroleum product can also cause major problems such as reduction of catalyst life[1] and corrosion.[2] Inorganic and metallic mercury are only moderately toxic and they are not passed efficiently through the marine food chain to man. However, some species of bacteria that live in sediments and ocean water containing very low concentrations of oxygen are able to convert some of the inorganic mercury dissolved in water to toxic methylmercury through a process called methylation. Mercury methylation also occurs in the organic-rich sediments of coastal salt marshes and wetlands. The major effects of mercury poisoning manifest as neurological and renal disturbances as it can easily pass the blood-brain barrier and affect the front brain. High concentration of Hg(II) cause impairment of pulmonary function and kidney, chest, pain, and dyspnousea. Various types of technology are available for removing of mercury in water and wastewaters including chemical precipitation, conventional coagulation, line softening, reverse osmosis, ion-exchange and activated carbon adsorption. The high cost of activated carbon has inspired a search for suitable low-cost adsorbents, such on clay minerals.

Several methods for removal of mercury from water and soil around platform have been proposed. These methods can be classified into two groups: hemical treatment and adsorption.

In chemical treatment, mercury reacts with some chemical and converts to a mercuric sulfide that is insoluble and easy to remove. The chemical substance used is usually a sulfur compound, such as alkali polysulfide. By this method, sulfur compound contacts and reacts with mercury compounds and converts to a mercuric sulfide. On the oher hand, adsorption is a common method that is used to remove mercury because it provides a high efficiency of mercury removal and does not contaminate with other chemical substance. However, some methods combine between chemical reaction and adsorption. The sulfur supported on the adsorbents such as activated carbon and alumina can be used. By this method mercury reacts with sulfur supported on the adsorbents and converts to a mercuric sulfide depositing.

## 1.2 Objective of research

The objective of this research is to study the effect of some parameters such as initial adsorbate concentration, pH, adsorbent dose, ionic strength, temperature and type and treatment of clay adsorbent and removal of mercury compounds by adsorption. The adsorbents are prepared by heat and chemical treatments. Mercuric chloride is used as model compound. Flow injection analysis mercury hydride system is a technique used for measurement of mercury. X-ray diffraction and FTIR are used for characterization of the adsorbents before and after treatment.

# CHAPTER II

# THEORY AND LITERATURE

## 2.1 Clay

Clay materials can be synthesized or taken from natural deposits. They comprise layer silicates which imbibe guest molecules between their siliceous layers causing their crystals to swell. Fuller's earth is an activated natural montmorillonite. Its pore size is altered and its surface area increased by acid treatment to 150-250 $m^2/g$. It is relatively inexpensive and can be used for refining edible and mineral oils, adsorbing toxic chemicals, removing pigments, etc. The cationic forms are capable of adsorbing a range of polar molecules and non-polar molecules if some water is present.

**Kaolinite** is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$. The basic building blocks are layers of silica tetrahedral (with four apical O) and layers of alumina octahedral (with two apical O shared with silica and four apical OH), in a 1:1 relationship. The main bonding forces between layers are hydrogen bonds between-OH on one layer and a bridging –O- the main constituent of china clay and ball clay.

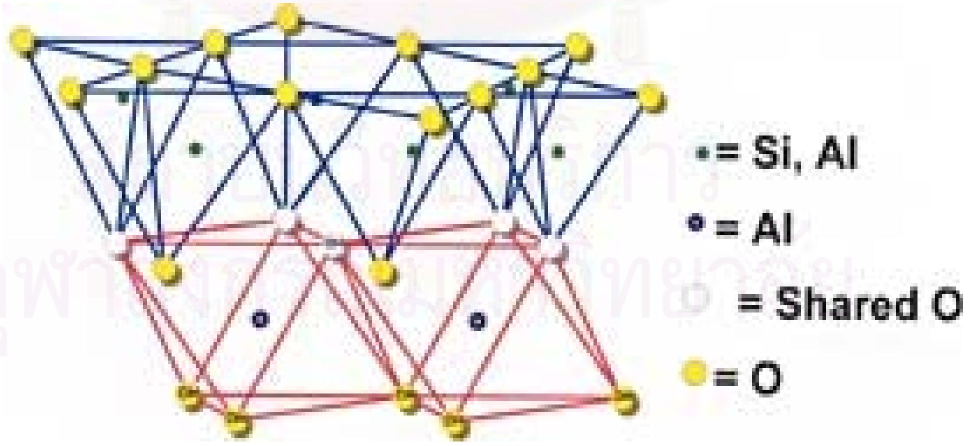


**Figure 2.1** Diagrammatic sketches of the structure of the kaolinite.

The mineral kaolinite forms a major component in both ball clay and china clay (which is also known as kaolin). The two materials are quite different from each other. China clay (mostly composed of kaolinite, mica and quartz minerals) remained in the place where it was formed as the feldspars in the granite decomposed. Ball clay is sedimentary clay - carried far from where the kaolinite was first formed. Rivers and streams washed away the decomposed granite, mixing it with other clay minerals, sands, gravels and vegetation as they flowed down from the uplands to form the deposits of ball clay in low lying basins. In ball clays, there are usually three dominant minerals: from 20 - 80% kaolinite; 10-25% mica, and 6-65% quartz. In addition, there are other 'accessory' minerals and some carbonaceous material (derived from ancient plants). The wide variation in minerals make-up and in the sizes of the clay particles result in different characteristics for individual ball clay seams.

**Montmorillonite $[Na_{0.6}Al_{3.4}Mg_{0.6}Si_8O_{20}(OH)_4]\cdot(H_2O)_x$** is main constituent of bentonite which are noted for their excellent swelling properties when wetting. It is composed of a sheet of octahedral coordinated gibbsite $[Al_2(OH)_6]$ sandwiched between two sheets of tetrahedral coordinated silicate $[SiO_4]^{4-}$ sheets shown in Figure 2.2. The three-sheet layer repeats itself, and the interlayer space holds the key to the chemical and the physical properties of the clay. An important and useful property of montmorillonite stems from its high degree of efficiency for $M^+$ cation exchange. This happens because of charge imbalances in its structure caused by exchange of $Al^{3+}$ for $Si^{4+}$ in the tetrahedral sheet, and of $Mg^{2+}$ for $Al^{3+}$ cation in the octahedral sheets.

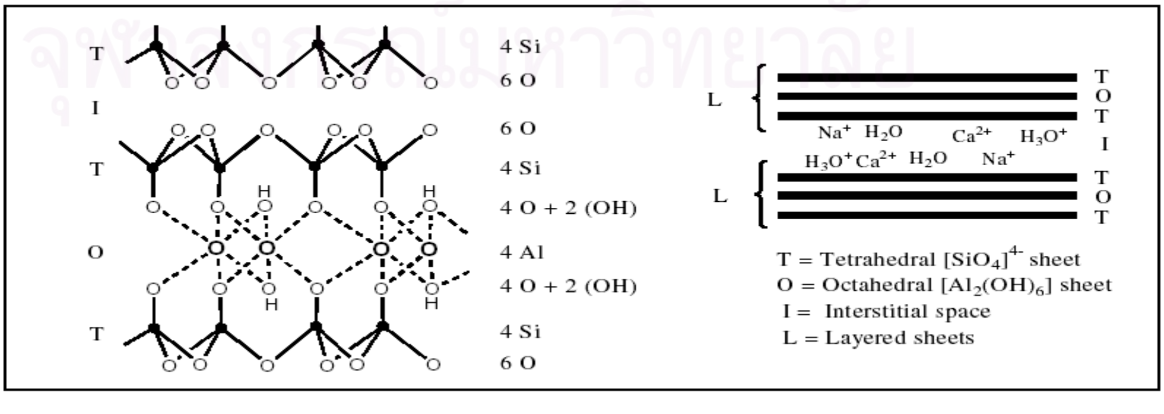


**Figure 2.2** Diagrammatic sketches of the structure of the bentonite layer.

## 2.2 Mercury

Mercury compounds are found in various forms. From a toxicological and environmental point of view, the most useful and commonly accepted classification is:

1. Metallic mercury, liquid and vapor.
2. Inorganic salts, such as sulfides, chlorides, nitrates and oxides.
3. Alkyl compounds, such as those containing an ethyl or methyl radical.
4. Alkoxyalkyl compounds.
5. Aryl compounds particularly the phenylmercurials.

Mercury is the only metallic element in that it is liquid at ordinary temperatures. Its atomic number is 80 and its atomic weight is 200.59. It has valences of 1 and 2. Mercury is capable of forming various compounds, e.g. dental fillings are essentially amalgams of mercury and silver. Mercury has a relatively high vapor pressure at ordinary temperatures. The rate of vaporization increases with increasing in temperature[3].

## 2.3 Mercury in petroleum

Mercury is a metal compound found in a wide range of petroleum industry such as natural gas, condensate, crude oil, water and soil around platform. Mercury compounds are found in various forms: elemental, ionic and organometallic forms. Form and quantities of mercury depend on the source. For example, amounts of mercury in natural gas and condensate were generally 10-3000 ppb[6] and 0.5-10 ppb in crude oil.[5] Distribution of mercury for South East Asian condensate is shown in Figure 2.3. Amounts of mercury in natural gas condensate of each boiling range of condensate fraction found in South-East Asian are different. For this particular condensate, the majority of mercury is found in the naphtha and kerosene fraction.

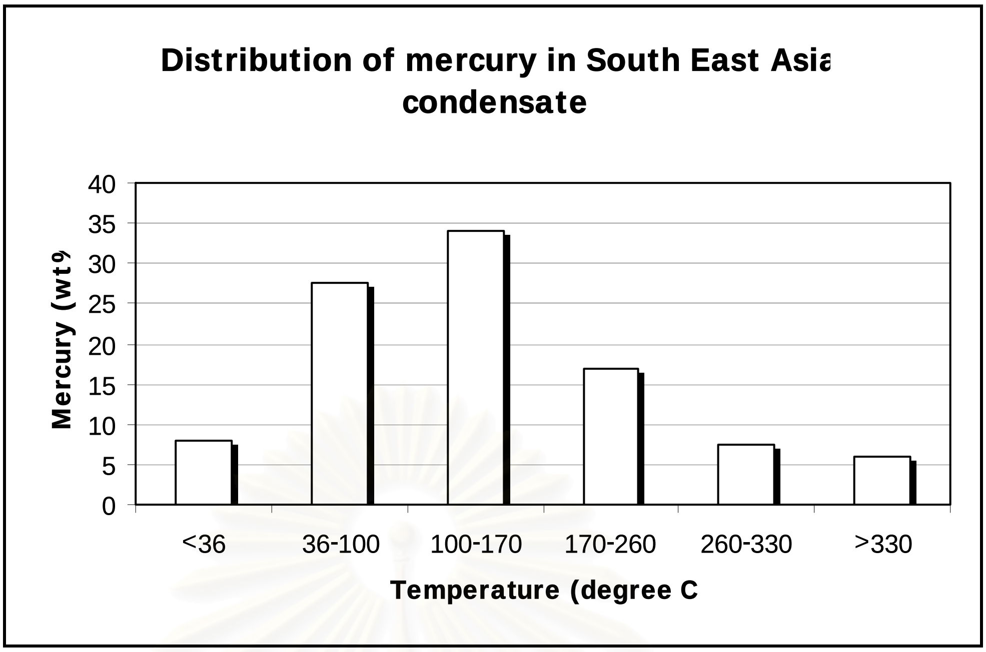


**Figure 2.3** Distribution of mercury in natural gas condensate found in South East Asia.[4]

The presence of contaminate mercury from petroleum drilling in neighbouring waters that would affect marine life in the Gulf of Thailand. Mercury substance was first found in petroleum drilled from the Gulf many years ago and the offshore gas production units have discharged mercury-contaminated produced water into the sea resulting in the increase of this heavy metal in aquatic animals around platforms.

## 2.4 Plant corrosion by mercury

Trace quantity of metallic mercury in natural gas can be a potential cause of problems in Liquefied Natural Gas (LNG) plant. The problems often take place in the presence of equipment constructed of aluminium. Mercury can form an amalgam with aluminium components causing stress fractures. Failures occurred at the LNG plant at Skikda, Algeria, from tube corrosion in the spiral wound exchangers. Corroded tubes contained white deposits: aluminium oxide, aluminium hydroxide and aluminium carbonates, with traces of elemental mercury.[1]

## 2.5 Rmoval of mercury

Elemental mercury is eliminated by using sulfur supported on solid material. Ionic or inorganic mercury can be removed by ion-exchange or reduced to elemental Hg using a reducing reagent such as Sn(II). However, ion-exchange cannot remove elemental mercury. The removal of all Hg species from hydrocarbon is more complicated because of organometallic compounds. Organometallic mercury cannot be removed by ion-exchange because of the covalent nature of Hg-C bonds.

Several methods have been proposed for mercury removal from soil and water around platform. They can be classified into two methods:

1. Chemical treatment
2. Adsorption

### Chemical treatment

Chemical treatment is a method that uses chemicals to convert from mercury compounds in petroleum to the form which easy to remove form sample. The chemical substance used is usually a sulfur compound. The reaction between mercury and sulfur compounds is shown below.

$$Hg + S_x^{2-} \longrightarrow HgS + S_{x-1}^{2-} \; ; \quad \text{where } x=3\text{-}6 \qquad (1)$$

Mercuric sulfide (HgS) occurred is solid material that cannot dissolve and can be removed easily. The disadvantage of chemical treatment method in removal of mercury is the contaminate of product with the chemicals used.

### Adsorption

The removal of mercury by adsorption provides a high efficiency of mercury removal and does not contaminate with other chemicals. The adsorption method is depending on type of adsorbent and condition used.

**Physisorption** (or physical adsorption) is adsorption in which the forces involved are intermolecular forces (Van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved.

**Chemisorption** (or chemical adsorption) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds. The problem of distinguishing between chemisorption and physisorption is basically the same as that of distinguishing between chemical and physical interaction in general. No absolutely sharp distinction can be made and intermediate cases exist, for example, adsorption involving strong hydrogen bonds or weak charge transfer.

## 2.6 Literature reviews

### 2.6.1 Removal of mercury by adsorption

Leeper (1980)[1] proposed corrosion of Liquid Natural Gas (LNG) plant caused by mercury and also method for removal of mercury. Natural gas contaminated with mercury is contacted with a fixed bed of metal sulfide on alumina-silica support with mercury is contacted with a fixed bed of metal sulfide on alumina-silica support.

Audeh (1989)[2] studied the removal of residual mercury in liquid hydrocarbon by mixing the hydrocarbon with aqueous polysulfide solution. The process was carried out at temperature of 70°F and used 0.5 $cm^3$ of sodium polysulfide which contained 22.2 wt% of sulfur. The mercury was decreased to less than 0.01 ppb from initial concentration of 13 ppb.

Yan (1990)[3] proposed a method for removing mercury from natural gas condensate by contacting them with dilution aqueous solution of alkali metal sulfide salt and recovering the treated liquid hydrocarbon. The alkali metal sulfide salt used was $Na_2S_x$. The mercury content in the condensate was 220 ppb. The study was carried out by mixing the condensate with $Na_2S_x$ and aqueous NaOH solution of varied concentration at temperature of 75°C. The result shows that the important factors in removing mercury from the condensate are speed of mixing, concentration of $Na_2S_x$, volume ratio of caustic solution of $Na_2S_x$ and efficiency of phase separation.

Ou (1990)[4] studied a method for removal of mercury by using an adsorbent. This method was directed to an effective way of removing elemental and ionic mercury from liquid hydrocarbon. The adsorbent used was reduced copper and zinc oxide and alumina Another adsorbent used was reduced nickel on clay, which reduced 90% mercury of Algerian condensate containing 32 ppb of mercury.

Yan (1991)[7] proposed the reaction of trace mercury in natural gas with polysulfide solution in a packed column. The residual mercury in the gas phase can be removed from about 0.1 to below 0.01 ppb. Polysulfide reacts with mercury in the gas phase to form insoluble mercuric sulfide, HgS, and thus removes mercury from gas.

Barradell (1991)[8] studied the vibrational Raman of methylmercury(II) nitrate in aqueous solution and of its complexes with dimethyl sulphide and dimethyl sulphoxide (DMSO). A quantitative determination of the $\nu$(HgO) and $\nu$(HgS) stretching band intensities using the $\nu$(HgC) stretching band as an internal standard for the $CH_3HgOH_2^+$ and $CH_3HgS(CH_3)_2^+$ species in aqueous solution has shown that the methylmercury(II) dimethyl sulphide complex cation is only partially dissociated in 0.01 M aqueous solution. An estimate of a factor of 2600 for the preference for sulphur coordination to oxygen coordination under these conditions has been made. The dimethyl sulphoxide complex of the methylmercury(II) cation has a mercury-oxygen bond and not mercury-sulphur as expected.

Bettmer (1993)[9] verified the suitability of different sulphur containing complexing reagents for the HPLC separation of ionic Pb and Hg compounds with subsequent photometric detection. The optimization of the separation such as pH value of the mobile phase, concentration of complexing reagent was done and compared different complexing reagent between mercaptoethanol and methyl thioglycolate. For mercaptoethanol, when increasing proton concentration and decreasing concentration of the complexing reagent in the mobile phase, the lead compounds decreased but mercury compounds were not affected. For separation, pH value of 6.7 and 0.02% (v/v) were suitable. On the other hand, for methyl thioglycolate the effect of pH and concentration were similar to the effects on mercaptoethanol. For separation, a pH of 5.8 and 0.02% (v/v) methyl thioglycolate was proved to be suitable.

Dias Filho (1995)[29] studied sorption and preconcentration of metals (Hg(II), Pb(II), Cd(II), Cu(II) and Mn(II) from an aqueous solution using 2-mercaptobenzothiazole treated clay as function of pH. Conditions for quantitative retention and elution were established for metal by batch and column methods. The chemically treated clay was very selective to Hg(II) in solution in which Zn(II), Cd(II), Pb(II), Cu(II) and Mn(II) were also present.

Sukkho (1995)[10] studied the removal of mercury compounds by adsorption on Cu-Zn adsorbent. The experiments were conducted at 30 to 50°C and pressure of 200 psig. Mercuric chloride was used as mercury compounds in ionic form. Phenylmercuric acetate and diphenylmercury were used as mercury compounds in organometallic form. Experimental resulted showed that removal of mercury was significantly dependent on temperature but independent of pressure. In addition, it was also depended on types of mercury compounds.

Sarkar (2000)[11] studied adsorption of Hg(II) by kaolinite as a function of solution pH, ionic strength and the competitive or complexation effects of ligands ($Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$) and metals ($Ni^{2+}$ and $Pb^{2+}$). The Hg(II) adsorption edge was described by a pH where 50% adsorption occurs is 3.4 and pH maximum is 4.4. Nickel and lead reduced the amount of Hg(II) adsorbed throughout the pH range examined. Ionic strength and the presence of $SO_4^{2-}$ and $PO_4^{3-}$ had relatively little impact on the Hg(II) adsorption.

Krishnan (2002)[12] compared adsorption of Hg from aqueous solutions and chlor-alkali industry effluent on steam activates and sulphurised steam activated carbons prepared from bagasse pith. The uptake of mercury(II) was maximum at the same concentration, pH and temperature of the solution. Batch studies indicated that the optimum pH range for the adsorption on sulphurised carbon was between 4 to 9 and for sulphur free carbon was between 6 to 8 at 30°C. Decrease in ionic strength and increase in temperature of solution has been found to improve the uptake of Hg(II). Complete removal of Hg(II) from synthetic and chlor-alkali industry wastewaters contained 20 and 50 mg/l.

Zhang (2002)[13] studied adsorption of stabilization/solidification (s/s) of Hg-containing solid wastes by activated carbon, powder reactivated carbon (PAC), and cement. Pretreatment of the PAC by soaking it in $CS_2$ significantly improved the mercury adsorption capacity of the PAC. The adsorption equilibrium was reached within 24 h. The optimum pH for the reaction was within the range of 5.0-5.5. After mercury stabilization by adsorption on the reactivated carbon, the mercury waste was mixed with cement for solidification. Surrogate with up to 1000 mg/kg were stabilized and solidified well enough to pass the Toxicity Characteristic Leached Procedure (TCLP) test. It can be seen that the amounts of mercury leached out from all stabilized surrogate samples were below the TCLP limit, 0.2 mg/l, this indicates that Hg(II) is strongly held onto PAC.

Manohar (2002)[14] studied a method for removal of mercury from aqueous solution and chlor-alkali industry wastewater by using 2-mercaptobenzimidazole-clay. The adsorption process follows a pseudo-second-order kinetics. Adsorption of Hg(II) increased with increased pH and reached a plateau value in the pH range of 4-8. The removal of Hg(II) was found to be >99% at an initial concentration of 50 mg/l. The adsorption of Hg(II) increased with increasing adsorbent dose and decreasing with adsorbent particle size.

Budinova (2003)[15] studied adsorption of mercury from aqueous solutions using three types of furfural-based carbon adsorbents (basic, mixture of furfural and tar and acidic adsorbent. Adsorbents with good adsorption capacities were obtained. Mercury adsorption follows a Langmuir isotherm. The mercury removal increases with an increase in pH from 2 to 5. The percentage of the recovery was 6% for the basic furfural adsorbent, 1% for the furfural adsorbent with acidic character, and 4% for the adsorbent from the mixture of furfural and tar.

Denizli (2003)[16] studied properties of poly(ethyleneimine) (PEI)-attached poly(2-hydroxy-ethylmethacrylate) (PHEMA) bead for $Hg^{2+}$ adsorption-desorption. Spherical PHEMA beads with an average size of 150-200 μm and specific surface area of 14.8 $m^2$/g. PEI chains could be covalently attached onto the PHEMA beads with equilibrium binding capacity up to 50 mg PEI/g beads. The adsorption process was fast; 90% of adsorption occurred within 45 min and equilibrium was reached at around 1 h. The maximum $Hg^{2+}$ adsorption capacity obtained was 1.67 mmol/g at pH 5.0. The metal-chelating beads can be regenerated by 0.1 N $HNO_3$ with higher effectiveness. The adsorption capacities from artificial wastewater were 1.32 mmol/g for $Hg^{2+}$.

Nam (2003)[17] studied the removal of mercury(II) from wastewaters (coal-fired utility plant scrubber solutions) using a thiol functional organoceramic composite (SOL-AD-IV). Equilibrium shows a mercury uptake capacity of 500 mg/g at a low mercury concentration of 0.5 mg/l and 726 mg/g at saturation. Adsorption is observed to be independent in the pH range 3-5. Selectivity is found to be in the order Hg(II) > Pb(II) ~ Cd(II) > As(V) > Cr(III). Regeneration of SOL-AD-IV is accomplished using 12 M HCl.

Yardim (2003)[18] studied adsorption of Hg(II) from aqueous solution at 0°C by activated carbon from polymerization of furfural following carbonization and activation of the obtained polymer material with vapor water at 800°C. Adsorption studies of Hg(II) were carried out varying condition, time, metal concentration, adsorbent amount and pH. The adsorption capacity of the carbon was 174 mg/g. It is determined that Hg(II) uptake increases with carbon dose. Metal ion adsorption increases sharply at a short contact time.

Antochshuk (2004)[19] studied incorporation of 1-benzoyl-3-propylthiourea group into siliceous mesopores of MCM-41 for mercury removal. This material was prepared via a two step modification by attachment of aminopropyl functionality and its subsequent conversion into a thiourea ligand. The material has a large surface area of 380 $m^2$/g and accessible mesopores of 3.0 nm in diameter. The maximum loading of mercury ion from aqueous solution for this material was 1.0 g $Hg^{2+}$/g or 5.0 mmol $Hg^{2+}$/g. A relatively weak mercury interaction with 1-benzoyl-3-propylthiourea ligand made the adsorbent’s regeneration under mild conditions via washing the mercury loaded samples with slightly acidified aqueous thiourea solution. The regenerated material retained over 70% of the initial adsorption capacity.

Kadirvelu (2004)[20] studied removal Hg(II) from aqueous solution onto activated carbon prepared from sago industry waste with $H_2SO_4$ and $(NH_4)_2S_2O_8$. The adsorption Hg(II) has been studied under varying conditions of agitation time, metal ion concentration, adsorbent dose, particle size and pH. Adsorption equilibrium was obtained in 105 min for 20 mg/l and 120 min for 20, 40 and 50 mg/l Hg(II) concentrations. The adsorption capacity of Hg(II) obtained from the Langmuir equilibrium isotherm model was found to be 55.6 mg/g at pH 5.0 for the particle size range of 125-250 μm. The percent removal increased with an increase in pH from 2 to 10.

### 2.6.2 Removal of other heavy metals by adsorption.

Aualiittia (1987)[21] studied the specific sorption of $Cd^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ by hydrous oxides ($\propto$-$MnO_2$, $Fe(OH)_3$ and $Al(OH)_3$) or clay mineral suspensions from acetate buffer solution containing 10 to 100 µg/l of each metal ion. It has been found that uptake can vary with pH, adsorbate concentration, and ratio of adsorbate to adsorbent and the presence of complexing ligands. The pH required for onset of sorption varied with solid phase composition with uptake subsequently increasing steadily with increasing pH. Affinity and relative uptake values followed the sequences: $Pb^{2+} > Cu^{2+} > Cd^{2+}$ and $\propto$-$MnO_2 > Fe(OH)_3 > Al(OH)_3 >$ clay > iron ores.

Orumwense (1996)[22] used kaolinite clay as adsorbent for the removal leads from water. Studies were carried out as a function of contact time (20 to 120 mins), initial lead concentration (5-10 mg/L), temperature (30-50°C) and pH (range of 3 to 9.5). The kinetics of adsorption as well as adsorption isotherms at different temperature was studied. The results show that lead removal is favored by low concentration, high temperature and acid pH.

Wang (2000)[23] studied vaporization of lead chloride ($PbCl_2$) on kaolinite and bentonite. The experiment was carried out at linearly rising temperatures in flowing nitrogen with the use of a thermogravimetric apparatus. A modeling method has been proposed to depict the vaporization rate of lead chloride and to calculate the fraction of lead chloride fixed on sorbent during heat-up. The results revealed that dehydrated kaolinite had a moderate ability to fix lead chloride while fresh kaolinite showed significantly increased fixation ability. Bentonite showed the moderate effectiveness for capturing lead chloride.

Harvey (2001)[24] studied adsorption characteristics, adsorption isotherms and ion selectivity of nitrate form of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) ion by ball clay. Adsorption of metals from the single-metal solution were in the order of: $Pb^{2+} > Cr^{3+} > Cd^{2+} \approx Zn^{2+} > Cu^{2+} > Ni^{2+}$ whereas those in the mixture solution were: $Cr^{3+} > Cd^{2+} \approx Cu^{2+} > Zn^{2+} \approx Pb^{2+}$. Adsorption of lead and nickel were severely suppressed by the presence of other metals. The reduction of lead was by ion competition, particularly by copper, whilst those of the nickel mainly by the pH of the solution.

Abollino (2003)[25] studied adsorption of metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) by Na-montmorillonite as function of pH and in the presence of ligand forming complexes of different stabilities with the metals of interest. The continuous column method was used to simulate natural condition. The adsorption decreases with decreasing pH. At $pH < 3.5$, the study metals were increasingly adsorbed in the following order: $Cu^{2+} < Pb^{2+} < Cd^{2+} < Zn^{2+} \leq Mn^{2+} \cong Cr^{3+} \cong Ni^{2+}$. The effect of ligand in solution influences the adsorption of heavy metals on clay. In this case the metal adsorption increases in the following order: $Cr^{3+} < Cu^{2+} < Ni^{2+} < Zn^{2+} \leq Cd^{2+} \leq Pb^{2+} \leq Mn^{2+}$.

Bansode (2003)[26] studied adsorption effectiveness of pecan shell-based granular activated carbons (GACs) in removing metal ions ($Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$) in municipal and industrial wastewater. Pecan shells were activated by phosphoric acid, steam or carbon dioxide activation methods. The results revealed that acid-activated pecan shell carbon adsorbed more lead ion and zinc ion than other carbons. Acid- and steam-activated pecan shell-based GACs are effective metal ion adsorbents.

Miranda-Trevino (2003)[27] used kaolinite clay as adsorbent for the adsorption of Pb, Zn and Cd. Studies were carried out as a function of exposure time (0.1, 1, 2, 4, 8, 12 and 24 h), initial lead concentration (1, 2 and 3 mmol/l). The kaolinite retained up to 10.0 μmol/g of Pb, 8.40 μmol/g of Zn and 6.00 μmol/g of Cd when it was mixed with the 3.0 mmol/l concentration of heavy metals. The sizes of the atomic radii are 1.81, 1.71 and 1.53 Å for Pb, Cd and Zn, respectively.

Boonamnuayvitaya (2004)[28] studied adsorption of metals ($Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$ , $Zn^{2+}$ and $Ni^{2+}$) by coffee residues binding with clay as adsorbent in pyrolysis temperature of 500°C, weight ratio of coffee residues to clay of 80:20 and particle size diameter of 4 mm. The adsorption increased in the order of $Cd^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+}$. The effects of solution pH and temperature on the adsorption of $Cd^{2+}$ were investigated. The $Cd^{2+}$adsorption increased with increasing pH and temperature. Desorption was easily achieved by leaching with distilled water which gave the recovery yield of 88-92%.

# CHAPTER III

# EXPERIMENTAL

In the present study of the adsorption of mercury chloride with clay, the experiment was divided into five steps.

1. Preparation and characterization of adsorbents.
2. Study of adsorption isotherm of mercury.
3. Study of the optimum conditions for mercury adsorption.
4. Study of real sample.
5. Desorption of mercury.

## 3.1 Preparation and characterization of adsorbents

### 3.1.1 Equipments

| Equipments | Brand | Model |
|---|---|---|
| Analytical balance | Mettler Toledo | AG 245 |
| Hot air oven | Sanyo Gallenleamp | OHF 097 XX1.5 |
| Magnetic stirrer | Heidoph | MR100 |
| Centrifuge | Hettich | Universal 32R |
| pH meter | Cyberscan | 500 |
| Heating bath | Haake | Circulator C10 |
| Muffle furnances | Sanyo Gallenleamp | FRM 009 XX2.5 |
| Vacuum pressure pump | Millipore | XX55 220 50 |
| UV Visible spectrometer | Perkin Elmer | Lambda 20 |
| Titrator | Mettler Toledo | DL 53 |

### 3.1.2 Chemicals

| Chemical | Supplier |
|---|---|
| 1. Mercuric standard solution, 1000 mg/L | Fisher chemical, AR grade |
| 2. Hydrochloric acid | Merck, Germany, AR grade |
| 3. Sodium hydroxide | Merck, Germany, AR grade |
| 4. Potassium permanganate | Merck, Germany, AR grade |
| 5. Sulfuric acid | Merck, Germany, AR grade |
| 6. Nitric acid | Merck, Germany, AR grade |
| 7. Potassium persulfate | Merck, Germany, AR grade |
| 8. Sodium borohydride | Merck, Germany, AR grade |
| 9. 2-Mercaptobenzothiazole | Fluka, AR grade |
| 10. Thiourea | Fluka, AR grade |
| 11. Ammonium sulfide | Merck, Germany, AR grade |
| 12. Sodium chloride | Merck, Germany, AR grade |
| 13. Hydroxylamine sulfate solution | Merck, Germany, AR grade |
| 14. Bentonite | Cernic International Co., Ltd. |
| 15. China clay | Cernic International Co., Ltd. |
| 16. Ball clay | Cernic International Co., Ltd. |
| 17. Silane | JJ-Degussa Chemicals (T) Ltd. |
| 18. Copper (II) chloride | Merck, Germany, AR grade |
| 19. Ethylenediamine | Merck, Germany, AR grade |

### 3.1.3 Analytical instruments

**- Flow Injection Mercury System (FIMS)**

Mercury analysis was carried out using FIMS Perkin Elmer at Intertek Testing Services (Thailand) Co., Ltd. The samples were prepared by digesting the samples with concentrated sulfuric acid, nitric acid, potassium permanganate and potassium persulfate. Detection limit is 0.04 µg/L. Flow Injection Mercury System (FIMS) combines the advantages of flow injection and atomic absorption measurement into a compact mercury analyzer. The flow injection principle used in the FIMS is illustrated in Figure 3.1.

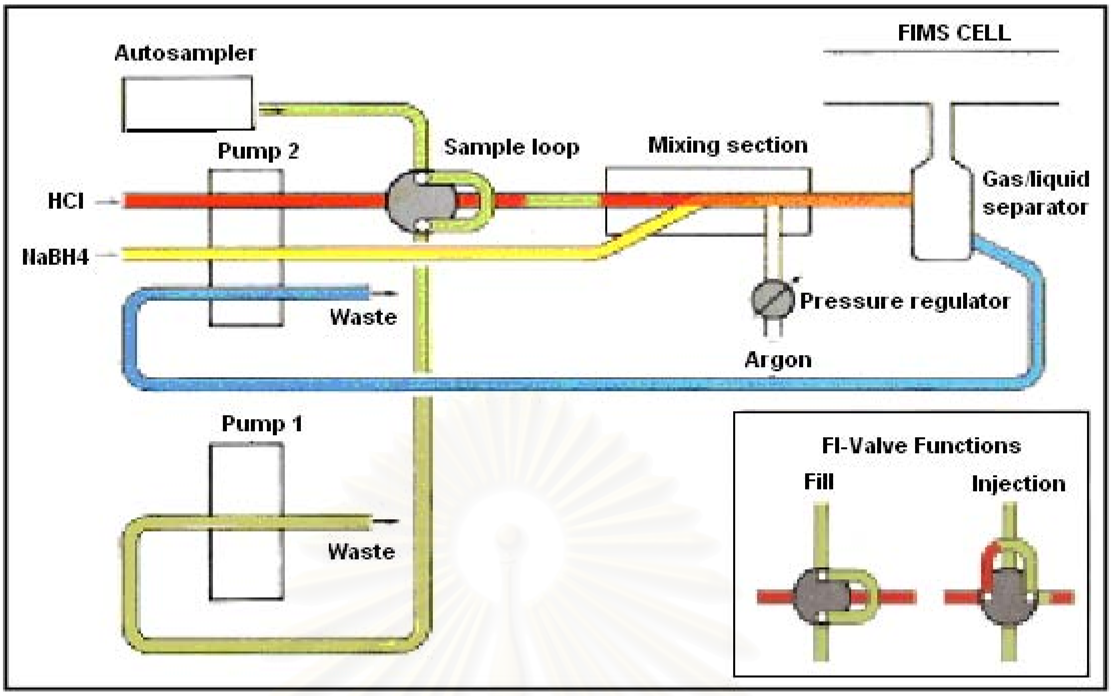


**Figure 3.1** Flow injection mercury flow diagram.

The peristaltic pumps are used to deliver the carrier and reductant streams and for waste removal. When the flow injection (FI) valve is in the FILL position, the sample loop is filled with an exact volume of sample. When the valve is switched to the INJECT position, the sample is introduced into the carrier stream and transported to the mixing section for reaction with $NaBH_4$. The resulting reaction mixture is then carried to a gas/liquid separator where the elemental mercury is liberated and, after passing through the polytetrafluoroethylene (PTFE) filter, is transported to the absorption cell by an argon carrier gas.

**- Fourier Transform Infrared Spectrometer**

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 $cm^{-1}$ to 4000 $cm^{-1}$ in transmittance mode.

**- X-Ray Diffractometer**

X-ray diffraction (XRD) technique is used to characterize samples of finely divided material. These techniques cover various investigations, including qualitative and quantitative analysis phase identification, determination of crystallinity, lattice-parameter determinations.

### 3.1.4 Acidity of clay[37]

The method used in the determination of acidity by value titration was modified as follow In this method, 0.1 grams of clay, dried at 120 °C for 6 h was taken in a conical flask to which 3 ml of 0.1 N NaOH was titrated with 0.1 N HCl. Acidity was determined as milliequivalents of NaOH used per 100 grams of clay.

$$\begin{array}{ll}\text{Acidity of clay} & \\ \text{(meq/100 g clay)} & \end{array} = \frac{(V_1\times [\mathrm{NaOH}])-(V_2 \times [\mathrm{HCl}]) \times 100}{\text{amount of clay}}$$

Where: $V_1$ = the volume of NaOH, mL

$V_2$ = the volume of HCl, mL

[NaOH] = NaOH concentration, N

[HCl] = HCl concentration, N

### 3.1.5 Cation Exchange capacity[42]

The cation exchange capacity (CEC) is one of the basic properties of clay minerals. The CEC quantifies of the soil's ability to exchange cation and retain nutrients and is a measure of the soil quality. The CEC influences the interaction of plants with nutrients but also with contaminants. This is a determination of the CEC with copper bisethylenediamine.

**Preparation of complex solution**

$[Cu(EDA)_2]^{2+}$ solution: A 1 M solution of $CuCl_2$ is prepared by dissolving 26.89 grams $CuCl_2$ in distilled water to give 200 mL. If the ethylenediamine requires purification, sodium hydroxide is added to adsorb traces of water. The amine is then distilled. A 1 M solution of ethylenediamine is prepared in distilled water to yield 500 mL. The complex is formed by adding 50 mL of the $CuCl_2$ solution to 102 mL of ethylenediamine solution. The slight excess of the amine ensure complete formation of the complex. The solution is diluted with water to one litre to give a 0.05 M $[Cu(EDA)_2]^{2+}$ solution.

**Cation exchange procedure**

0.3 to 0.5 grams of dry clay are weighed in a centrifugal tube. 2 to 5 mL of the complex solution is diluted with distilled water to 25 mL and added to the clay. The samples were shaken for 30 min and then centrifuged. The concentration of the complex remaining in the supernatant is determined by visible spectrophotometry at $\lambda_{max} = 548$ nm.

$$\underset{\text{(meq/g clay)}}{\text{CEC of clay}} = \frac{(C_1-C_2) \times V \times 2}{1000 \times g}$$

Where: $C_1$ = the initial concentration of $[Cu(EDA)_2]^{2+}$ solution before exchange, mM

$C_2$ = the concentration of $[Cu(EDA)_2]^{2+}$ solution after cexchange, mM

$V$ = mL of $[Cu(EDA)_2]^{2+}$ used

$g$ = amount of clay, grams

### 3.1.6 Heat treatment

Approximately 20 grams of clay (bentonite, china clay and ball call) were heated at temperature of 150, 250, 350, 450 and 550°C for 6 h.

### 3.1.7 Acid treatment[29]

The clay was treated with 10 mL of 6 M $H_2SO_4$ and 30 ml of 0.5 M $KMnO_4$. The mixture was gently shaken for 4 h at 80°C and then filtered, washed with deionized water and dried at 80°C overnight. The material was ground and sieved.

### 3.1.8 Sulfide treatment

Clay (10 grams) was treated with 250 mL of 0.1 M acetone solution of sodium sulfide and stirred 30 min. The solvent was evaporated. The material was then washed repeatedly with deionized water until the washing water appeared clear. Finally the product was dried at 80°C overnight.

### 3.1.9 Thiourea treatment[19]

The natural clay was loaded with thiourea and used for the removal of Hg(II). The structure of the thiourea is given in Figure 3.2.

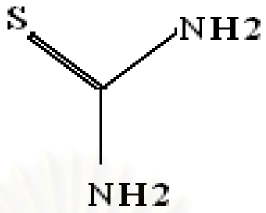


**Figure 3.2** Structure of thiourea.

Clay (10 grams) was dried at 150°C for 6 h. 50 mL of 5 M solution of thiourea was added. The mixture was stirred overnight. Then treated clay was washed with deionized water and dried at 80°C overnight.

### 3.1.10 2-Mercaptobenzothiazole treatment[30]

The 2-mercaptobenzothiazole loaded natural clay was prepared for the removal of Hg(II) from aqueous media. The structure of the 2-mercaptobenzothiazole is given in Figure 3.3.

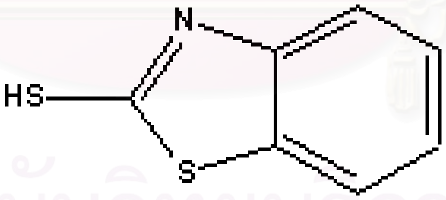


**Figure 3.3** Structure of 2-mercaptobenzothiazole

The clay (20 grams) was treated with 10 mL of 6 M $H_2SO_4$ and 30 mL of 0.5 M $KMnO_4$. The mixture was gently shaken for 4 h at 80°C and then filtered, washed with deionized water and dried at 80°C overnight. About 15 grams of this treated clay was immersed in 15 ml of 2-mercaptobenzothiazole in acetone solution (10% w/v) and shaken for 4 h and then the solvent was evaporated at room temperature. The material was then washed repeatedly with deionized water to remove any non-adsorbed reagent until the washing water appeared clear. Finally the product was dried at 80°C overnight**.**

## 3.2 Study of adsorption isotherm of mercury

### 3.2.1 Mercury analysis by cold vapor technique

**Cold vapor technique**

In the analysis of mercury by cold vapor technique, mercury in the sample solution is reduced to the elemental state and aerated to purge the mercury vapor. The vapor is swept through a long path cell where the absorbance at 253.7 nm is measured. This significantly simplifies the instrumentation required in that the need for a nebulizer and a burner system is eliminated.

Flow injection mercury hydride system (FIMS) is a high sensitivity and suitable technique for measurement of mercury. The technique involves the reaction of acidified aqueous sample with a reducing agent such as sodium borohydride. The sodium borohydride acid reduction generates hydrides as shown in equation (2).

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8H \qquad (2)$$

This reaction generates volatile hydride which was transported to a quartz cell by argon carrier gas. In the quartz cell, the hydrides were converted to gaseous metal atoms. Thus technique is capable of detecting, not organomercury. As a consequence, organic mercury compounds must be converted to inorganic mercury prior to determination. Digestion of sample was necessary in order to obtain the ionic form and reduce analytical interferences. Samples are digested with permanganate-persulfate solution, nitric acid and sulfuric acid, method from The United States Environmental Protection Agency (US EPA) 7470A[32] for liquid sample and US EPA 7471A[33] for solid or semisolid sample. The FIMS uses a hydrochloric acid carrier solution, sodium borohydride solution as the reductant, and includes a long path flow cell with a 253.7 nm source. The detection limit was 0.04 μg/L.

### 3.2.2 Adsorption isotherm

The condition of 10-100 µg/L of 50 mL mercury solution at pH 6.0 and room temperature was used for determination of adsorption isotherm. The amount of adsorbent used was 0.01 grams. Adsorption time of 30 min was used for batch method.

## 3.3 Study of the optimum conditions for mercury adsorption

### 3.3.1 Optimum condition for adsorption of mercury

The adsorption of mercury was examined by batch and column experiments performed in duplicate. The test solution was prepared by diluting 1000 mg/L $HgCl_2$ in deionized water. The kinetic and adsorption isotherm of three types of clay (bentonite, china clay and ball clay) were studied. The effect of pH on Hg(II) adsorption was studied using Hg(II) concentrations of 100 µg/L, by varying the initial pH of the solution between 3 and 8 using HCl and NaOH for pH adjustment. Tests were also made to find out the effect of NaCl concentration on Hg(II) adsorption. The effect of adsorbent dose was tested using Hg(II) concentration of 100 µg/L by varying the adsorbent dose between 0.2 and 10 g/L. The temperature of adsorption was studied between room temperature and 90°C.

### 3.3.2 Comparison of batch and column methods

**Batch method**[26]

Batch adsorption studies are carried out with 0.05 grams of treated clay and 25 mL of mercury solution with desired concentration at pH 6.0 (with HCl and NaOH) in 100 mL conical flasks, displayed in Figure 3.4.

**Figure 3.4** Apparatus in batch method.

The treated clay slurry was stirred at 500 rpm on a magnetic stirrer for 30 minutes. After 30 minutes, an aliquot of the solution was filtered through filter paper No.1 to remove treated clay. The filtrate was analyzed for mercury concentration by FIMS.

**Column method**[29]

In the column experiment, a glass column of 12 cm height and 1.0 cm internal diameter was packed with 10 grams of treated clay, displayed in Figure 3.5.

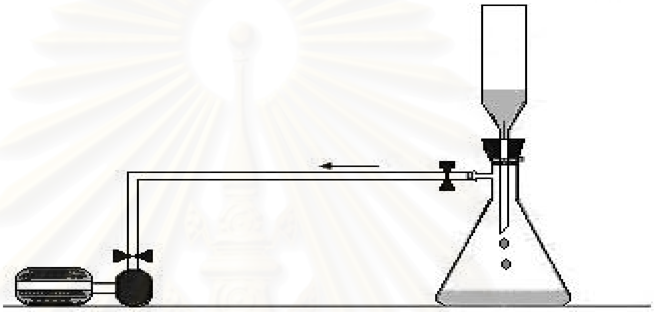


**Figure 3.5** Apparatus in column method.

About 25 mL of mercury standard solution at pH 6.0 and room temperature was passed through the column with a flow rate between 0.5 and 1.0 mL min$^{-1}$. Collected solution which passed column was collected for analysis of mercury concentration.

### 3.4 Study of real sample

### 3.4.1 Sample preparation for liquid sample [32]

100 mL of sample was transferred to a 300 ml BOD bottle. 5 ml of $H_2SO_4$ and 2.5 ml of concentrated $HNO_3$ were added into the bottle. The mixture was gently shaken. 15 ml of potassium permanganate solution and 8 mL of potassium persulfate were added to each sample bottle. Shake and stand for at least 15 min. Heat for 2 h in a water bath maintained at 95°C. Cool and 6 ml of sodium chloride-hydroxylamine sulfate was added to reduce the excess permanganate.

### 3.4.2 Sample preparation for solid sample [33]

0.2 grams portions of sample place in the BOD bottle. 5 ml of reagent water and 5 ml of aqua regia (3 volumes of hydrochloric acid and 1 volume of nitric acid) were added to each bottle. Heat 2 min in a water bath at 95°C. Cool; then 50 ml reagent water and 15 ml potassium permanganate solution were added to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

### 3.5 Desorption of mercury[12]

**3.5.1 Desorption for batch method:** spent adsorbent obtained from the adsorption experiment was stirred in 25 mL of 6 M HCl for 24 h. Sample was centrifuged and kept before analysis.

**3.5.2 Desorption for column method:** spent adsorbent obtained from the adsorption experiment was washed with 25 mL of deionized water. The adsorbed mercury was eluted with 25 mL of 6 M HCl and the effluent was collected for analysis of mercury.

# CHAPTER IV

# RESULTS AND DISCUSSIONS

Study on removal of mercury compounds was conducted in a batch reactor. In each experiment, 50 mL of mercury solution (as mercury chloride) is used as adsorbate. Adsorbents used are bentonite, ball clay and china clay. These adsorbents were treated by various ways: heat treatment, acid treatment or chemical treatment; 2-mercaptobenzothiazole, thiourea and sulfide. After each experiment, sample and spent adsorbent were separated by centrifugation then digested with permanganate-persulfate solution. After digestion, permanganate was reduced with hydroxylamine. Mercury content was determined by cold vapor technique Atomic Absorption Spectroscopy (AAS).

## 4.1 Characterization of adsorbents from chemical treatment

### 4.1.1 The chemical composition of clays

The chemical compositions of clays are presented in Table 4.1 (Information was obtained from Cernic International Co., Ltd.).

**Table 4.1** Origin and chemical compositions of clays

| **Clay** | **Bentonite** | **China clay** | **Ball clay** |
|---|---|---|---|
| Origin | Chantaburi | Lampang | Suratthani |
| $SiO_2$ (%) | 63.60 | 44.85 | 51.5 |
| $Al_2O_3$ (%) | 17.60 | 37.98 | 23.0 |
| CaO (%) | 3.00 | 0.06 | 0.37 |
| MgO (%) | Trace | 0.12 | 0.12 |
| $TiO_2$ (%) | - | 0.07 | 0.63 |
| $Fe_2O_3$ (%) | 3.10 | 0.97 | 1.42 |
| $Na_2O$ (%) | 3.40 | 0.04 | 0.22 |
| $K_2O$ (%) | 0.50 | 1.23 | 0.92 |
| $H_2O$ (%) | - | 0.65 | - |
| Loss on ignition (%) | 5.80 | 13.94 | 19.60 |

### 4.1.2 Surface area of clay

BET methods determined surface area of clays and results were displayed in Figure 4.1

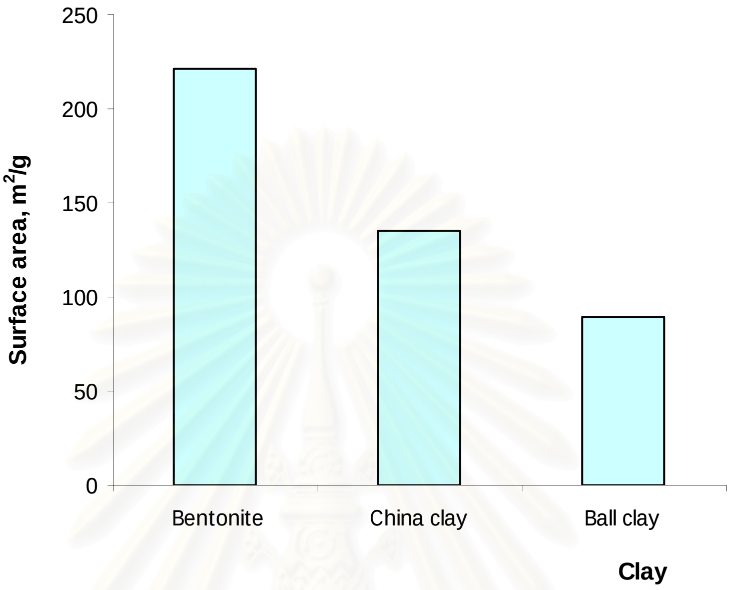


**Figure 4.1** Surface areas of clays.

### 4.1.3 Acidity of clay

The total acidity of clay (determined by NaOH titrations and expressed in meq of NaOH used per 100 grams of clay) in section 3.4 is presented in Table 4.2.

**Table 4.2** Comparison of acidity for raw and treated clays.

| Clay | Raw | Acid treated | Heated treated |
|---|---|---|---|
| Bentonite | 57.21 | 77.27 | 57.28 |
| China clay | 54.45 | 57.31 | 54.52 |
| Ball clay | 52.63 | 55.15 | 53.01 |

Bentonite exhibited the maximum acidity followed by china clay and ball clay, respectively. Because the acid treatment replaces exchangeable $K^+$, $Na^+$, $Ca^{2+}$ by $H^+$ in the interlayer space thus rendering the clay physically more porous and electrochemically more active. Trend of acidity and surface area are the similar.

### 4.1.4 The cation exchange capacity (CEC)

The determination of the cation exchange capacity (CEC) was done by copper bisethylenediamine method. The concentration of complex remaining in the supernatant is determined by UV-VIS at $\lambda_{max}$ = 548 nm. The CEC results were presented in Tables 4.3 and 4.4.

**Table 4.3** UV-VIS data of standard $Cu(EDA)_2^{2+}$ complex at $\lambda_{max}$ 548 nm

| Concentration of $Cu(EDA)_2^{2+}$ (mM) | Absorbance |
|---|---|
| 2.5 | 0.165 |
| 5.0 | 0.316 |
| 7.5 | 0.487 |
| 10.0 | 0.641 |
| 12.5 | 0.796 |

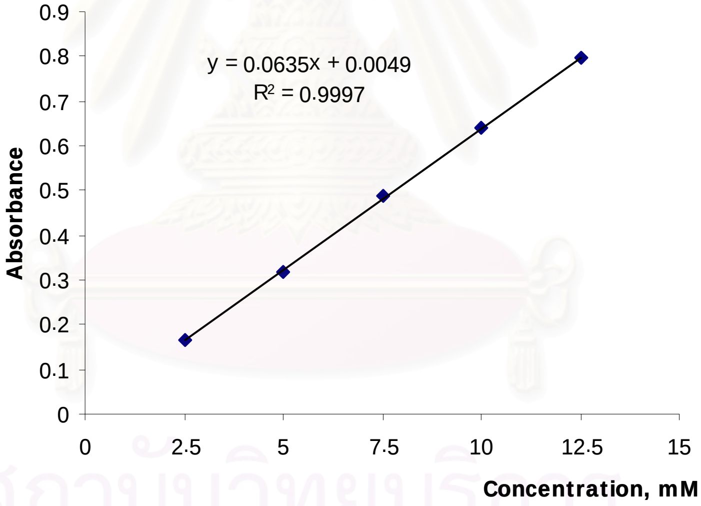


**Figure 4.2** CEC calibration curve

**Table 4.4** The cation exchange capacity of clays

| Clay | CEC (meq/g) |
|---|---|
| Bentonite | 0.756 |
| China clay | 0.225 |
| Ball clay | 0.217 |

From Table 4.4, the cation exchange capacity (CEC) of three types of clays were determined twice. The CEC of bentonite is higher than that of ball clay and china clay. This is in good agreement with their structure and charge. The bentonite is classified as montmorillonite group, has a 2:1 layer type. The layers of kaolinite are electronically neutral (1:1 layer type) but it shows some CEC, this might be because its clay crystals have broken edges.

### 4.1.5 Chemical treated clays

Clays (bentonite, china clay and ball clay) were treated chemically with sulfide, thiourea and 2-mercaptobenzothiazole. Then they were characterized by spectroscopic technique and XRD.

#### 4.1.5.1 Analysis by Fourier Transform Infrared Spectrometer (FT-IR)

The infrared spectroscopy is an effective method to identify chemical compound. It is sufficient to characterize the functional groups. The spectra of parent natural clay (bentonite, china clay and ball clay) and treated clays with chemical treatment are shown in Table 4.5 and Figures 4.3-4.17.

**Table 4.5** Characteristic FTIR bands of clays after chemical treatment

| Clay | Wave number (cm$^{-1}$) | | | | | Assignment |
|---|---|---|---|---|---|---|
| | Raw | Acid | Sulfide | Thiourea | MBT | |
| Bentonite | 3619 | 3625 | 3625 | 3625 | 3625 | O-H stretching |
| | 1637 | 1642 | 1643 | 1642 | 1641 | O-H deformation |
| | - | - | 1123 | 1124 | 1124 | S=O stretching |
| | 1036 | 1045 | 1045 | 1046 | 1047 | Si-O stretching |
| | 913 | 918 | 918 | 923 | 913 | Al-O vibration |
| China clay | 3614 | 3623 | 3620 | 3619 | 3630 | O-H stretching |
| | 1632 | 1637 | 1637 | 1638 | 1642 | O-H deformation |
| | - | - | 1121 | 1120 | 1121 | S=O stretching |
| | 1031 | 1043 | 1042 | 1045 | 1044 | Si-O stretching |
| | 913 | 918 | 915 | 918 | 918 | Al-O vibration |
| Ball clay | 3615 | 3621 | 3620 | 3619 | 3635 | O-H stretching |
| | 1637 | 1640 | 1642 | 1641 | 1647 | O-H deformation |
| | - | - | 1123 | 1121 | 1122 | S=O stretching |
| | 1037 | 1046 | 1046 | 1047 | 1048 | Si-O stretching |
| | 908 | 915 | 913 | 912 | 923 | Al-O vibration |

FT-IR spectra of all clays showed a band corresponding to the stretching vibration of structural hydroxyl group appeared at 3600-3700 cm$^{-1}$ and a broad band centered near 3400 cm$^{-1}$ was attributed to the O-H stretching vibration of water present. Similar behavior was shown by the deformation band nearby 1638 cm$^{-1}$, which may be used to indicate the amount of water in clay. The band at 1120-1125 cm$^{-1}$ in the spectrum of chemical treatment represents the S=O stretching vibrations are due to the surface sulphur groups bonded to the clay, it is assumed that the clay surface is modified with sulphur groups. The Si-O band shift to higher wave number indicated that acid treatment affected the raw clay structure. The band around 910 cm$^{-1}$ corresponding to the Al-O bending deformation became very weak for bentonite, china clay and ball clay, suggesting significant depopulation of the octahedral sheet.[34]

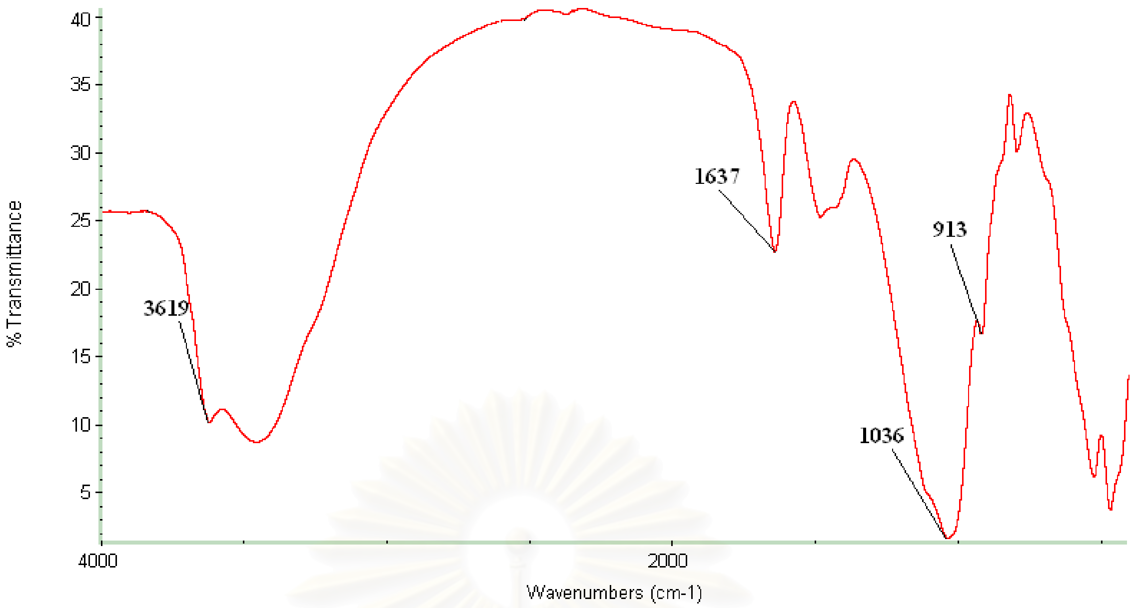


**Figure 4.3** IR spectrum of raw bentonite

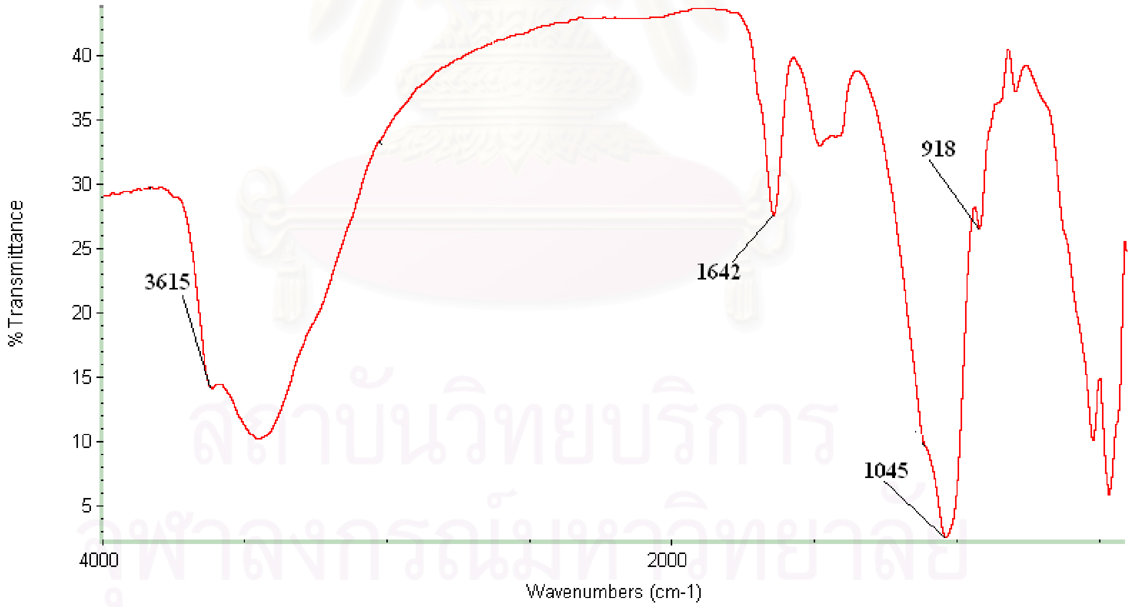


**Figure 4.4** IR spectrum of acid treated bentonite

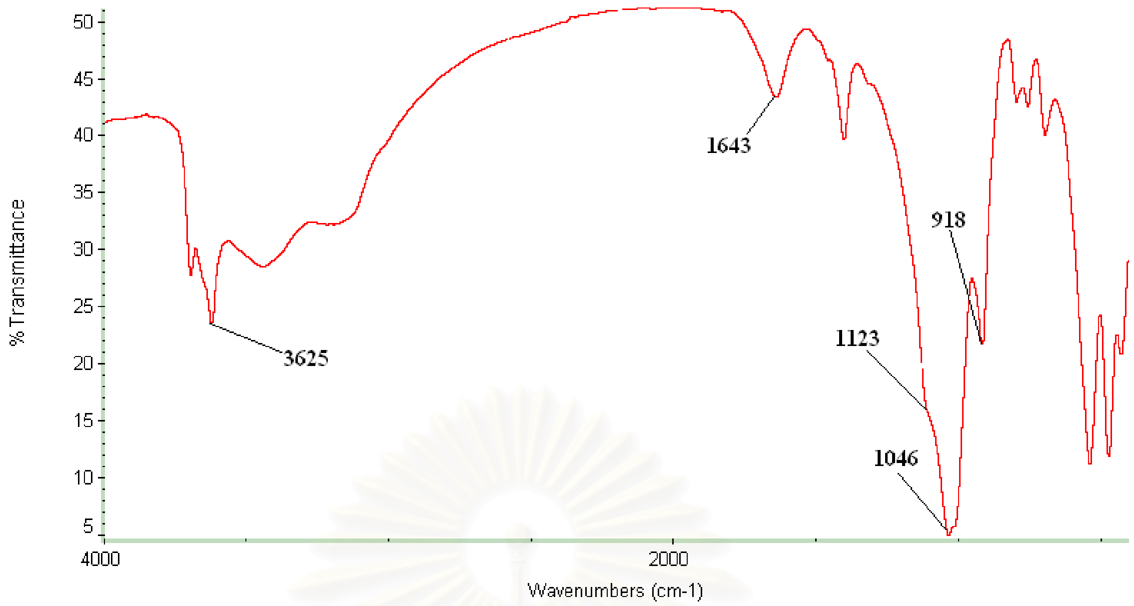


**Figure 4.5** IR spectrum of sulfide treated bentonite

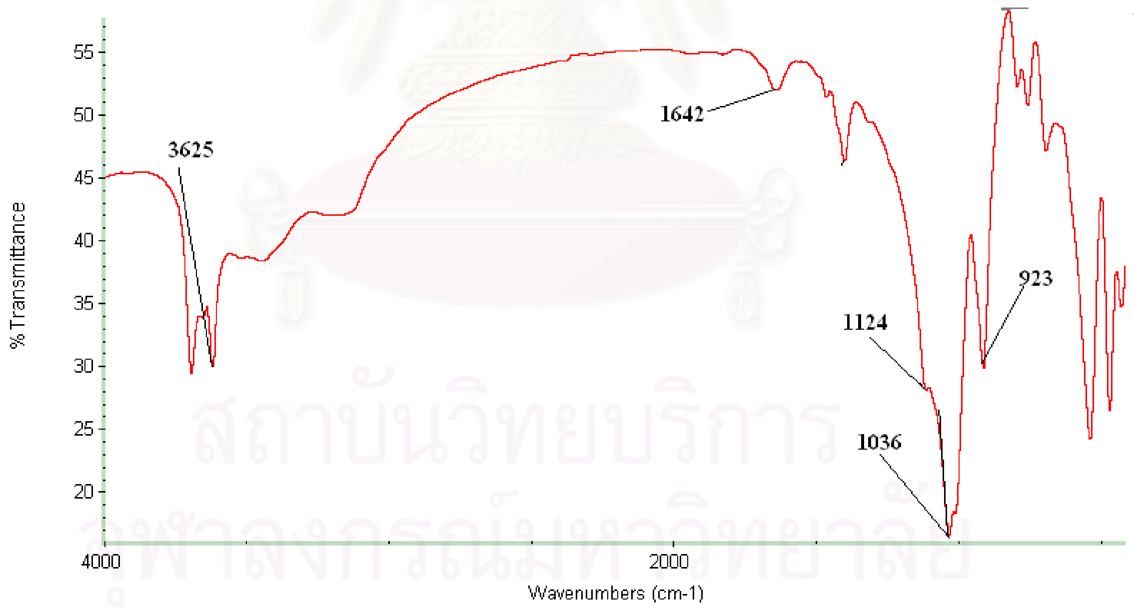


**Figure 4.6** IR spectrum of thiourea treated bentonite

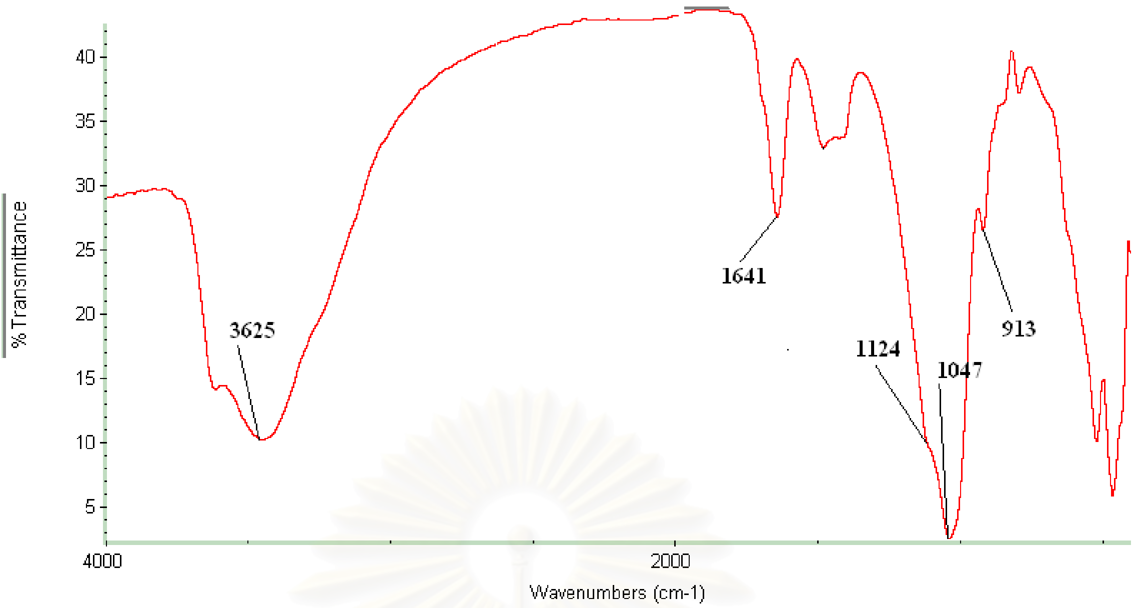


**Figure 4.7** IR spectrum of MBT treated bentonite

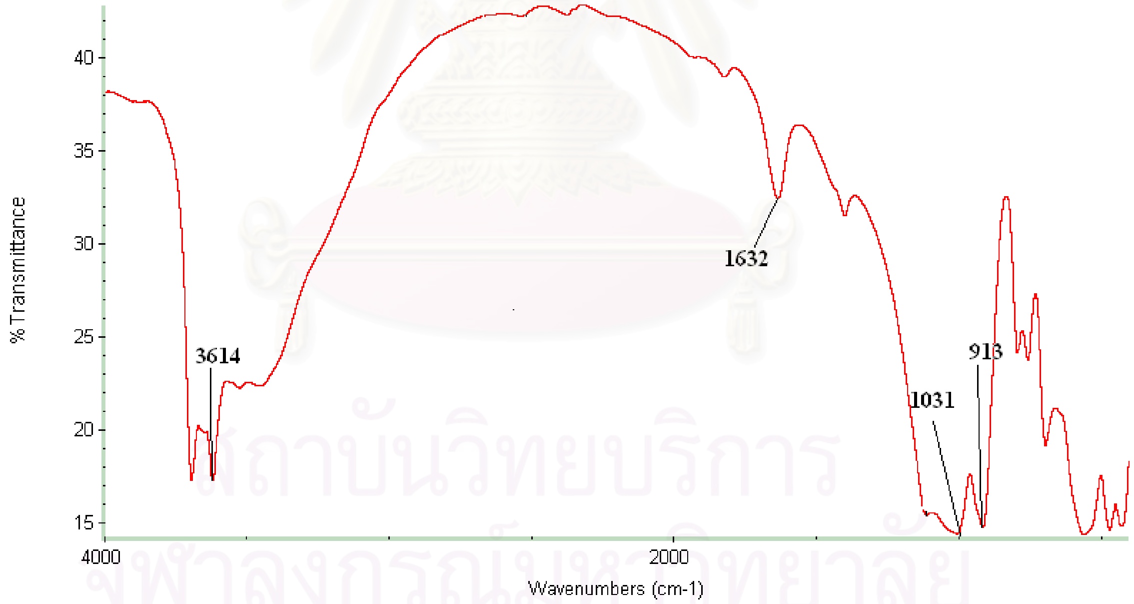


**Figure 4.8** IR spectrum of raw china clay

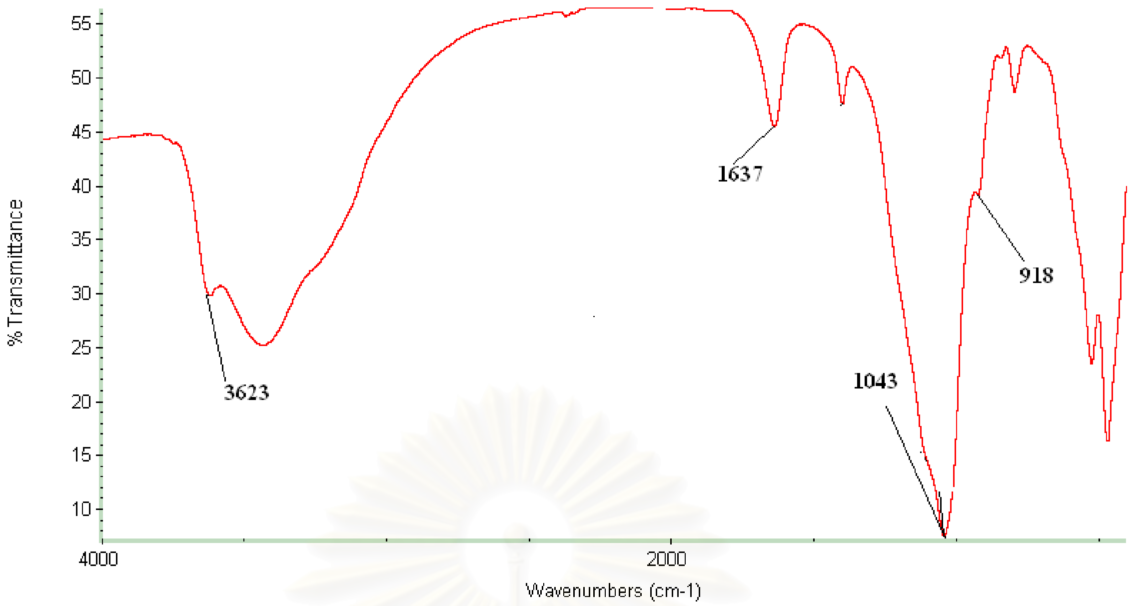


**Figure 4.9** IR spectrum of acid treated china clay

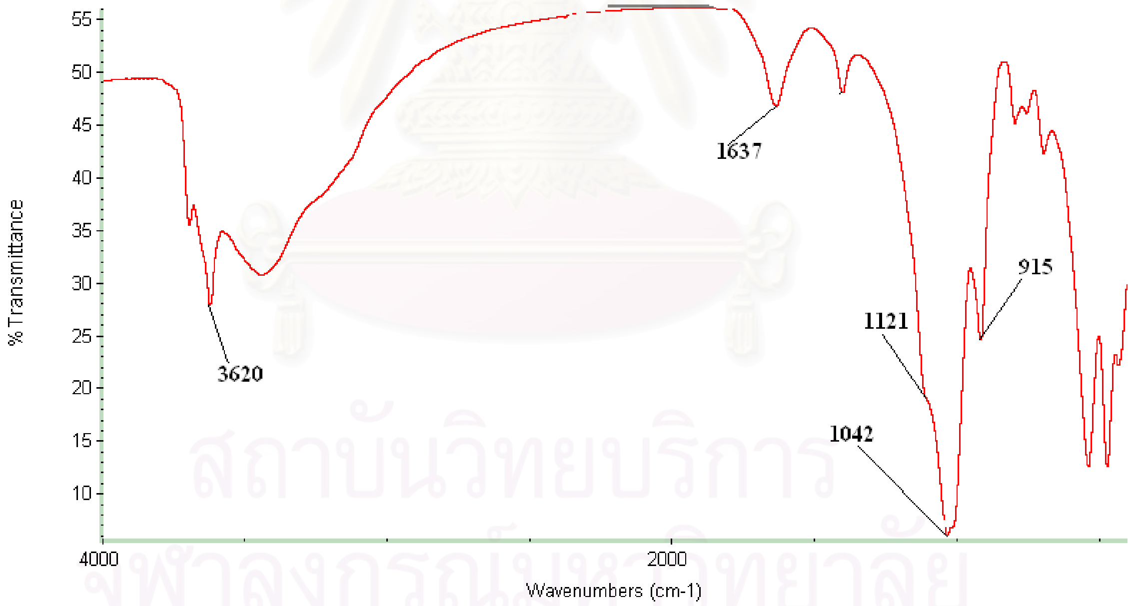


**Figure 4.10** IR spectrum of sulfide treated china clay

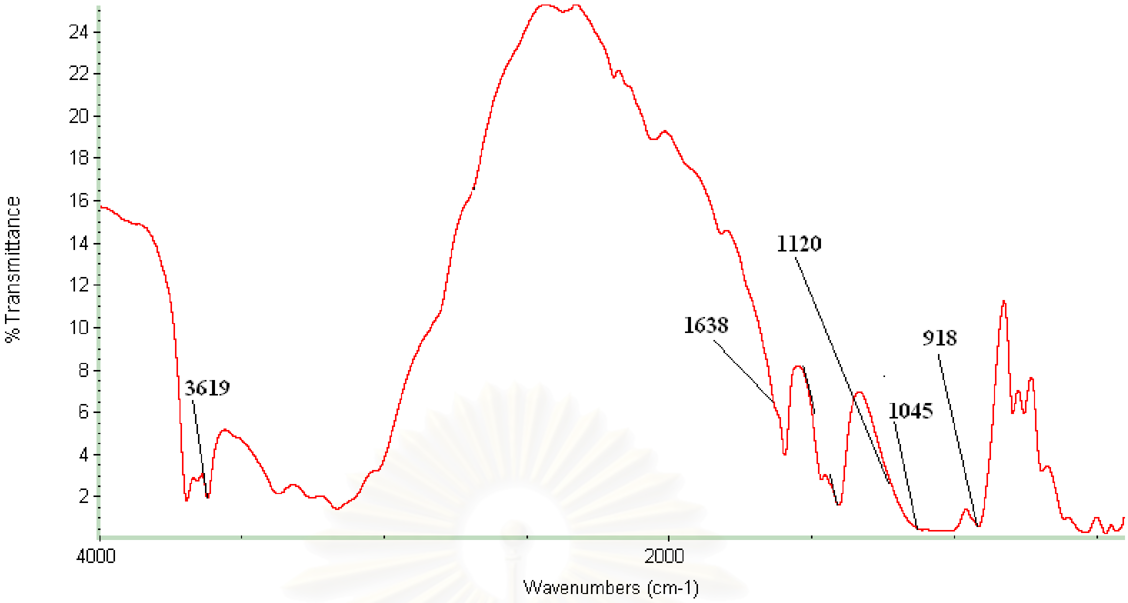


**Figure 4.11** IR spectrum of thiourea treated china clay

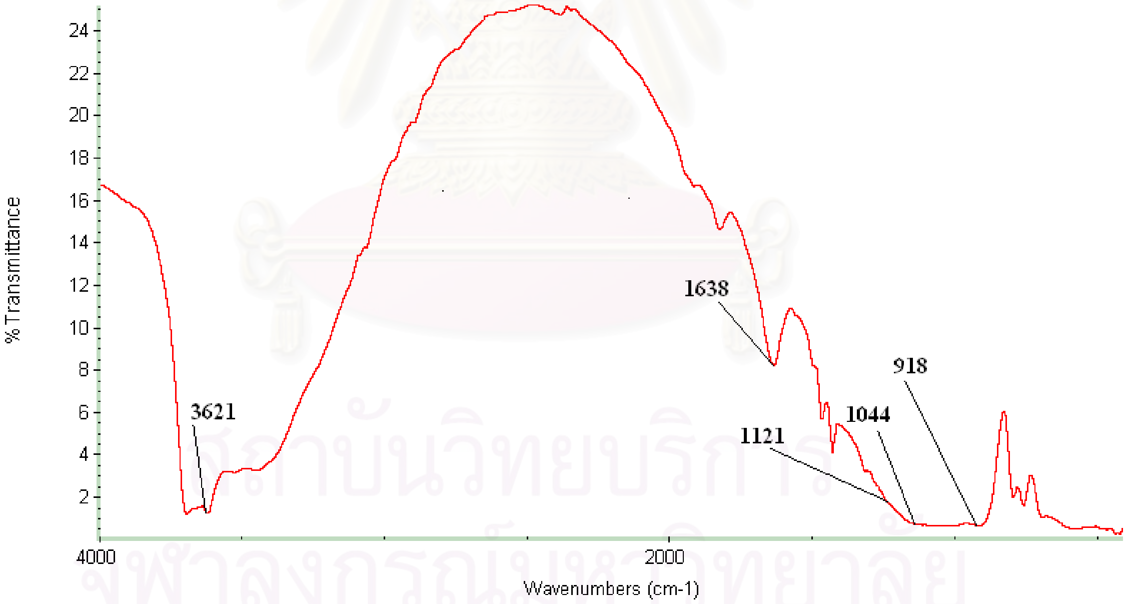


**Figure 4.12** IR spectrum of MBT treated china clay

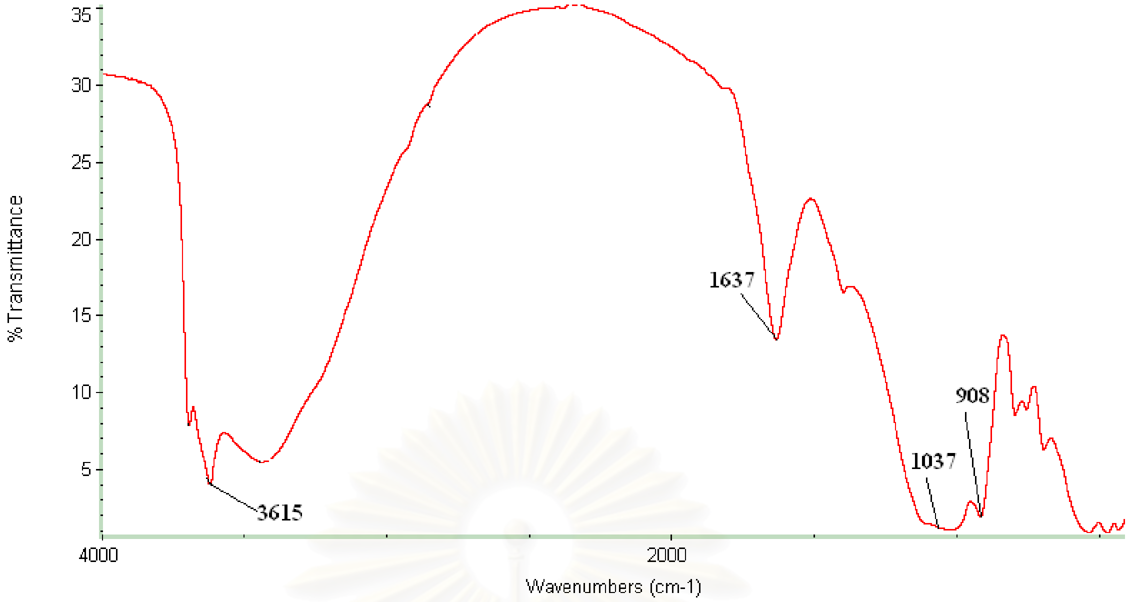


**Figure 4.13** IR spectrum of raw ball clay

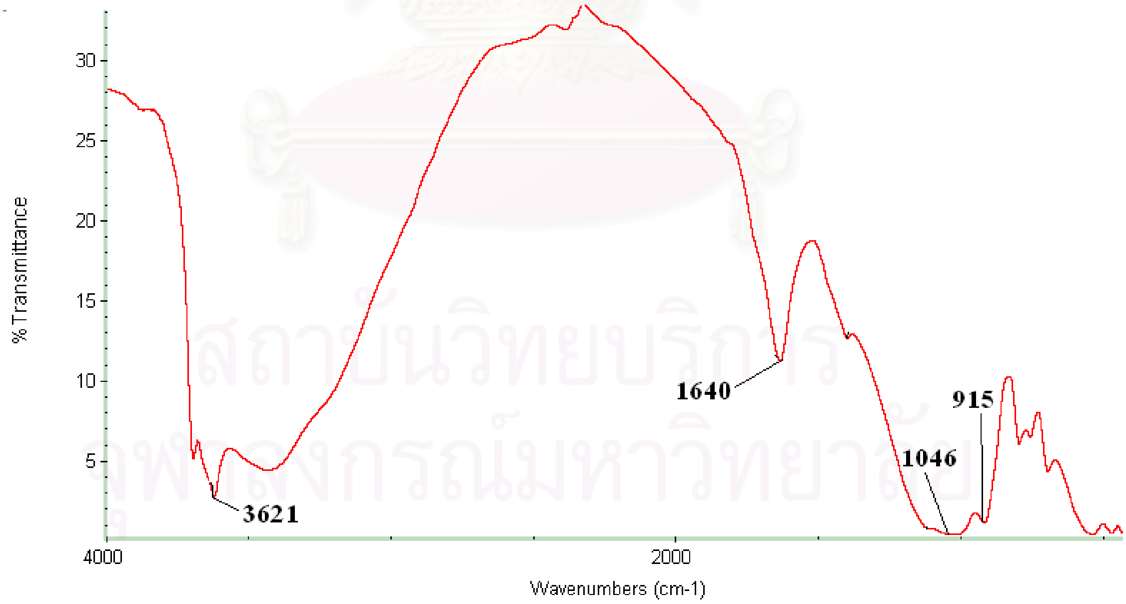


**Figure 4.14** IR spectrum of acid treated ball clay

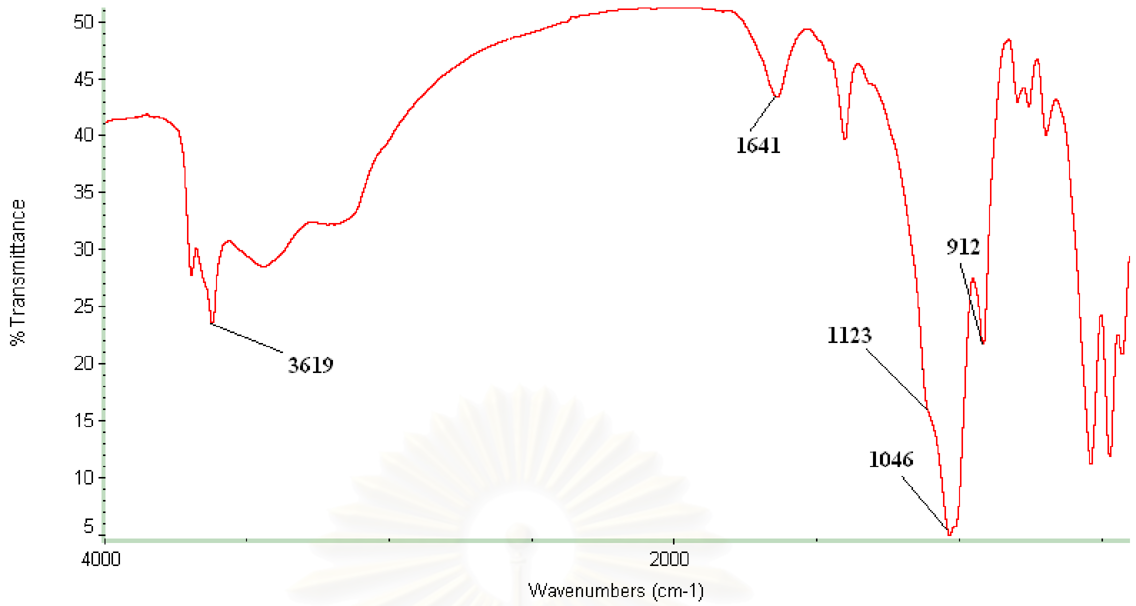


**Figure 4.15** IR spectrum of sulfide treated ball clay

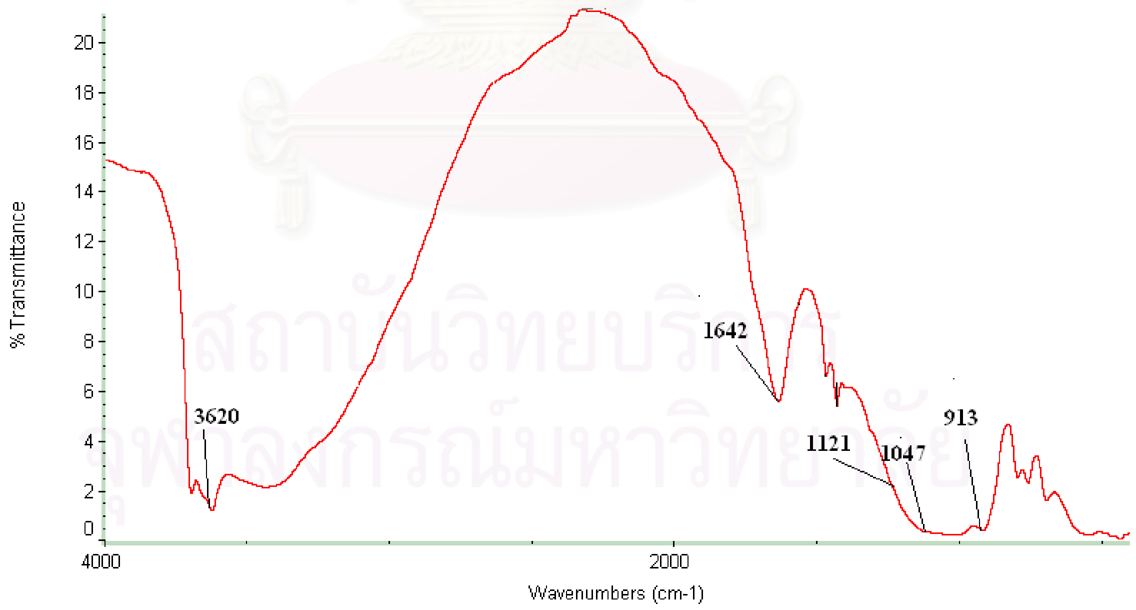


**Figure 4.16** IR spectrum of thiourea treated ball clay

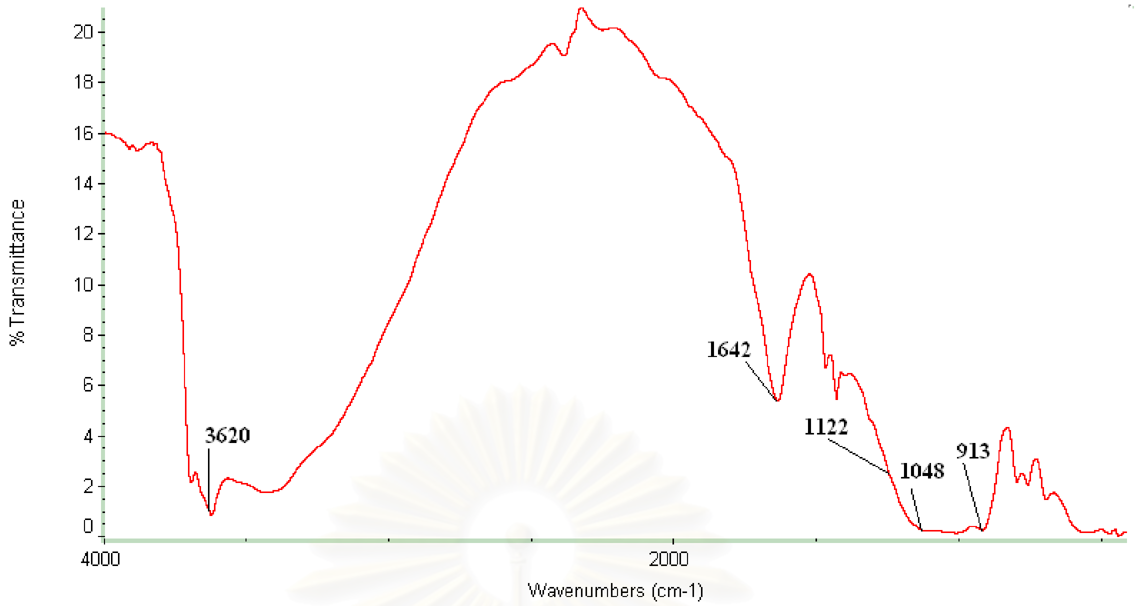


**Figure 4.17** IR spectrum of MBT treated ball clay

### 4.1.5.2 Analysis by X-Ray Diffractometer

The X-ray patterns, for either raw or treated clays, were taken by using General Electric diffractometer model XRD-5 with a graphite monochromator, using CuKα radiation (40 kV/30mA).

The crystallinity and the basal spacing of the clay can be identified by XRD spectra. Each of the clay samples consists of a primary phase and some minor phases. Structures of clays were investigated by XRD technique, XRD patterns of raw clays are shown in Figure 4.18 and Table 4.6.

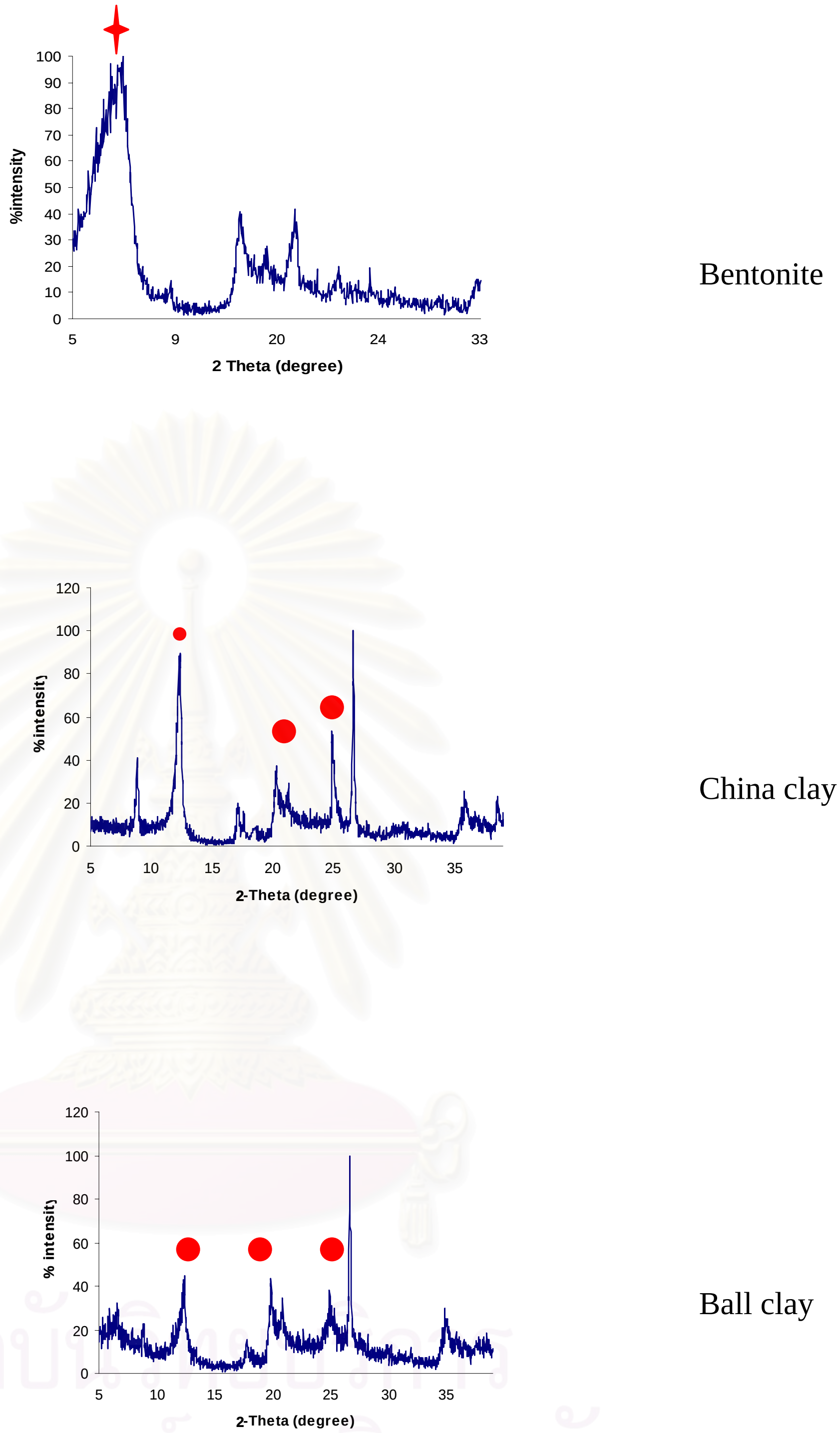


**Figure 4.18** XRD patterns of raw clays

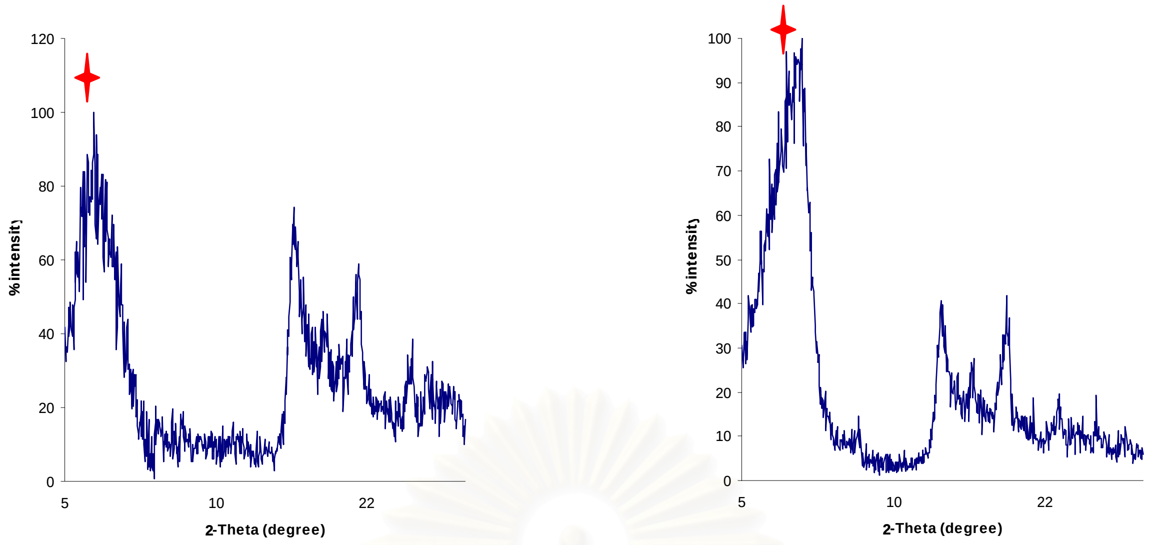
**Table 4.6** Characteristic XRD for raw clays

| Clay | 2 Theta (Degree) | d(Å) |
|---|---|---|
| Bentonite | 27.80 | 3.20 |
| | 6.48 | 12.69 |
| | 6.96 | 13.63 |
| Ball clay | 26.64 | 3.34 |
| | 19.88 | 4.46 |
| | 12.38 | 7.14 |
| China clay | 26.66 | 3.34 |
| | 24.90 | 3.57 |
| | 12.36 | 7.15 |

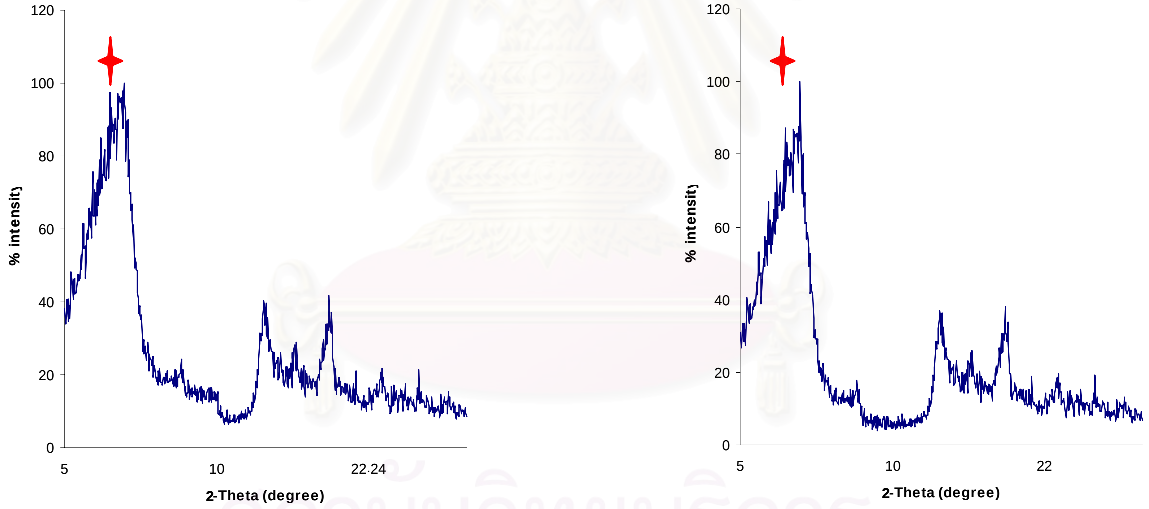
The summarized XRD data of chemical treated clays (acid, sulfide, thiourea, and MBT treatments) are shown in Table 4.7 and Figures 4.19-4.21.

**Table 4.7** Characteristic XRD are of clays after chemical treatments

| Clay | 2 Theta | | | | d(Å) | | | |
|---|---|---|---|---|---|---|---|---|
| | Acid | Sulfide | Thiourea | MBT | Acid | Sulfide | Thiourea | MBT |
| Bentonite | 27.78 | 27.80 | 27.80 | 26.66 | 3.21 | 3.21 | 3.21 | 3.34 |
| | 6.54 | 6.96 | 6.96 | 6.54 | 13.51 | 12.87 | 12.69 | 13.50 |
| | 5.97 | 6.86 | 6.48 | 5.96 | 14.82 | 12.96 | 13.63 | 14.86 |
| Ball clay | 26.66 | 26.65 | 26.64 | 26.62 | 3.34 | 3.34 | 3.34 | 3.35 |
| | 19.94 | 19.96 | 19.86 | 19.86 | 4.49 | 4.44 | 4.47 | 4.49 |
| | 12.36 | 12.41 | 12.28 | 12.34 | 7.16 | 7.12 | 7.20 | 7.17 |
| China clay | 26.64 | 26.62 | 26.66 | 27.02 | 3.34 | 3.35 | 3.34 | 3.30 |
| | 24.64 | 24.96 | 24.93 | 24.93 | 3.61 | 3.56 | 3.57 | 3.57 |
| | 12.28 | 19.86 | 12.26 | 26.66 | 7.20 | 4.47 | 7.21 | 3.34 |

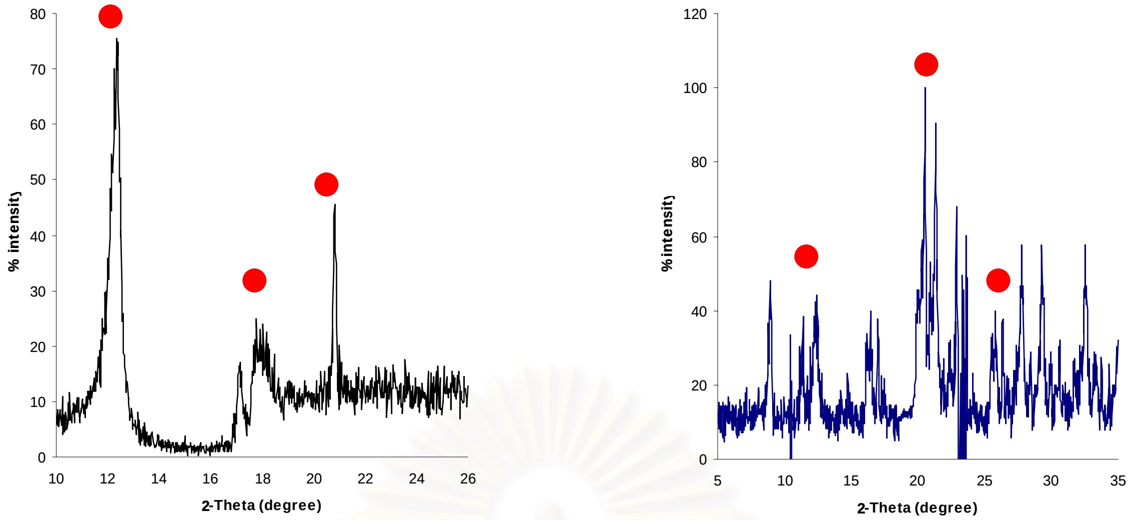


a) Acid treatment b) Sulfide treatment



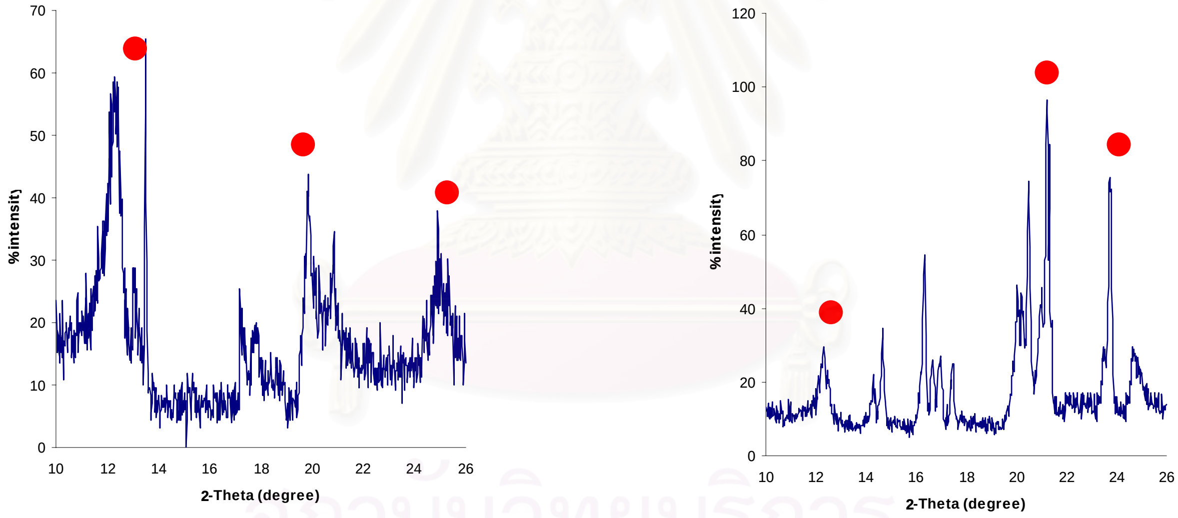
c) Thiourea treatment d) MBT treatment

**Figure 4.19** XRD patterns of chemical treated bentonite



a) Acid treatment

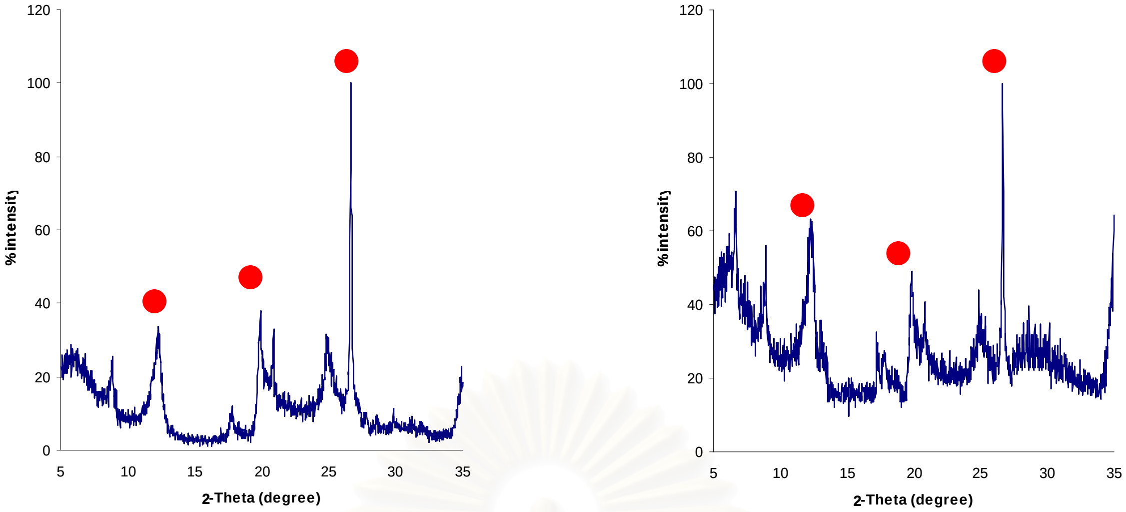
b) Sulfide treatment



c) Thiourea treatment

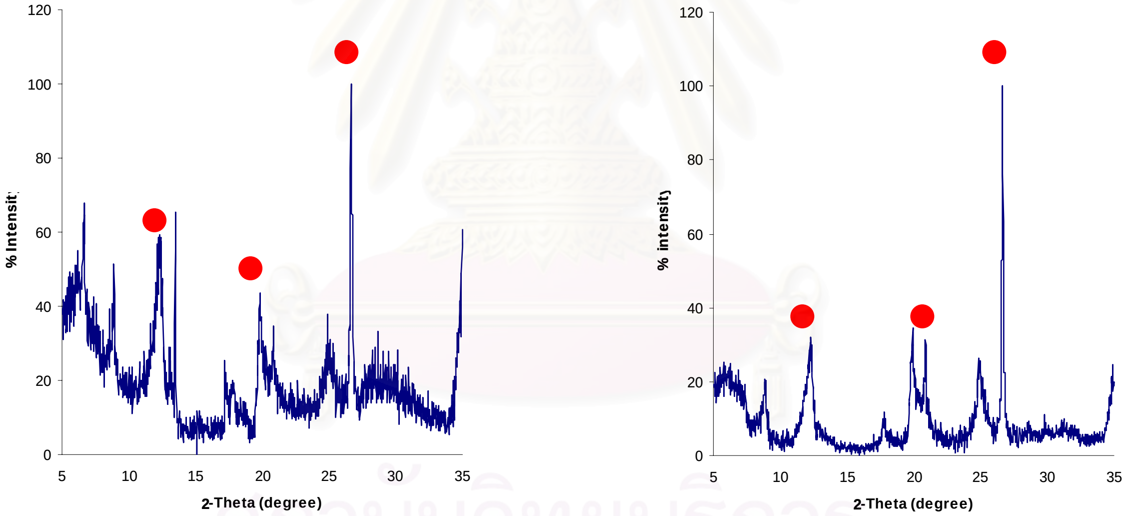
d) MBT treatment

**Figure 4.20** XRD patterns of chemical treated china clay



a) Acid treatment

b) Sulfide treatment



c) Thiourea treatment

d) MBT treatment

**Figure 4.21** XRD patterns of chemical treated ball clay

When XRD patterns of raw clays were compared with these of treated clays (Table 4.6 and Table 4.7), d-spacing was not changed significantly. This shows that chemicals added for the treatment have no effect on the clay structure.

## 4.2 Adsorption isotherm for mercury adsorption

### 4.2.1 Adsorption kinetics

The adsorption kinetic properties are important for assessment of the suitability of clay to serve as an adsorbent. The kinetic curves display in Figure 4.22 show the adsorption of Hg(II) on MBT treated bentonite using 10-100 µg/L of 50 mL mercury solution at room temperature. The amount of adsorbent used was 0.01 grams and contact time is 0-90 min.

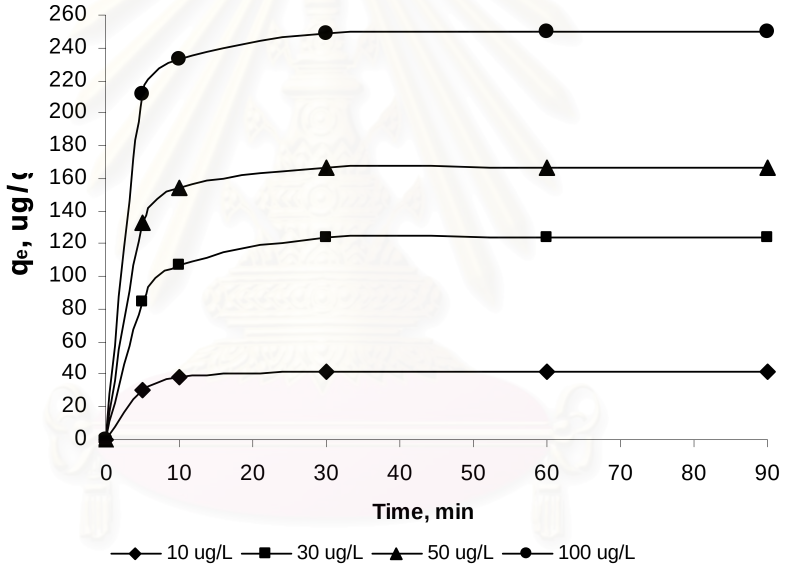


**Figure 4.22** Kinetic of mercury adsorption on MBT treated bentonite

Figure 4.22 shows typical kinetic curves for the adsorption of mercury on the MBT treated bentonite. Hg(II) ion adsorption increases sharply at a short time and slows down gradually with approaching equilibrium at 30 minutes. This behavior can be attributed to the relative decrease in the number of available sites on the adsorbent surface as the process proceeds. The kinetic curves are smooth and continuous, leading to saturation, suggesting the possibility of the formation of monolayer coverage of Hg(II) on the surface of the adsorbent.[15,18] Tend of kinetic curves of other adsorbent is the same. (Figure A2-A16)

### 4.2.2 Adsorption isotherm

The study of adsorption isotherm is useful for determining the maximum adsorption capacity of adsorbate for the given adsorbent. The adsorption isotherms in Figure 4.23 show comparison of the adsorption isotherm of chemical treated bentonite, china clay and ball clay using 10-100 μg/L of 50 mL mercury solution at room temperature. The amount of adsorbent used was 0.01 grams and contact time is 0-90 min.

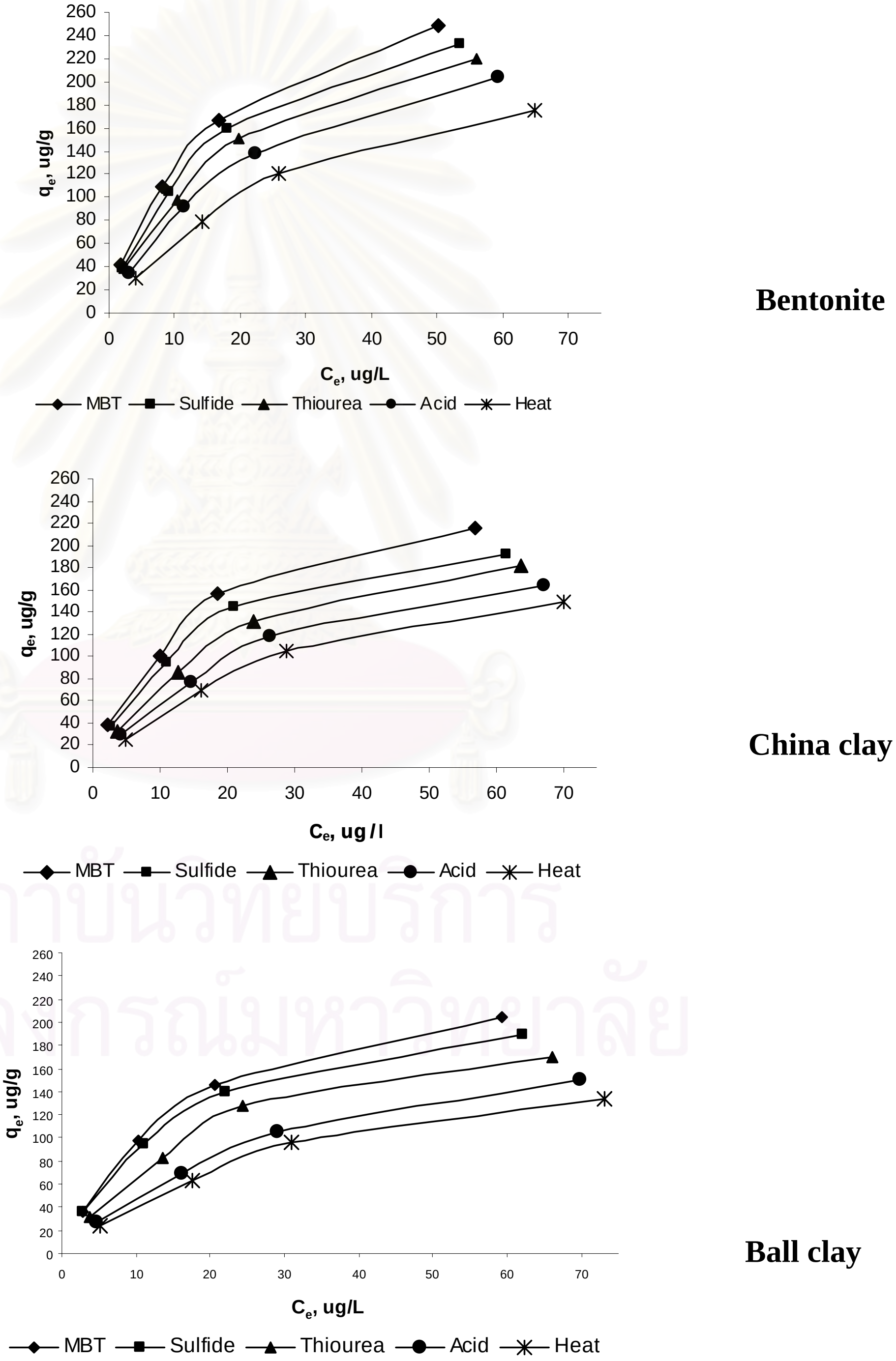


**Figure 4.23** Adsorption isotherm of Hg(II) on different modification of clays.

Figure 4.23 illustrates a comparison of the adsorption of Hg(II) on different treated of clays. The amount of mercury ion adsorbed at equilibrium per clay mass, $q_e$, is represented as a function of the equilibrium mercury ion concentration, $C_e$. Adsorption isotherms are regular, positive and concave to the concentration axis for all clays. Initial adsorption is quite rapid, which is followed by a slow approach to equilibrium at high concentrations. The results indicate that the adsorption efficiency in the order of: 2-mercaptobenzothiazole > sulfide > thiourea > acid > heat. As a result, Langmuir plot isotherms of 2-mercaptobenzothiazole treated clays were determined. The isotherms of Hg(II) adsorption on these treated clay follow type L of Giles 'classification.[39] L-type isotherms reflect adsorption at higher contaminant concentrations, corresponding to the completion of a monolayer in the experimental concentration range.

The adsorption data exhibit a Langmuir type isotherm, which can be described by the following equation:

$$C_e/q_e = 1/Q_0b + C_e/Q_0$$

(3)

Where $C_e$ = the equilibrium concentration (μg/L)

$q_e$ = the amount of Hg(II) adsorbed at equilibrium (μg/g)

$Q_0$ = the maximum adsorption capacity (μg/g)

b = intensity of adsorption (L/μg)

The model is frequently used to interpret adsorption from dilute solutions. The value of $Q_0$ gives the limit toward which adsorption from solution of pollutants and *b* can be considered as a measure of the adsorption energy.[41]

The linear plot of $C_e/q_e$ versus $C_e$ shows that the adsorption obeys Langmuir isotherm model, shown in Figure 4.24, $Q_0$ and b values were determined from the slope and intercept of the plot and are presented in Table 4.8.

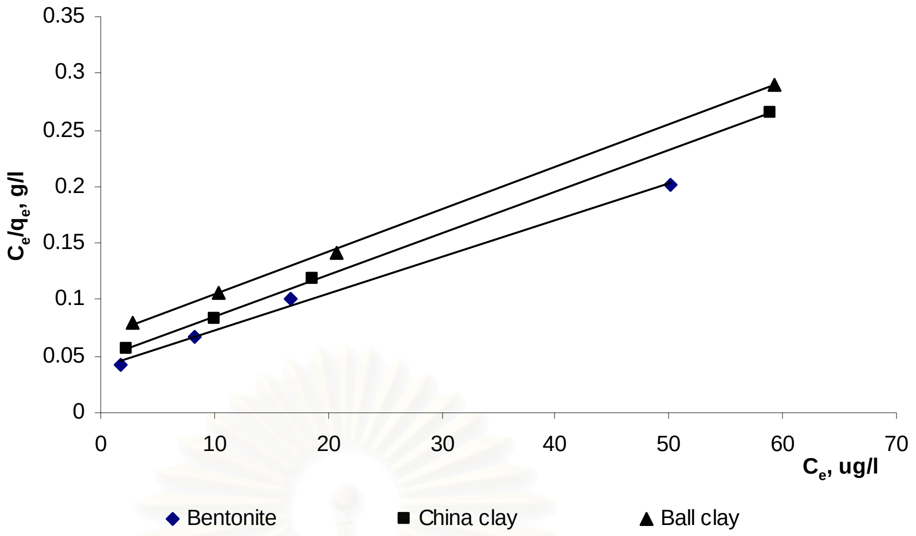


**Figure 4.24** Langmuir plots for Hg(II) adsorption on MBT treated clays.

**Table 4.8** Data for mercury adsorption obtained from Langmuir plots

| MBT treated clay | $r^2$ | $Q_0$ (μg/g) | b (L/μg) |
|---|---|---|---|
| Bentonite | 0.9963 | 312.5 | $7.9\times10^{-2}$ |
| China clay | 0.9998 | 270.3 | $7.7\times10^{-2}$ |
| Ball clay | 0.9994 | 263.2 | $5.7\times10^{-2}$ |

Table 4.8 shows the determined values of $Q_0$, 312.5, 270.3 and 263.2 μg/g for MBT treated bentonite, china clay and ball clay, respectively. These results show that the order of mercury adsorption capacity of clays is bentonite > china clay > ball clay. As expected of the quantity of mercury taken up increases with increasing adsorbent surface area.[15] Thus MBT treated bentonite was used for next experiments.

### 4.3 Heat treatment

Adsorption efficiency of clay (bentonite, china clay and ball clay) with heat treatment at various temperature of 150 to 550°C was studied. The adsorption reached contact time at 30 minutes and pH 6.0 of 100 µg/L mercury solution. Using 0.01 grams adsorbent and 50 mL of Hg(II) solution. The results are collected in Table 4.9.

**Table 4.9** Adsorption of mercury at various temperatures of adsorbent

| Temperature | 150°C | 250°C | 350°C | 450°C | 550°C |
|---|---|---|---|---|---|
| Bentonite, µg/g | 159.2 | 159.9 | 160.3 | 160.7 | 160.9 |
| China clay µg/g | 149.3 | 149.8 | 150.2 | 150.5 | 150.8 |
| Ball clay µg/g | 133.9 | 134.2 | 135.1 | 135.6 | 134.2 |

The pyrolyzed clays adsorbed Hg(II) in the range from 150-550°C were 159.2-160.9 µg Hg(II)/g adsorbent for bentonite, 149.3-150.8 µg Hg(II)/g adsorbent for china clay and 133.9-134.2 µg Hg(II)/g adsorbent for ball clay. These Table 4.9, it can be seen the amount of Hg(II) adsorbed at equilibrium nearly constants when increasing temperature for pyrolysis process indicated that temperature range from 150-550°C almost had no effect on the adsorption. Therefore 150°C was selected as pyrolysis temperature in further study.

### 4.4 Results on the optimum condition for mercury adsorption

#### 4.4.1 Effect of pH

The pH of the aqueous solution is one of the important controlling parameters in the adsorption process. The adsorption of mercury compound was studied by varying pH between 3 and 8 with hydrochloric acid or sodium hydroxide using 2-mercaptobenzothiazole treated bentonite (0.05 grams) and 25 mL of 100 µg/L initial Hg(II) concentration.. Contact time was 30 minutes, at room temperature. The results are shown in Figure 4.25.

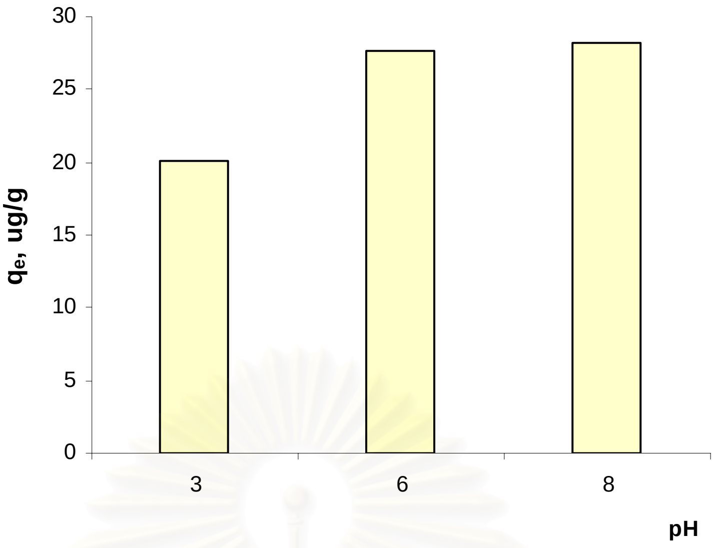


**Figure 4.25** Adsorption efficiency at various pHs

From the result it can be seen that the amount of Hg(II) adsorbed at equilibrium increases at pH 6-8. At low pH, both the adsorbent and adsorbate are positively charged ($H^+$ and $Hg^{2+}$) and therefore, the net interaction is that of electrostatic repulsion.[40] $H^+$ ions present in the reaction mixture competes with the positively charged Hg(II) ions for the surface adsorbing sites, resulting in a decrease in the removal of Hg(II). Others[20, 14] have reported similar results for the adsorption of Hg(II) from aqueous solution by activated carbon made from sago waste and 2-mercaptobenzimidazole treated clay, respectively.

### 4.4.2 Effect of temperature

Temperature has a direct influence on the amount of the sorbed substance. In this research, the experiments were conducted at various temperatures (30 to 90°C). Adsorbents used was 0.01 grams of 2-mercaptobenzothiazole treated bentonite and 50 mL of 0-100 µg/L initial Hg(II) solution. The contact time was 30 minutes. The Langmuir parameters for the adsorption isotherms obtained from different temperature were calculated from Ce/qe versus Ce plot. The results are shown in Figure 4.26 and Table 4.10.

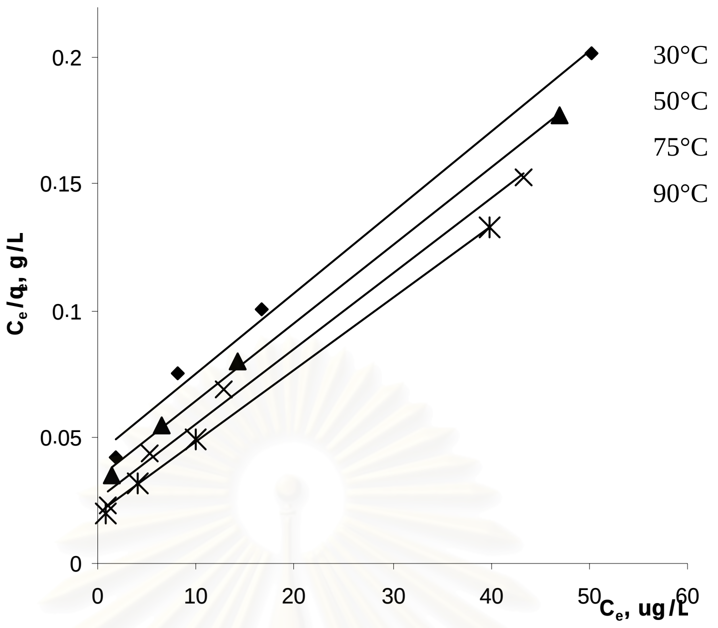


**Figure 4.26** Langmuir plot for adsorption of Hg(II) at various temperatures.

**Table 4.10** Data for mercury adsorption at various temperatures from Langmuir plot

| Temperature, °C | $Q_0$ (µg/g) | b (L/µg) |
|---|---|---|
| 30 | 312.5 | $7.3\times10^{-2}$ |
| 50 | 322.6 | $9.3\times10^{-2}$ |
| 75 | 333.3 | $1.2\times10^{-1}$ |
| 90 | 344.8 | $1.5\times10^{-1}$ |

It is observed that maximum capacity of Hg(II), $Q_0$, increases with increasing temperature. The increase of b with temperature indicates that the affinity for Hg(II) ion is more favorable at high temperature. Based on Langmuir isotherm, at high temperature the active sites are activated more than at low temperature. Heat of adsorption ($\Delta H$) which indicates the mechanism of adsorption can be estimated using the following equations:

$$\Delta G = -RT \ln b \qquad (4)$$

and

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

then

$$\ln b = -\Delta H/RT + \Delta S/R \qquad (6)$$

Where $\Delta G$ is changes of free energy (J/mol), $\Delta H$ is enthalpy (J/mol), $\Delta S$ is entropy (J/mol·K) and R is the universal gas constant (8.3144 J/mol·K). Here b is obtained from the conventional Langmuir equation. The linear plot of ln b versus 1/T is presented in Figure 4.27.

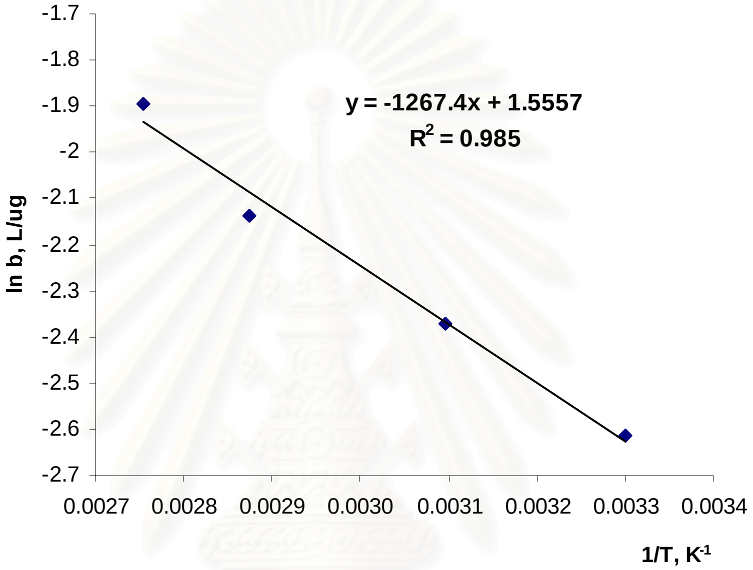


**Figure 4.27** A plot of ln b against 1/T.

The $\Delta H$ value, as determined from the slope of the plot was found to be 10,537 J/mol( 2.52 kcal/mol) which indicated that adsorption process is endothermic in nature. This data conform to the literature using various temperature from 30-80°C to adsorb $Cd^{2+}$ using coffee residues binding with clay as adsorbent. The maximum adsorption at 80°C gives the highest adsorption.[28] However, in this work, room temperature was chosen because high temperature is not suitable for real sample.

### 4.4.3Effect of ionic strength

The ionic strength of the solution is of significance for its effect on the adsorption. The adsorption of mercury compound was studied by varying ionic using sodium chloride 0.00, 0.05, 0.1, 0.5 and 1.0 M in 100 µg/L mercury concentration. Adsorbent used was 2-mercaptobenzothiazole treated bentonite at pH 6.0 and room temperature. The contact time was 30 minutes. The results are collected in Figure 4.28.

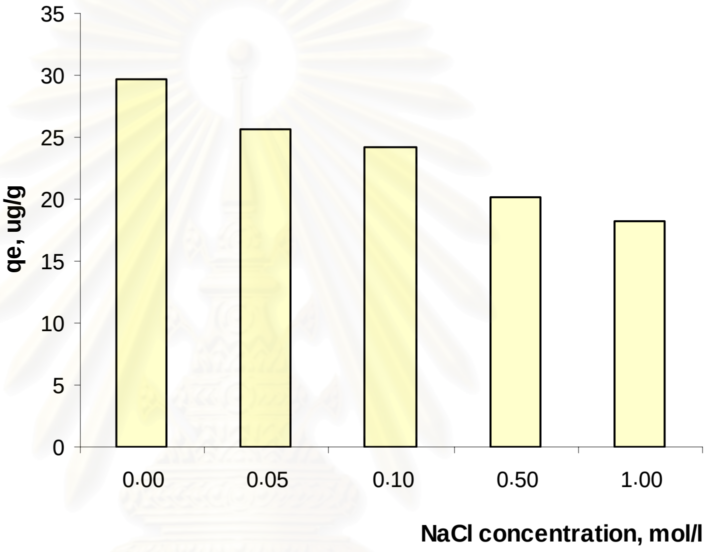


**Figure 4.28** Adsorption efficiency at various NaCl concentrations.

From the results, it was found the adsorption of Hg(II) from solution decreased with increasing ionic strength. Adsorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism. Thus, it seems that electrostatic attraction plays an important role in the removal Hg(II). The reduction in Hg(II) adsorption can be explained by the fact that the presence of $Na^+$ ions which compete for metal binding.

### 4.4.4 Initial concentration and contact time

Initial concentration and contact time are of important parameters for economical treatment application. The adsorption of mercury compound was studied by varying initial concentration of Hg(II) 10-100 µg/L. Adsorbent used was 2-

mercaptobenzothiazole treated bentonite at pH 6.0 and room temperature. The contact time was 0-90 minutes. The results are collected in Figure 4.29.

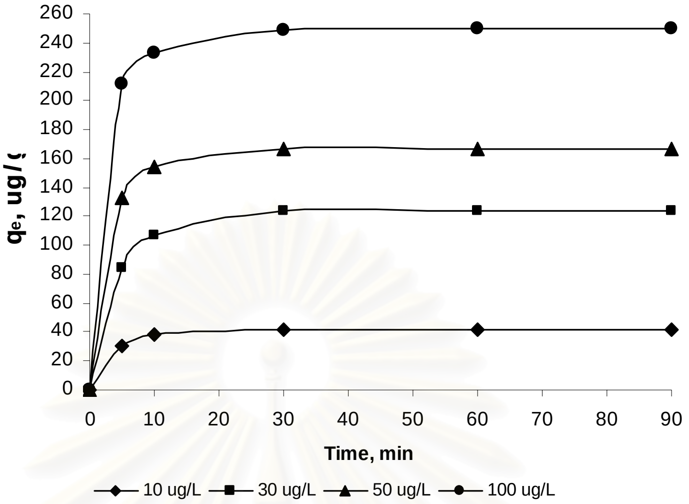


**Figure 4.29** Adsorption efficiency at various initial concentration and contact time.

Figure shows that the adsorption of mercury increases with an increase in contact time and equilibrium in 30 min. The contact time required for the Hg(II) removal is very short. The curves were single, smooth and continuous leading to the saturation indicating monolayer adsorption mercury on the treated clay.

## 4.5 Comparison of adsorption efficiency between batch and column methods

In previous experiments, batch method was used. Now, for comparison, column method was investigated. In the column experiment, a glass column was packed with 2-mercaptobenzothiazole treated bentonite. About 25 mL of mercury standard solution was passed through the column. The column was washed with deionized water and eluted with HCl solution and the effluent collected for analysis of mercury. The adsorption efficiency of batch and column methods are 49.1 µg/g and 48.8 µg/g respectively. This indicates that the batch method is slightly better than column method. This might be due to the use of vacuum pump for suction which causes mercury loss from adsorbent.[29]

## 4.6 Desorption

Desorption of adsorbed 100 ppb Hg(II) from the spent adsorbent was also studied. The adsorbent with adsorbed mercury was stirred in 6 M HCl solution for 4

h. The results of the adsorption and desorption of mercury 2-mercaptobenzothiazole treated clay are shown in Table 4.11.

**Table 4.11** Desorption efficiency of clays using HCl solution

| Adsorbent | Hg concentration, µg/L | | %Desorption |
|---|---|---|---|
| | Adsorption | Desorption | |
| Bentonite | 99.8 | 97.3 | 97.5 |
| China clay | 99.0 | 96.7 | 97.7 |
| Ball clay | 97.8 | 94.9 | 97.0 |

The results show that the percentages of mercury desorbed from 2-mercaptobenzothiazole treated clay are around 97%.

### 4.7 Adsorption efficiency of mercury form water from offshore

Hydrocarbons, both gas and condensate, produced from certain natural gas fields have been found to contain significant amounts of mercury. The gas and condensate from one field, for example, are found to have mercury content of about 250 and 200 µg/L, respectively. The presence of mercury in the gas and condensate causes both processing and environmental concerns.

Produced waters from gas and oil wells may contain significant amounts of mercury. For example, concentrations of 70-150 µg/L of mercury have been observed in water produced from gas wells in certain natural gas fields.[35] In the Gulf of Thailand, water from oil production is contaminated with hydrocarbon, arsenic and mercury in high level. It must be clean to meet Thailand’s strict discharge specifications before disposal, or it can be transported to a nearby platform where it can be injected into a disposal well. Produced waters usually include dissolved salts and organic compounds, oil hydrocarbons, trace metals, suspensions, and many other substances from the reservoir or from the drilling and other production operations. Besides, produced waters can mix with the extracted oil, gas, and injection waters from the wells. All of the above make the composition of the discharged produced waters very complex. Produced water after separated from the hydrocarbons, treated, and then either discharged into the sea or injected back into the wells.

Produced water and discharged water from platform in the Gulf of Thailand at the same depth were sampling and adsorption of mercury using the method found from this work was studied, in this study, 0.05 grams of MBT treated bentonite and 50 mL of samples were used. Batch method was carried out at room temperature. The sample condition and results are collected in Table 4.12.

**Table 4.12** Results of mercury adsorption in water from platform

| Station | Sample type | pH | Hg content, µg/L | | %Adsorption |
|---|---|---|---|---|---|
| | | | Before treatment | After treatment | |
| 1 | Discharged water | 7.8 | 40.7 | 1.8 | 95.6 |
| 2 | Discharged water | 6.0 | 42.3 | 2.4 | 94.3 |
| 3 | Produced water | 5.9 | 110.1 | 5.4 | 95.1 |
| 4 | Produced water | 6.0 | 95.7 | 3.5 | 96.3 |
| 5 | Produced water | 6.7 | 68.7 | 3.5 | 94.9 |

From the results, it can be seen that the efficiency of mercury removal in both discharged and produced waters from platform is high (94-97% adsorption).

In addition, in the drilling operation, some drilling wastes contain mercury, they are called drilling mud and cutting, based on their appearance, muddy or sandy, respectively. Drilling cuttings are removed from drilling muds and cleaned in special separators. The amount of oil left on cuttings after cleaning is much higher when using oil-based fluids. Separated drilling muds and cleaning fluids used to treat cutting are partially returned to the circulating system. Drilling cutting and the rest of the drilling muds are either dumped overboard or transported to the shore for further treatment and disposal, depending on the situation and ecological requirements. Recently, a technology was developed to remove the drilling wastes, especially cuttings, by reinjecting their slurry into a geological formation. Drilling discharges also contain many heavy metals (mercury, lead, cadmium, zinc, chromium, copper, and others).

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In this work, adsorption of mercury from drilling mud and cutting was studied at room temperarure, using 0.05 grams of MBT treated bentonite and 0.2 grams of solid sample. The samples were randomly sampling at varied depth. The sample condition and results are collected in Table 4.13.

**Table 4.13** Results of mercury adsorption in solid from drilling process

| Station | Sample type | Depth (ft.) | Hg content, µg/L | | %Adsorption |
|---|---|---|---|---|---|
| | | | Before treatment | After treatment | |
| 1 | Cutting | 5000 | 167.0 | 33.8 | 79.7 |
| 2 | Cutting | 6000 | 309.5 | 68.9 | 77.7 |
| 3 | Cutting | 7000 | 345.8 | 70.7 | 79.6 |
| 4 | Mud | 9000 | 656.9 | 146.7 | 77.7 |

%Adsorption of mercury in solid from drilling process is about 77-79%. Comparison of Table 4.12 and Table 4.13, it can be observed that %adsorption of liquid samples is higher than that of solid samples. This is due to the fact that liquid samples are more homogeneous than muddy sample, so that the adsorption from solid samples can be quite difficult.

# CHAPER V

# CONCLUSION AND SUGGESTION

## 5.1 Conclusion

In this research, adsorption of mercury was carried out by using clay as adsorbent. Three types of Thai clay: bentonite, china clay and ball clay were investigated. First, clays were heated, treated with acid and chemicals: sulfide, thiourea, and 2-mercaptobenzothiazole. The treated clays were characterized using FTIR, XRD techniques. The results confirm the remaining of clays structure and the inclusion of chemicals which were used for the treatment. Other properties of clays: cation excharge capacity, acidity and surface area were also determined. The influences of various parameters were studied to find an optimum condition for adsorption: pH, temperature, ionic strength, adsorbent dose and initial concentration of mercury.

Experimental results indicate that 2-mercaptobenzothiazole treated bentonite gives highest adsorption of mercury at pH 6.0 and 100 µg/L mercury concentration in 30 minutes. Increasing temperature increases adsorption efficiency. The adsorption isotherms follow Langmuir isotherm. Heat of adsorption indicated that adsorption on clay was an endothermic reaction. The efficiency of batch method is a little higher than column method. After adsorption, the spent adsorbent can be regenerated easily by eluting with dilute hydrochloric acid. The percentage of desorption is high (97%).
This method is also used for treatment of mercury from real samples: water or soil.

## 5.2 Suggestion for further work

For the future work, modification of adsorbents by mixing clay with some chemicals or waste should be investigated for improving the adsorption efficiency. In addition, methods to regenerate should be attempted the adsorbent.

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# APPENDIX A

## Experimental Data

**Table A1** Calibration curves of mercury standard.

| Sample no. | Concentration, mg/L | %RSD | Mean Abs. |
|---|---|---|---|
| Cal. Blank | - | 34.06 | 0.00 |
| Standard 1 | 1.0 | 1.01 | 0.01 |
| Standard 2 | 5.0 | 0.66 | 0.08 |
| Standard 3 | 10.0 | 0.53 | 0.14 |
| Standard 4 | 30.0 | 0.28 | 0.43 |
| Standard 5 | 60.0 | 0.12 | 0.84 |
| Standard 6 | 90.0 | 0.23 | 1.31 |

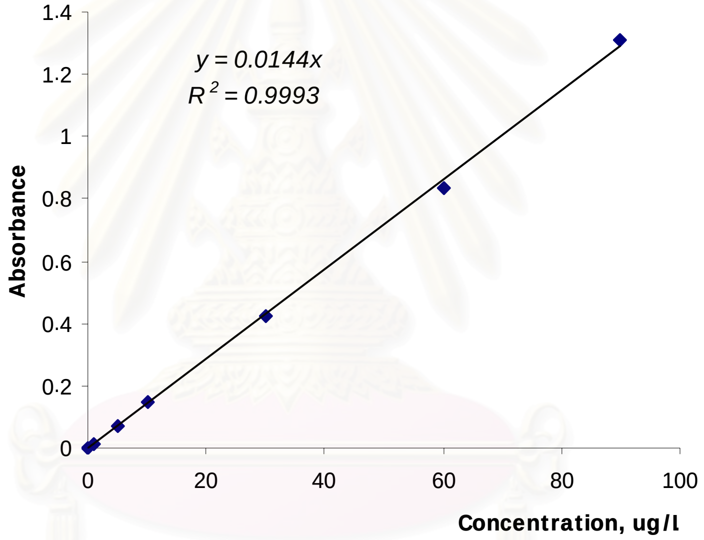

**Figure A1** Calibration curve of mercury

**Table A2** Table of acidity data for raw, acid and heat treated clay

| **Clay** | **Process** | **Amount of clay, g** | **mL of NaOH** | **[NaOH], N** | **mL of HCl** | **[HCl], N** | **Acidity meq/100 g clay** |
|---|---|---|---|---|---|---|---|
| Bentonite | Raw | 0.1020 | 3.0 | 0.103 | 2.56 | 0.098 | 57.21 |
| | Acid | 0.1031 | 3.0 | 0.103 | 2.34 | 0.098 | 77.27 |
| | Heat | 0.1011 | 3.0 | 0.103 | 2.56 | 0.098 | 57.28 |
| China clay | Raw | 0.1086 | 3.0 | 0.103 | 2.55 | 0.098 | 54.45 |
| | Acid | 0.1065 | 3.0 | 0.103 | 2.53 | 0.098 | 57.31 |
| | Heat | 0.1033 | 3.0 | 0.103 | 2.58 | 0.098 | 54.52 |
| Ball clay | Raw | 0.1099 | 3.0 | 0.103 | 2.56 | 0.098 | 52.63 |
| | Acid | 0.1032 | 3.0 | 0.103 | 2.57 | 0.098 | 55.15 |
| | Heat | 0.1045 | 3.0 | 0.103 | 2.59 | 0.098 | 53.01 |

**Table A3** Adsorption efficiency of mercury at various pHs

| pH | Amount of Hg adsorbed per weight of adsorbent, µg/g | | | Mean µg/g | SD |
|---|---|---|---|---|---|
| | #1 | #2 | #3 | | |
| 3 | 20.149 | 20.149 | 20.144 | 20.147 | 0.003 |
| 6 | 27.618 | 27.619 | 27.6195 | 27.619 | 0.001 |
| 8 | 28.17 | 28.1715 | 28.172 | 28.171 | 0.001 |

**Table A4** Adsorption efficiency of mercury at various ionic strength

| [NaOH] | Amount of Hg adsorbed per weight of adsorbent µg/g | | | Mean µg/g | SD |
|---|---|---|---|---|---|
| | #1 | #2 | #3 | | |
| 0.00 | 29.6435 | 29.644 | 29.6435 | 29.644 | 0.000 |
| 0.05 | 25.6045 | 25.6055 | 25.606 | 25.605 | 0.001 |
| 0.10 | 24.189 | 24.186 | 24.1875 | 24.188 | 0.001 |
| 0.50 | 20.1945 | 20.193 | 20.194 | 20.194 | 0.001 |
| 1.00 | 18.2275 | 18.229 | 18.226 | 18.228 | 0.001 |

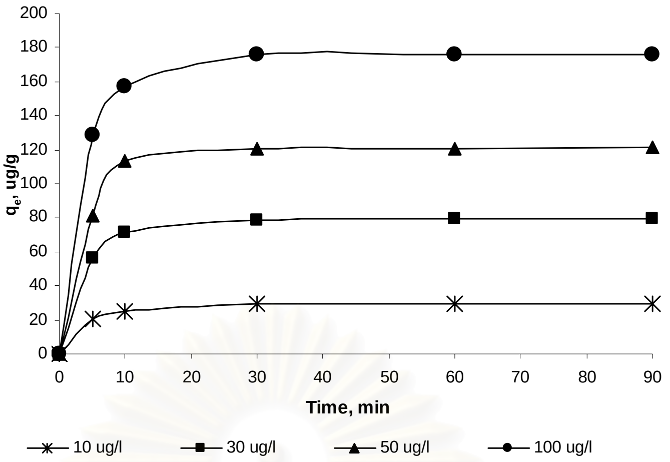

**Figure A2** Kinetics curve on heat treated bentonite

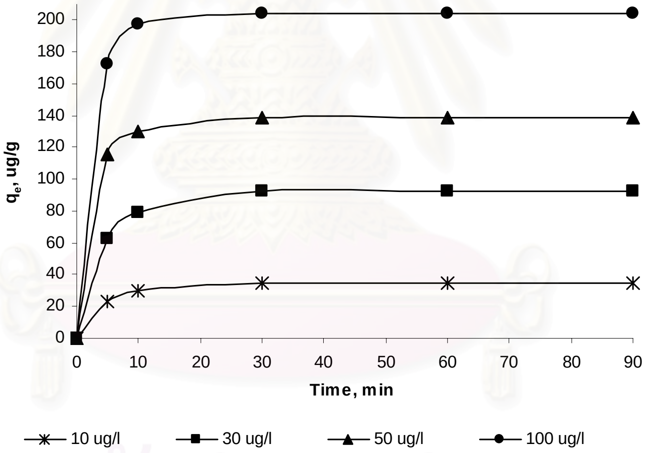

**Figure A3** Kinetics curve on acid treated bentonite

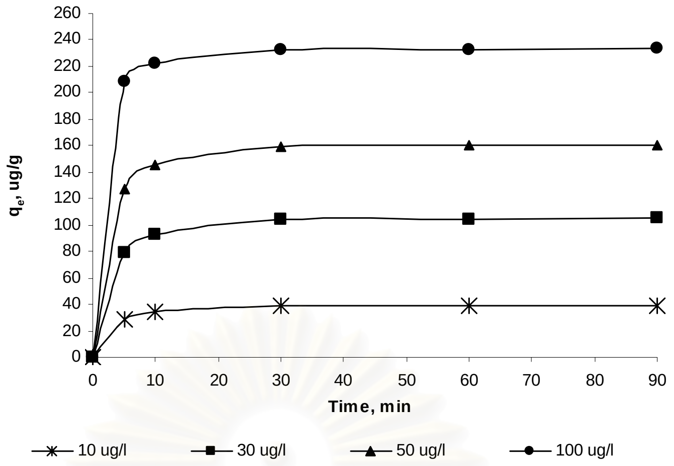

**Figure A4** Kinetics curve on sulfide treated bentonite

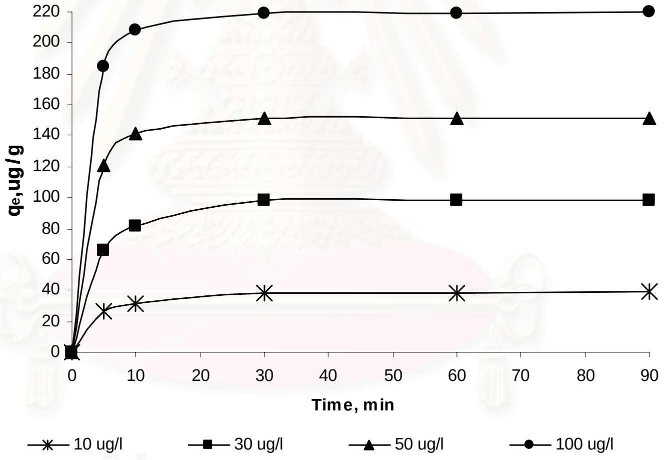

**Figure A5** Kinetics curve on thiourea treated bentonite

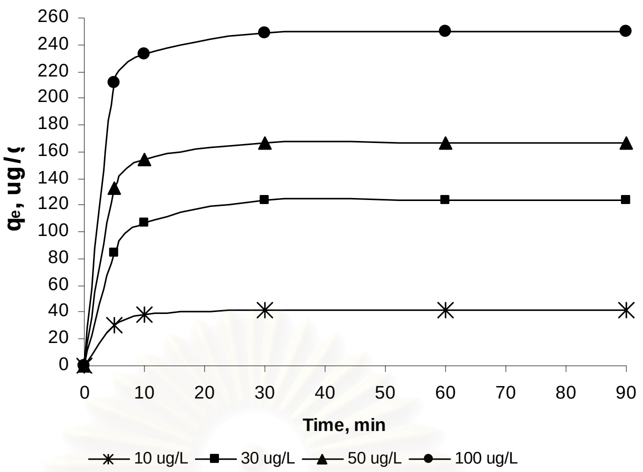

**Figure A6** Kinetics curve on MBT treated bentonite

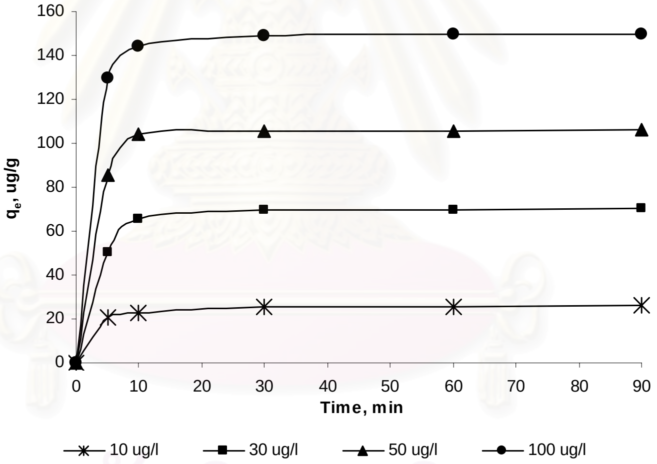

**Figure A7** Kinetics curve on heat treated china clay

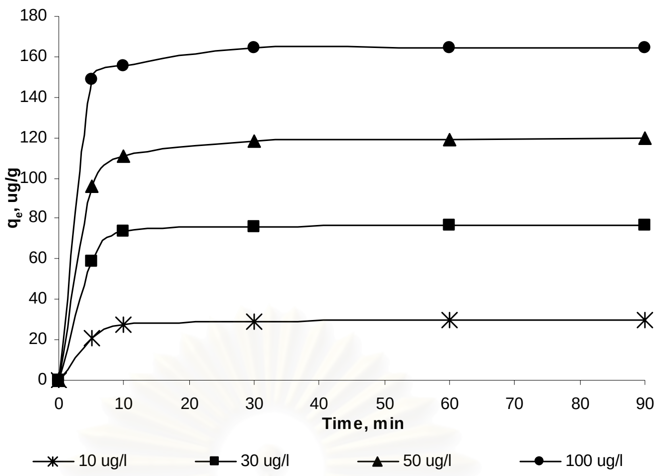

**Figure A8** Kinetics curve on acid treated china clay

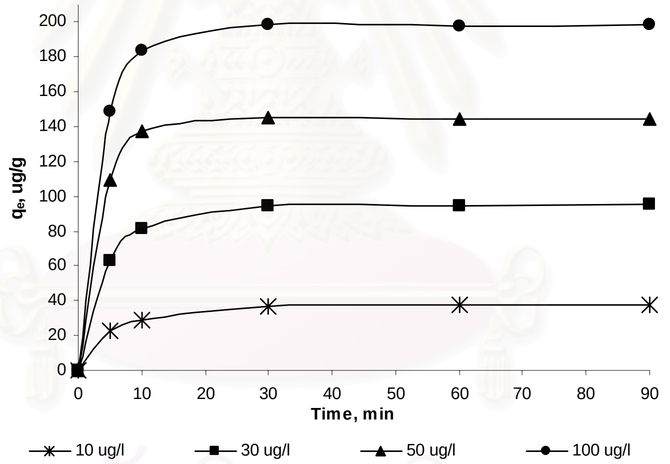

**Figure A9** Kinetics curve on sulfide treated china clay

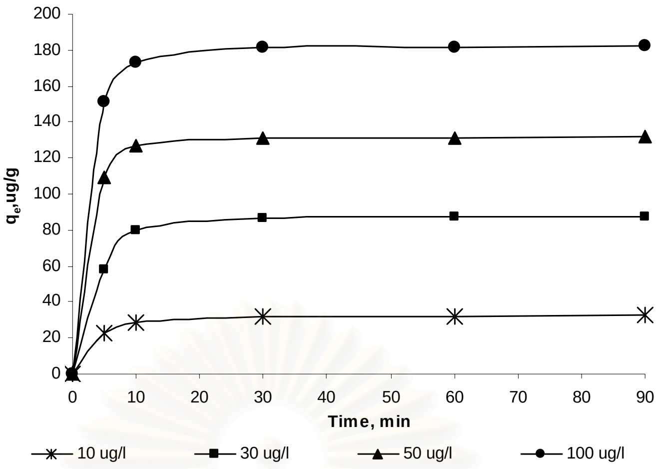

**Figure A10** Kinetics curve on thiourea treated china clay

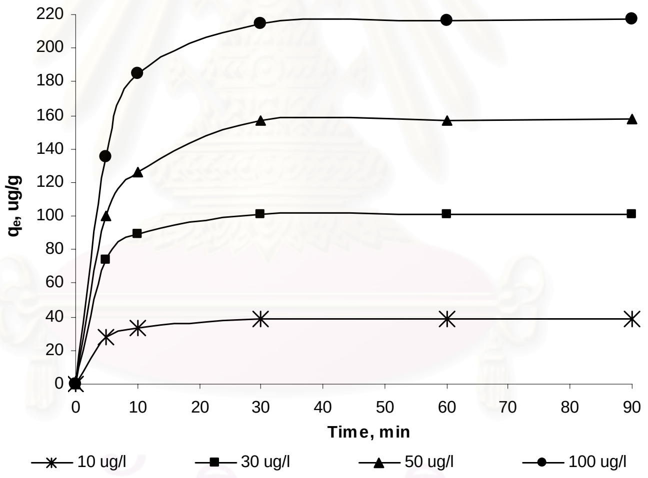

**Figure A11** Kinetics curve on MBT treated china clay

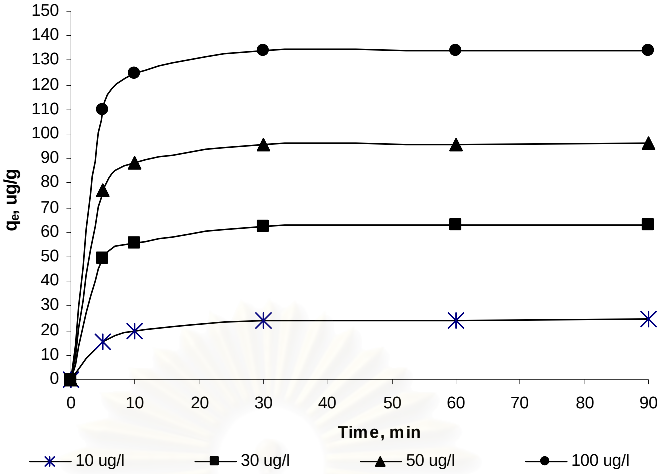

**Figure A12** Kinetics curve on heat treated ball clay

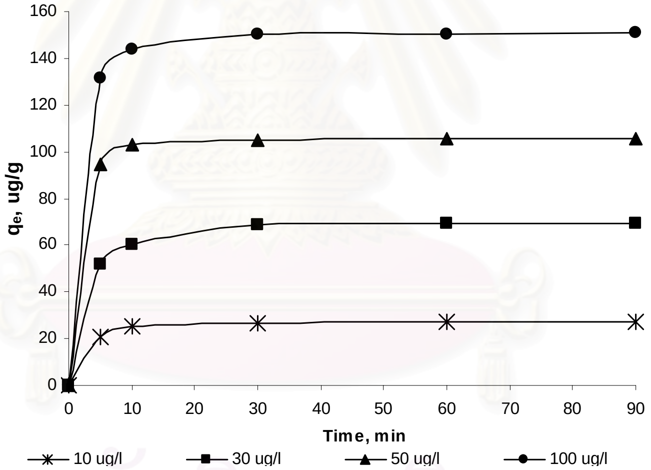

**Figure A13** Kinetics curve on acid treated ball clay

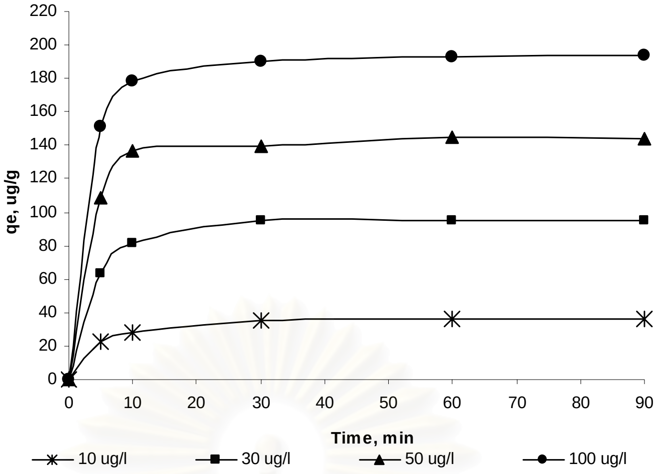

**Figure A14** Kinetics curve on sulfide treated ball clay

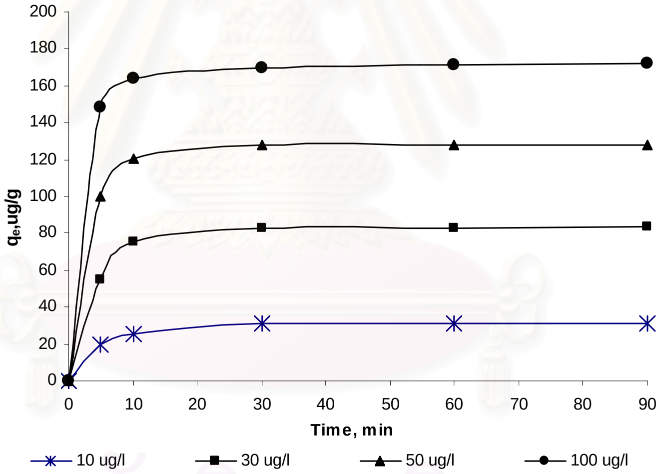

**Figure A15** Kinetics curve on thiourea treated ball clay

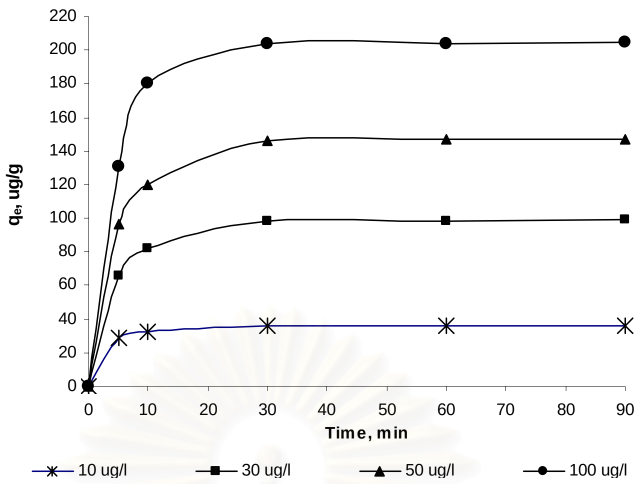

**Figure A16** Kinetics curve on MBT treated ball clay

**Table A5** Adsorption efficiency of treated bentonite at room temperature and pH 6. Contact time 30 mins. Using 0.01 grams of clay and 50 ml of Hg solution.

| **Clay** | **Initial Hg content μg/L** | **Remained Hg content, μg/L** | **Amount of Hg adsorbed μg/g** |
|---|---|---|---|
| MBT | 10 | 1.7 | 41.3 |
| | 30 | 8.2 | 109.2 |
| | 50 | 16.8 | 166.2 |
| | 100 | 50.2 | 249.0 |
| Sulfide | 10 | 2.1 | 39.3 |
| | 30 | 9.1 | 104.3 |
| | 50 | 18.0 | 159.8 |
| | 100 | 53.4 | 232.9 |
| Thiourea | 10 | 2.3 | 38.6 |
| | 30 | 10.3 | 98.2 |
| | 50 | 19.8 | 150.8 |
| | 100 | 56.1 | 219.4 |
| Acid | 10 | 3.04 | 34.8 |
| | 30 | 11.5 | 92.5 |
| | 50 | 22.3 | 138.4 |
| | 100 | 59.2 | 203.7 |
| Heat | 10 | 4.1 | 29.5 |
| | 30 | 14.2 | 79.0 |
| | 50 | 25.9 | 120.5 |
| | 100 | 64.9 | 175.5 |

**Table A6** Adsorption efficiency of treated china clay at room temperature and pH 6. Contact time 30 mins. Using 0.01 grams of clay and 50 ml of Hg solution.

| **Clay** | **Initial Hg content μg/L** | **Remained Hg content, μg/L** | **Amount of Hg adsorbed μg/g** |
|---|---|---|---|
| MBT | 10 | 2.2 | 39.0 |
| | 30 | 9.9 | 100.8 |
| | 50 | 18.6 | 157.1 |
| | 100 | 57 | 215 |
| Sulfide | 10 | 2.67 | 36.7 |
| | 30 | 11.0 | 94.9 |
| | 50 | 21.0 | 144.9 |
| | 100 | 60.3 | 198.8 |
| Thiourea | 10 | 3.6 | 32.0 |
| | 30 | 12.8 | 86.2 |
| | 50 | 23.8 | 130.9 |
| | 100 | 63.7 | 181.6 |
| Acid | 10 | 4.1 | 29.3 |
| | 30 | 14.8 | 76.2 |
| | 50 | 26.3 | 118.6 |
| | 100 | 67.1 | 164.4 |
| Heat | 10 | 4.9 | 25.8 |
| | 30 | 16.0 | 69.9 |
| | 50 | 28.9 | 105.6 |
| | 100 | 70.1 | 149.3 |

**Table A7** Adsorption efficiency of treated ball clay at room temperature and pH 6. Contact time 30 mins. Using 0.01 grams of clay and 50 ml of Hg solution.

| **Clay** | **Initial Hg content µg/L** | **Remained Hg content, µg/L** | **Amount of Hg adsorbed µg/g** |
|---|---|---|---|
| MBT | 10 | 2.8 | 35.8 |
| | 30 | 10.4 | 98.0 |
| | 50 | 20.7 | 146.5 |
| | 100 | 59.2 | 204.0 |
| Sulfide | 10 | 2.9 | 35.8 |
| | 30 | 11.0 | 94.9 |
| | 50 | 22.1 | 139.4 |
| | 100 | 62.0 | 190.0 |
| Thiourea | 10 | 3.8 | 31.0 |
| | 30 | 13.5 | 82.5 |
| | 50 | 24.5 | 127.7 |
| | 100 | 66 | 170.0 |
| Acid | 10 | 4.64 | 26.8 |
| | 30 | 16.2 | 68.9 |
| | 50 | 29.0 | 105.2 |
| | 100 | 70.0 | 150.3 |
| Heat | 10 | 5.2 | 24.1 |
| | 30 | 17.5 | 62.6 |
| | 50 | 30.8 | 95.8 |
| | 100 | 73.2 | 133.9 |

# APPENDIX B

## Certificate of Chemicals

**Table B1** Certificate of 2-Mercaptobenzothiazol

| | |
|---|---|
| Chemical formula | $C_7H_5NS_2$ |
| Color and appearance | Yellow-brown powder |
| Molecular weight | 167.25 |
| Assay | 100.0% rel. |
| Melting point | 175.4°C |
| Residue on ignition | ≤2% |

**Table B2** Certificate of thiourea

| | |
|---|---|
| Synonyms | Thiocarbamide sulfourea |
| Chemical formula | $CH_4N_2S$ |
| Molecular weight | 76.12 |
| Residue on ignition | ≤0.05% (as $SO_4$) |
| Melting point | 174-177 °C |
| Sulfate ($SO_4$) | ≤50 mg/kg |

# VITA

Miss. Nartwara Chirandorn was born on October, 24 1976 in Songkhla, Thailand. She received a Bachelor's Degree of Science, majoring in Chemistry from Prince of Songkla University, Songkhla, Thialand, in 1999. Presence, she has worked as a chemist in the laboratory division, Intertek Testing Services (Thailand) Co., Ltd. Since 2002 she has been a graduate student in the program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in 2004.