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Modified Organoclay Containing Chelating Ligand for Adsorption
of Heavy Metals in Solution

A thesis
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Master of Science in Chemistry

by
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December 2011

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Keywords: Montmorillonite, Kaolin, Organoclay, Heavy metal cations, Adsorption,
Environmental protection, Chelating Ligand, Mesoporous material

ABSTRACT

Modified Organoclay Containing Chelating Ligand for Adsorption of Heavy Metals in Solution

by

Mary Akuyea Addy

Presence of a chelating ligand in the clay structure significantly improves its ability to immobilize heavy metals from contaminated sludge or wastewater. Two-step modification procedure comprising sequential pillaring and grafting of chelating agent to the modified clay is involved.

Montmorillonite and kaolin were chosen as typical examples of expandable and non-expandable clays, correspondingly. Modifications with silica and ferric oxide were targeted on development of mesoporous structure. Laboratory tests of the organoclay efficiency for purification of wastewater were conducted with the most promising sample, i.e. organoclay with the highest specific loading of chelating agent. Experiments were conducted with model wastewater containing either individual or mixed cations of heavy metals.

The modified organoclay displayed a high adsorption capacity on heavy metal cations even in acidic media. The method of modification presented in this work can be used for synthesis of efficient adsorbents for applications in contaminated areas.

DEDICATION

This piece of work is dedicated to my dear parents Mr. and Mrs. Addy, my husband Benjamin and daughter Priscilla, my pastor Rev. Amelia, and the entire family for their constant support both physically and spiritually.

ACKNOWLEDGEMENTS

My profound gratitude and thanks go to THE MOST HIGH GOD for the courage and strength given me to choose and work on this topic.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
BET Method	Brunauer, Emmett, and Teller Method
BJH Method	Barrett, Joyner, and Halenda
DR Method	Dubinin-Radushkevich
DSC	Differential Scanning Calorimetry
H	Hour
FT-IR	Fourier Transform Infra-Red
TEOS	Tetraethoxysilane
TCI	Trimethylstearylammmonium chloride
TGA	Thermogravimetric Analysis
TMS-EDTA	N-[3-trimethoxysilyl]propyl]ethylene diaminetriaceticacidtrisodium salt

CHAPTER 1

INTRODUCTION

General Review on Pollution

In the mid-20th century, eutrophication was acknowledged as a pollution problem in North America and European lakes and rivers. Research shows that 54% of lakes in Asia are eutrophic, 28% in Africa, 53% in Europe, 48% in N. America, and 41% in S. America.

Research into waste water treatment has been a topic of interest due to the increasing rate of organics, heavy metals, and micronutrients pollution in rivers and lakes which brings about eutrophication, groundwater contamination, and traditional water pollution. Waterbodies contaminated with heavy metals like lead and mercury are a current problem worldwide and high concentration of such metals pose threat to human life and the environment. Environment protection requires economically feasible, highly effective materials for adsorption of heavy metals [1].

Composition of Sewage Sludge

In the US, use of sewage sludge from industries has been an environmental problem of concern. The sludge usually contain N (1-3%), P (1-2%), K (0.5-1.2%), and significant quantity of microelements like heavy metals. Due to this composition, the convenient method of recycling sludge is transforming it into biosolids by biothermal treatment and later used as fertilizers. In Europe, sewage treatment plants produce 8.106 t of sludge each year and the application of the sludge to soil is the commonest way of getting rid of it.

However, the treated sludge contains a high content of heavy metals that usually accumulate during the treatment. The presence of heavy metals in the sludge limits the possibility of their

recycling as fertilizer because their disposal on the lands may cause a serious effect on microbial communities, threaten ground water aquifers, and also change the natural solubility equilibrium for clays by complexation mechanism and ion exchange [2].

Effect of Heavy Metals in Living Organism (Man)

Unfortunately, heavy metals are some of the natural components of the Earth's crust that cannot be degraded or destroyed. However, heavy metal pollution is basically from industrial discharges such as mining ores and contaminated waste from industries [3].

Because heavy metals bioaccumulate, they are dangerous, and their accumulation in man may either be acute or chronic depending on the term of exposure. They accidentally get to our bodies through contaminated food, drinking water, and air.

Some of these metals like copper, zinc, and iron are essential in maintaining the metabolism of the human body. Nevertheless, high concentration in man leads to poisoning. Small amount may cause damage to the brain and the central nervous system and growth retardation in unborn babies and little children. Depending on the term of exposure in adults, heavy metals can cause damage to most of the organs in the body. For example, long-term exposure of lead can damage the central nervous system of humans, that of cadmium is associated with renal dysfunction, and high exposure can lead to obstructive lung disease that has been linked to lung cancer and damage to human's respiratory systems. Although essential to man, high concentration of copper causes anemia, liver and kidney damage, and stomach and intestinal irritation. Mercury causes damage to the brain and the central nervous system.

Some Sources of These Metals

- Cadmium metals are from batteries, burning fuel
- Copper metals are from bearing wear, engine parts, brake emissions
- Chromium metals are from air conditioning coolants, engine parts, brake emissions
- Iron metals are from auto body rust, engine parts
- Lead metals are from leaded gasoline, tire wear, lubricating oil and grease, bearing wear
- Nickel metals are from diesel fuel and gasoline, lubricating oil, brake emissions
- Zinc metals are from tire wear, motor oil, grease, brake emissions, corrosion of galvanized parts [4].

Metals Found in Tennessee Waterbodies

In Tennessee, reservoirs and lakes are normally used as domestic water supply, livestock and wildlife watering, industrial water supply, navigation, irrigation, fish and aquatic life, and recreation, so any pollutant in such waterbodies can make its way in man through the food chain. From the Tennessee Department of Environment and Conservation, one of the frequent pollutants in reservoirs and lakes are metals. These metals get into the waterbodies by legal activities, atmospheric deposition, or industrial discharges. Example, Cu, Fe, and Zn deposition is mainly by mining operations. The most common metals impacting Tennessee waters include mercury, iron, manganese, arsenic, and lead. Zinc, copper, and chromium levels can also violate water quality standards [5].

Purification Techniques

Water purification is the means by which chemical, biological, and/or material contaminants are removed from water in order to make it safe for use or reuse. There are many conventional techniques like flocculation and coagulation, chlorination, ion exchange, bioresins,

activated sludge, and natural zeolites which water and wastewater are treated to remove heavy metals. Most of these techniques are expensive, labor intensive, and also not effective for concentrations below 100 ppm. These conventional precipitation techniques usually rely on precipitate being formed from addition of chemical agents, then collection and processing, and finally burial of sludge that contains toxic metals. The cost and energy use involved in these steps is substantial because of the amount of materials involved and that need to be handled.

There are two possibilities to improve the quality of the sludge or soil: removal of heavy metals or irreversible immobilization [6-12]. The most cost-effective strategy of remediation of contaminated soils is based on the irreversible immobilization of heavy metals. In this method, the risks related to the presence of soluble or available heavy metal ions are reduced, although the metals are still present. However, heavy metals are converted into an insoluble state that reduces the risk of leaching from the ground and makes them available for further bioremediation. No waste processing or disposal is necessary in this case, which is a significant economic advantage. For the adsorption of heavy metals, the application of low-cost materials seems to be a suitable option for waste water treatment. Recent studies illustrated that some materials can be effective for immobilizing heavy metals from sludge. For example, Ciccu et al. showed that addition of fly ash and red muds (bauxite ore processing waste) significantly reduced heavy metal ion (Pb, Zn, Cd, Cu, As) contents in ground water [13]. Querol et al. successfully immobilized Zn, Pb, As, Cu, Sb, Co, Tl, and Cd on zeolite materials synthesized from coal fly ash [14]. Raicevic et al. used apatite minerals to adsorb Pb, Cd, as well as other toxic metals from polluted soils [15]. Clay materials (Na-bentonite, Ca-bentonite, and zeolite) were used for immobilization of heavy metals (Zn, Cd, Cu, and Ni) in sewage sludge-contaminated soil [16, 17]. The extractability of these metals was significantly decreased.

Heavy metals can have different mobility when they are present in their various forms. Simple and complex cations are the most mobile, and exchangeable cations in organic and inorganic complexes are of medium mobility, while chelated complexes are less mobile. Ravishankar et al. evaluated several contaminated sludge to study bioleaching processes [18, 19]. They concluded that the most stable sludge contained higher contents of organically bound metals. The degree of immobilization on inorganic materials is not sufficiently high. This means that metals are **the most stable** and show **the lowest leaching** if they are **organically** bound. In contrast, leaching was more severe when they were adsorbed on inorganic materials [15]. However, up to now immobilized organic substances were not used for contaminated sludge treatment.

Clay (MMT and Kaolin)

Clay is a naturally occurring compound of aluminum silicate ($(\text{AlO})_2 \text{SiO}_3$) composed of fine grained minerals. These minerals, Andalusite, Sillimanite, and Kyanite, although polymorphic, the chemical composition is the same [20, 21].

By the gradual chemical weathering of rocks over long periods of time, the minerals are formed, mainly silicate-bearing, by low concentrations of carbonic acid and other diluted solvents. These acidic solvents pass through the weathering rock after leaching through the upper weathered layers. Also, some clay minerals are formed by hydrothermal activity. The minerals are hydrous aluminum phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations. Clay deposits are mostly composed of clay minerals, a subtype of phyllosilicates minerals that impact plasticity and harden when fired or dried [22]. Clay deposits may be formed in place as residual deposits in soil, 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 like large lakes and marine deposits.

Basically, the differences in size and mineralogy can be used to distinguished clay from other types of fine-grained soils. Comparatively, clay particle sizes are smaller than those of silts, nevertheless there is some overlap in both particle size and other physical properties, and there are many naturally occurring deposits that include both silts and clays.

Generally, there are four main groups of clays, namely kaolinite, montmorillonite-smectite, illite, and chlorite. Thirty different types of "pure" clays make up these four categories, but most "natural" clays are mixtures of these different types, along with other weathered minerals. Clays are of two distinct structural units; Tetrahedral (1:1) and Octahedral (2:1), and each different type falls within one of them.

The structure of kaolinite is well known, and it is build up by an octahedral layers (sheet) of Al_2O_3 and tetrahedral layers of SiO_4 , which varies in 1:1 ratio. The main constituent of kaolin, also called China clay (Figure 1), is kaolinite with its chemical structure, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (39.8 % alumina, 46.3% silica, 13.9% water) and its crystallochemical formula is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$.

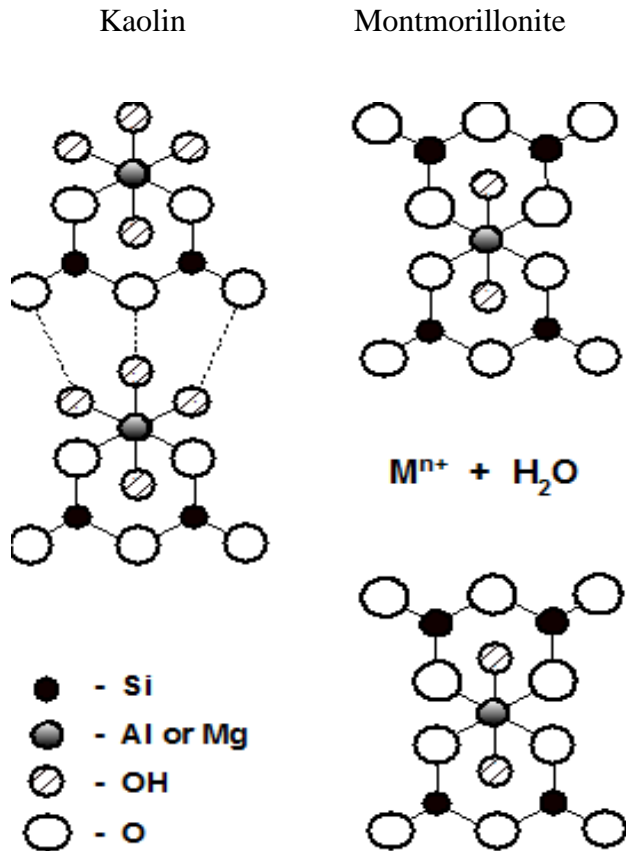


Figure 1. Structure of hydrated MMT and Kaolin Clay

Kaolinite is build up from pseudohexagonal triclinic crystals with diameter between 0.2–10 μm , with thickness of 0.7 nm, molecular weight of 258.073 g/mol and its density is 2.6 g/cm³. Thus, the 1:1 sheet structure of kaolinite can be expressed as $[Si_2O_5]_2$ sheet and $[Al_2(OH)_4]_2$ sheet with pseudo-hexagonal symmetry. The kaolin crystal has a plate-like morphology. An ideal cell of the kaolinite is electrically neutral. The first model of the structure kaolinite was designed by Brindley et al. [23]. Because the layers between the sheets are close one to other, the water molecules could not get between the sheets.

Montmorillonite structure (Figure 1) is an octahedral laminated sheet that is sandwiched between tetrahedral silicate layers (sheet). Research shows that it can form many

nanocomposites with different organic compounds within an interlayer spacing of ca. 0.9 – 1.2 nm due to its excellent cation exchange properties. Montmorillonite clay has an excellent sorption property and possesses sorption sites available within its interlayer space as well as on the outer surface and edges. This is a very soft phyllosilicate group of minerals that typically form in microscopic crystals which forms clay. Montmorillonite is a member of the smectite (2:1 clay) family, which means it has 2 tetrahedral sheets that sandwich a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1 μm [24].

Montmorillonite has variable water content and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Potassium, iron, and other cations are common substitutes; the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite, and kaolinite [24].

Research Using Clay

Research shows that some types of clay have catalytic or adsorptive properties [25-31]. Example, bentonite that has adsorptive properties, has been used to remove a number of chemicals species like amines, organic pigments, cations (Ni, Zn), phenols, and ketones, and other contaminants. Kaolin, for instance, is still been used in treating some heavy fractions in hydrocracking process developed over 80 years ago. In addition to treatment, it is used as an additive in resent residual fluid catalytic cracking (RFCC) catalyst. Naturally occurring abundant clays have very good potential, hindered however by weak adsorption of heavy metal directly on the clay's surface. Such adsorption occurs mainly by ion-exchange mechanism, i.e. cations of clay are reversibly exchanged for cations of heavy metals. Cation exchange capacity

of untreated clay is not enough for wide scale applications [32]. Metals' adsorption by clays strongly depends on pH of media and becomes much less effective from acidic solutions.

Much stronger binding of heavy metals might be achieved with the help of chelating agents. For adsorption purposes, chelating agents should be immobilized on the solid carriers. This type of adsorbents may potentially extract heavy metals from acidic media. The main obstacle to use clays as a chelates' carrier is relatively small surface available for ligand immobilization.

Treatment of lamellar clays to improve porosity is known as pillaring, i.e. formation of intercalation compounds in which distance between lamellas increase by insertion of host compound. The obligatory requirements for pillared clays are robustness of the intercalation compound to prevent collapse on dehydration or during application. Spacing between pillars should be large enough to allow access of molecules of interest [33-39].i.e. chelating ligands in our case. The production process should be scalable and cheap [40]. Because clays are natural product variation of their properties might be significant; therefore, the production process should be adoptable to reasonable variation of the properties and composition of the raw clay.

In a review of [19], the authors summarized various routes of the pillaring. The most widely traditional route is pillaring with inorganic cations of multivalent elements such as iron, aluminum, zirconium, chromium, etc. Inorganic cations might be used individually or as a mixture [16, 41-47]. All these publications by Canzares et al., Aouad et al., Mahboub et al., Moreno et al., Occelli et al., Perez-Vidala et al., Sychev et al., and Yan et al., reported significant increase of BET surface area. In the work of [48], the final product combined micro- and mesopores with overall BET surface area of 383 m²/g was prepared. Increase of overall

BET surface area from 35.1 to 323.2 m²/g by montmorillonite pillaring, with TiCl₄ in alkaline media was described by Yuan et al. [49].

Less widely used but promising route of pillaring in prospective of ligand grafting is based on various modifications of sol-gel process [1, 50-53]. Literature data showed that total BET surface by this process might exceed 700 m²/g. Solution of tetraethoxysilane (TEOS) in low molecular weight alcohol applied to the clays dispersion. Alkaline or acidic hydrolysis leads to formation of silicate-ions, with formation of amorphous silica three-dimensional network. Amorphous silica might form pillars between the lamellas of clay. However, no reasons for silica domains to be localized only in the intragallery space were found in literature.

Introduction of surfactants into TEOS process allows making a template heterostructure. In the work in [54], the use of cetyltrimethyl ammonium bromide was described to achieve bimodal mesoporous structure of montmorillonite in hydrothermal process. Octadecylamine has also been used to intercalate a fine and a coarse grained Mg-Vermiculite, and into montmorillonite [55-56]. Loading of surfactant exceeded critical micellization concentration for the extent at which rod type micelles were formed. Intercalation of these micelles into intragallery space and further loading and hydrolysis of TEOS resulted in formation of silica bulk layer penetrated by micelles [57]. Calcination at moderate temperature eliminated the organic component with formation of porous clay heterostructure.

The clays' structures are well documented in literature. According to classification presented in [58], kaolin falls into a category of materials with rigid, i.e. non-expandable structure in contrast to expandable montmorillonite. Structures of kaolin and hydrated montmorillonite are presented in Figure 1. As one can see, interlayer distance for kaolin is

about twice smaller than the similar parameter for montmorillonite (7.2 vs. 15 Å [59]), which leaves no space for kaolin swelling. In contrast to montmorillonite, kaolin layers are strongly bonded with hydrogen bonds [60]. A major part of literature devoted to pillaring considers various types of montmorillonite. Much less was published about modification of kaolin. Application of modified kaolin and montmorillonite for adsorption of heavy metals from water has been reported [61]. The authors concluded that application of clays is economically feasible for adsorption of heavy metals. Modification of clays significantly increased adsorption capacity.

Organoclays are very prospective materials that might find numerous applications in various fields of science and engineering [17, 62]. In the present work, we study modification of clays with two step-processes, i.e. sequential pillaring and ligand grafting. We choose clays modification by combining of pillaring with grafting of chelating agents to the surface of two abundant clays, i.e. montmorillonite and kaolin. Use of kaolin and montmorillonite disclose impact of swelling tendency on effectiveness of the final organoclay adsorbent for heavy metals. The work is focused on clays modification to make them suitable for adsorption of heavy metals from diluted wastewater.

CHAPTER 2

EXPERIMENTATION / METHODOLOGY

Materials Used

Kaolin, tetraethoxysilane (TEOS), $(C_2H_3O_2)_2Ni \cdot 4H_2O$, $(C_2H_3O_2)_2Cd \cdot 2H_2O$, and $(C_2H_3O_2)_4Pb$ were purchased from Sigma-Aldrich (St. Louis, MO).

Montmorillonite K-10 was purchased from Acros Organic (Geel, Belgium). $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnCl_2$ were purchased from Fisher Scientific (Pittsburgh, PA). Octadecyltrimethylammonium Chloride (TCI America, Portland, OR) was used as a template (Appendix A). A chelating ligand, N-[3-(trimethoxysilyl)propyl]ethylenediaminetriacetic acid trisodium salt (TMS-EDTA) (Appendix C), was obtained from Gelest Inc. (Morrisville, PA).

Methods

Modification by Ferric Oxide

Ferric oxide was introduced into clays (samples **2** and **5** in Table 1) using a slightly modified method in [63]. Raw clay **1** or **4** (10 g) was suspended in 55 mL of deionized water at 1000 rpm stirring. Na_2CO_3 (6.5 g) was dissolved in 50 mL of 0.2 M $Fe(NO_3)_3$ at constant stirring until homogenous mixture was formed. The mixture was aged during 26 hours. Then it was added dropwise to the clay suspension at stirring for two hours at 60 °C. The sample was allowed to age for 20 h at room temperature, washed with deionized water, filtered, dried, and calcined on air at 300 °C for 3 h.

Table 1. Properties of Raw and Modified Clays

Sample	Clay	Oxide	Amount of introduced oxide, %	BET surface area, m ² /g	Total pore volume, cc/g	Micro-pore volume, cc/g	Average pore radius, A	Loading of TMS-EDTA, mmol/g	Average TMS-EDTA density, molecules/nm ²
1	Montmorillonite	-	-	219	0.282	0.189	16.5	0.05	0.14
2		Fe ₂ O ₃	42	277	0.320	0.237	16.5	0.21	0.45
3		SiO ₂	177	96	0.194	0.087	16.4	1.25	7.80
4	Kaolin	-	-	18	0.034	0.016	16.0	0.04	1.30
5		Fe ₂ O ₃	42	102	0.204	0.091	25.4	0.11	0.65
6		SiO ₂	68	91	0.049	0.058	16.5	1.04	6.80

Modification by Silica

Raw clay **1** or **4** (10 g) was suspended in 64 mL of deionized water and then stirred vigorously at 1000 rpm. A solution of TEOS (60 g), (Appendix B) and octadecyltrimethyl ammonium chloride (9.7 g) in 20 mL of 2-propanol (Templating approach, Figure 2) was slowly added to the clay suspension, which then formed a gel. The pH of the reaction mixture was adjusted to 10 by adding NH₄OH solution, and then stirred for two hours. The product (**3** and **6** in Table 1) was filtered, washed with deionized water, dried, and calcined on air at 300°C for 3 h.

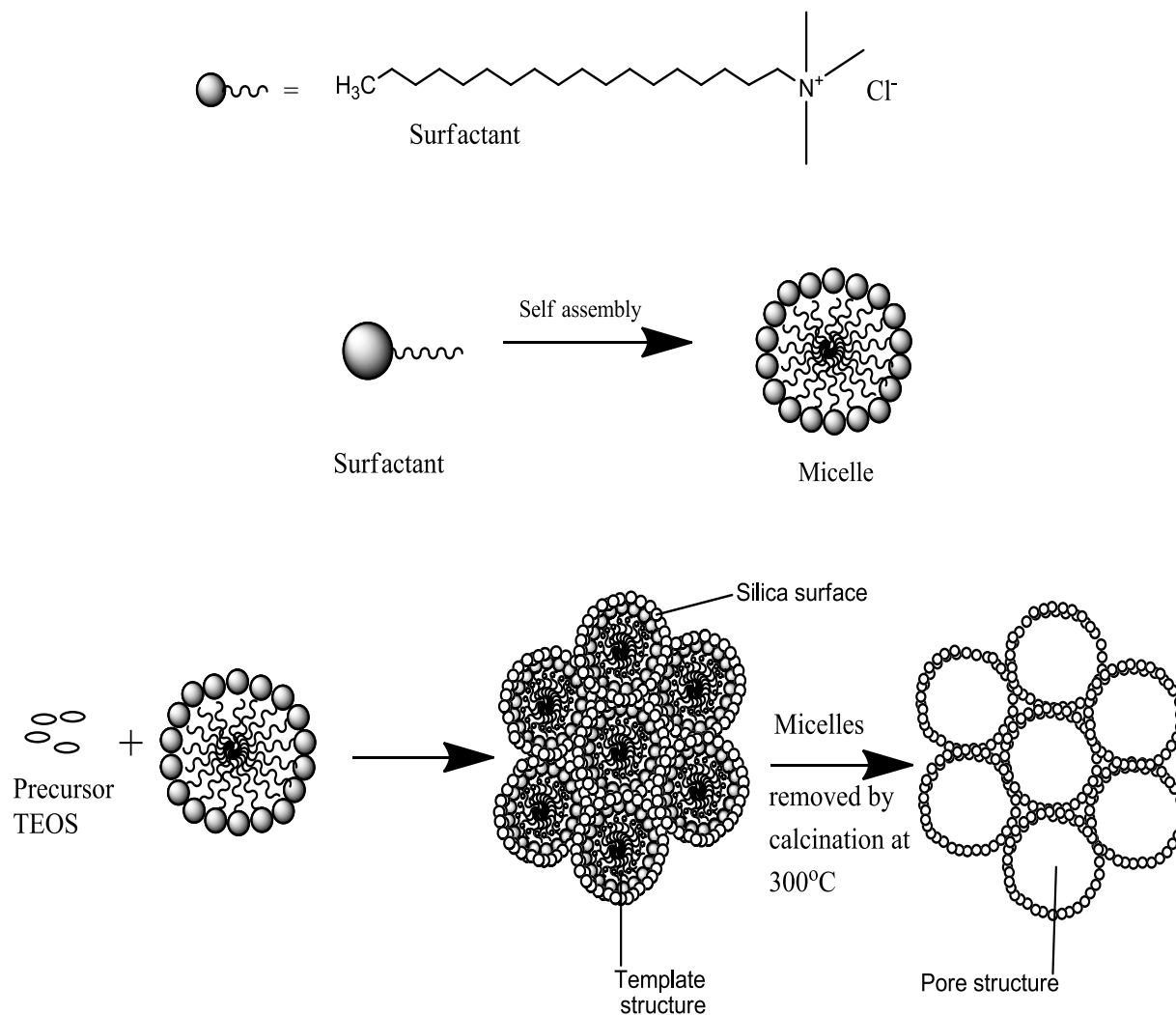


Figure 2. Templating Approach for Silica Pillaring

Mass Increments after Pillaring

This analysis was done by taking small amount of the raw clays, weighing them, and then introducing the oxides into them. The weights of the raw clays were noted and after the introduction of the oxides, the pillared clays were dried at 300°C using the BET analyzer. The weights of the dried pillared clays were determined and recorded as shown in Figure 3.

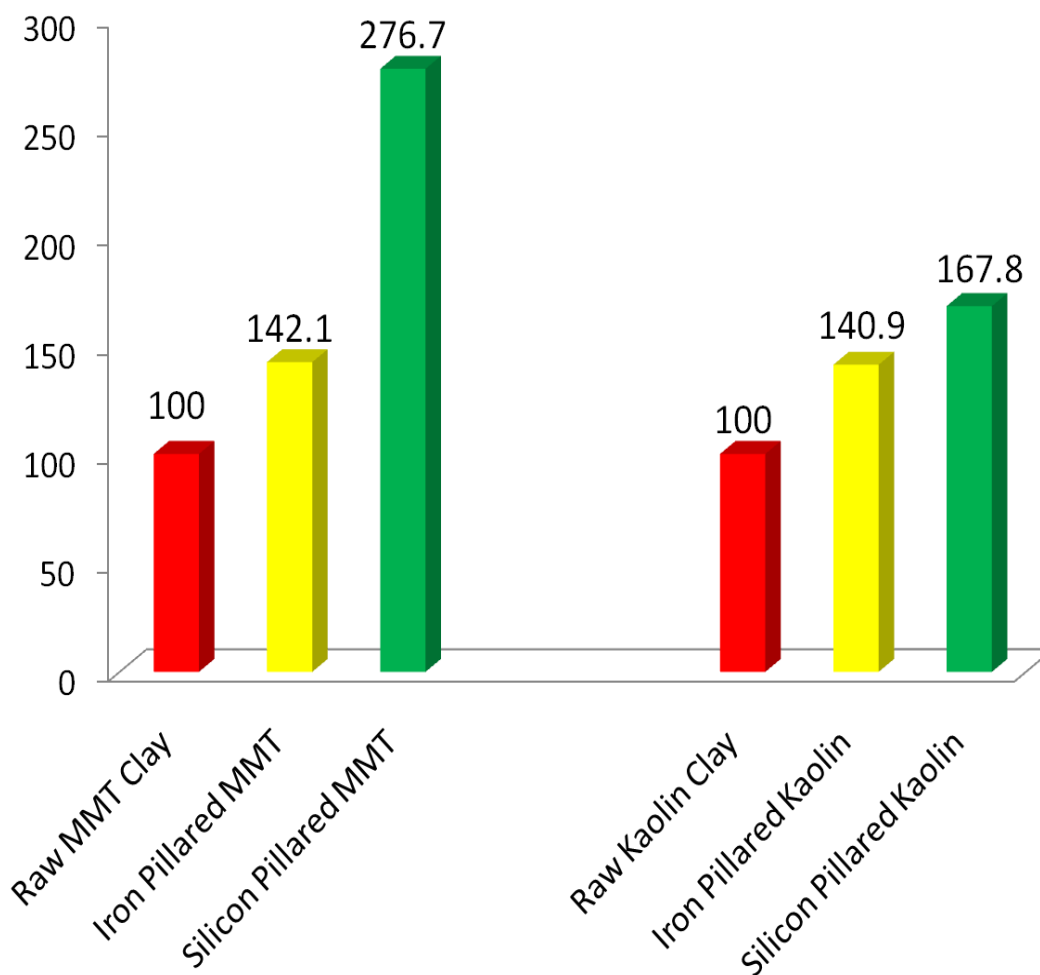


Figure 3. Mass Increments after Pillaring of MMT and Kaolin Clays

Immobilization of Chelating Ligand

Grafting of the ligand to the surfaces of modified clays was conducted according to the procedure described by Vasiliev et al. [64]. The sketch in Figure 4 illustrates grafting process and the structure of product **7**. Finally bulk sample of just montmorillonite silica pillared clay was prepared for the adsorption of heavy metals analysis.

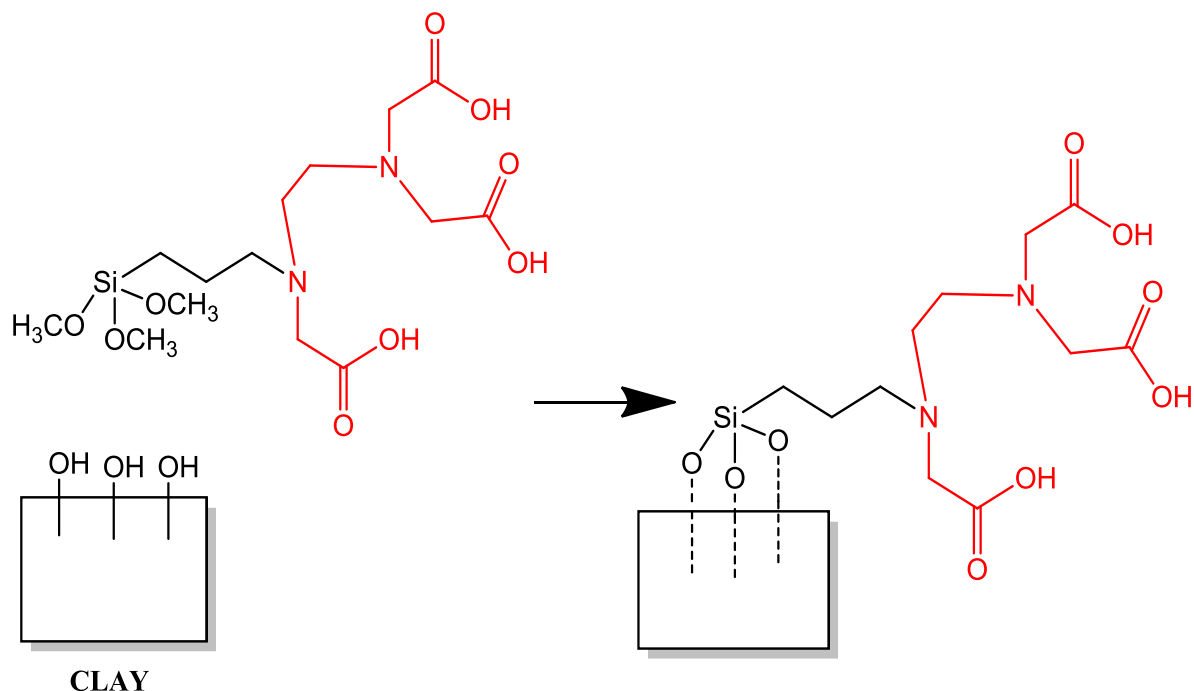


Figure 4. Immobilization of Ligand on Pillared Clay Surface

Adsorption of Heavy Metals

For adsorption studies, solutions of an individual metal salts with metal concentrations of 5.0 ppm were prepared. In the case of Pb^{4+} solution concentration of 71.0 ppm was chosen due to higher detection limit of the instrument (AAS) on this metal. All metal salts except $(C_2H_3O_2)_4Pb$ were dissolved in deionized water. In order to prevent hydrolysis, $(C_2H_3O_2)_4Pb$ was acidified by a solution of HNO_3 to $pH=3.8$. For study of relative adsorption capacity on different metals, a solution containing mixture of six metal salts with total metal ions concentration 42.3 ppm (5 ppm of each metal), and 120.3 ppm (20 ppm of each metal) were prepared in an acidified water solution. The solutions were passed through the column filled with modified clay **7** (0.75 g) using a Carter Cassette peristaltic pump (Thermo Fisher Scientific, Barrington, IL) as in Figure 5, at the constant average rate of 15 mL/min.

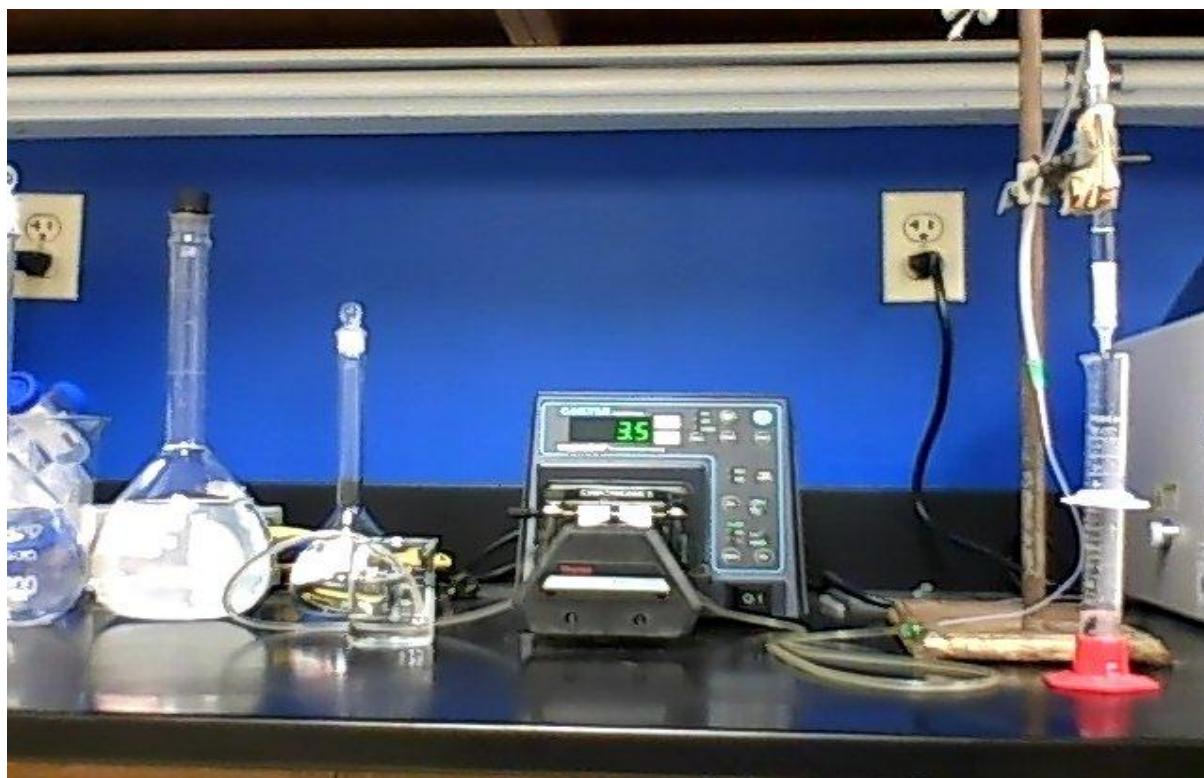


Figure 5. Set Up for the Adsorption of Heavy Metals

The aliquots of the output solutions were taken every hour for six different times and analyzed for residual metal content using the AAS. Using a calibration curve, the concentration of all the output on the solutions was determined. Finally, the concentrations of the single (5 ppm), and mixed metals of 5 ppm and 20 ppm individual salt, were plotted against time/h. Concentrations of heavy metals were measured using an AA-6300 Atomic Absorption Spectrophotometer (Shimadzu Corp., Kyoto, Japan).

Characterization Techniques

Porosimetry

Porous structure of the clays was studied on a Quantachrome Nova porosimeter (Boynton Beach, FL). The measurements were conducted by BET adsorption of N₂ at -196 °C as in the equation below:

$$\frac{P}{V_a (P - P^0)} = \frac{(C-1) (P/P_0)}{V_m C} + \frac{1}{V_m C}$$

where P/P_0 = relative pressure of adsorbate

V_a = volume of gas adsorbed at pressure, P

V_m = volume of gas required to form monolayer

C = BET constant (relative to energy of adsorption of 1st layer)

Prior to measurements, the samples were degassed in vacuum at 300 °C for 3 h. Total pore volume and pore size distribution were calculated using BJH method. Micropore volume was determined by DR method.

Elemental Analysis

Amount of the ligand immobilized on clay surface was calculated from contents of C, H, and N. Elemental analysis was provided by Robertson Microlit Lab. (Ledgewood, NJ).

FT-IR Analysis

IR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer (Shimadzu Corp., Kyoto, Japan).

Thermal Stability

DSC data were acquired on a Perkin Elmer Diamond DSC instrument (Waltham, MS). TGA analysis was carried out on a Perkin Elmer TGA-7 (Waltham, MS). Thermoanalysis

studies were conducted under nitrogen blanket at heating rate 10 °C/min. The range of temperatures was 20-600 °C for DSC and 20-700 °C for TGA.

Concentrations of heavy metals were measured using an AA-6300 Atomic Absorption Spectrophotometer (Shimadzu Corp., Kyoto, Japan).

CHAPTER 3

RESULTS AND DISCUSSION

Results

Modification of Clays with Oxides

Amount of Oxides Introduced to Clays. As seen in Table 1, montmorillonite (**1**) had a significantly higher capacity on both oxides (Fe_2O_3 and SiO_2) than kaolin (**4**). For both types of clays, the amount of introduced silica was higher than amount of ferric oxide as seen in Figure 3. In the product **3**, its amount exceeded the amount of the raw clay used for modification.

Porous Characteristics of the Clays

Adsorption / desorption isotherms of all raw and modified clays were determined as in Appendix D and E. BET surface areas of samples **1-3** are significantly higher than corresponding samples **4-6**. However, modification of **1** with silica reduced BET surface (sample **3**). The average pore radius did not change after experiments except modification of kaolin by ferric oxide. The data on the samples porosity are shown in Table 1.

Immobilization of Organic Ligand

Starting materials **1** and **4** had little capacities on the ligand (Table 1). Ferric-modified clays (**2** and **5**) showed higher TMS-EDTA loading while modification with silica resulted in increase of immobilization capacity (**3** and **6**) as in Figure 6.

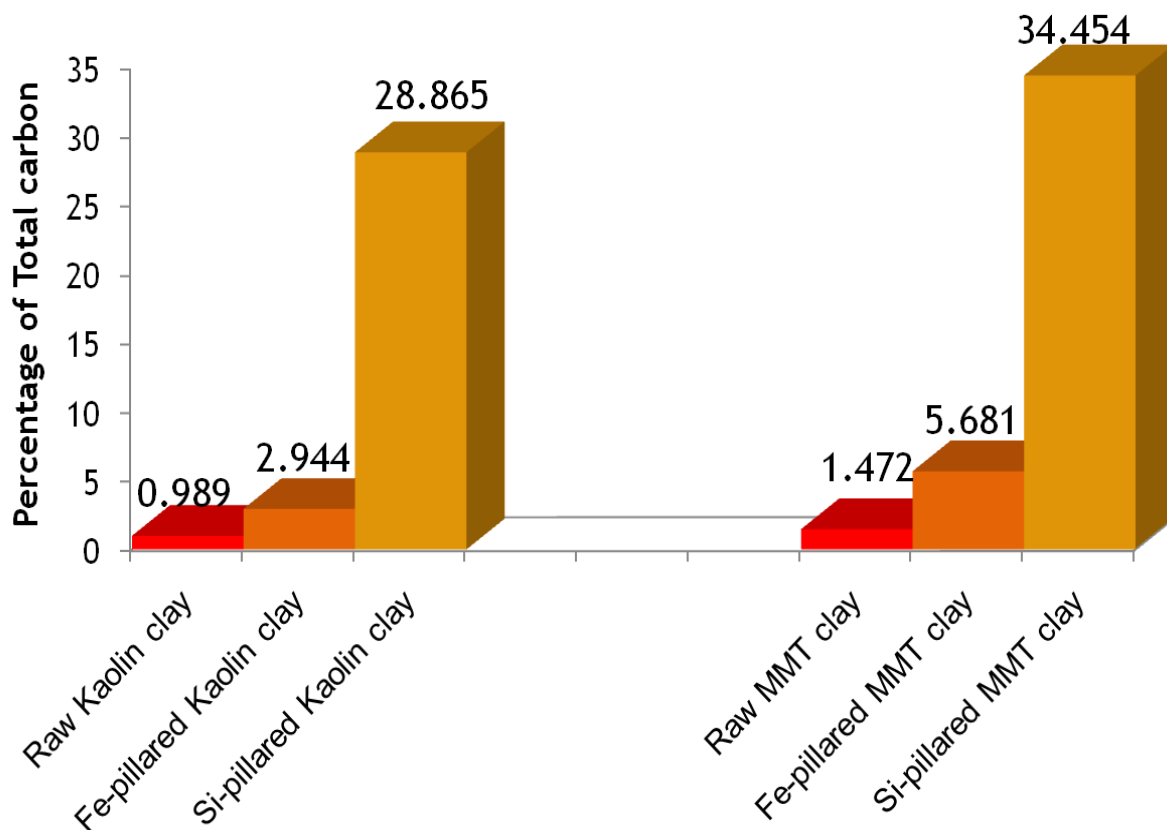


Figure 6. Loading of the Ligand on Silica and Iron Pillared Clay

In all experiments montmorillonite had higher immobilization capacity than kaolin. Thus, the loading of TMS-EDTA on sample **3** was 20.2 % higher than on sample **6**.

Thermoanalysis Data

DSC curve displayed three endothermic effects at the following temperatures (ΔH , J/g): 213 (6.9); 318 (3.7); 350 (3.8) (Appendix F). TGA thermogram of this sample showed a slight loss in mass at heating to 180 °C (0.5%) [65]. In the range 180-317 °C the weight loss was

12.8%. Then the rate of weight loss became slower and the total weight loss up to 700 °C was 22% (Appendix G).

FT-IR Spectroscopy

IR spectra of all samples have characteristic bands of aluminosilicate network at 792-806 cm^{-1} ($\nu_{\text{s}}\text{Si-O}$) and 1051-1053 cm^{-1} ($\nu_{\text{s}}\text{Si-O-Si}$). In the spectra of organically modified samples, the first band can also be attributed to $\nu_{\text{as}}\text{Si-C}$ of immobilized TMS-EDTA. Additionally, their spectra contain weak bands attributed to vibrations of organic groups (cm^{-1}): 2852 and 2920 (νCH_2), 1560 and 1655 (νCOO^-) (Appendix H).

Adsorption of Heavy Metals

Contents of metal ions in solutions of single metal salts and their mixture are shown in Tables 2-3. After passing through the column, concentrations of all individual metals significantly reduced. In the case of the metal mixture, prevalent adsorption of Fe^{3+} cations was observed.

Table 2. Concentrations of Heavy Metals after Adsorption from Solutions of Single Salts

Time, h	Concentration, ppm						
	Cu^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}	Fe^{3+}	Pb^{4+}	
Initial	5.00	5.00	5.00	5.00	5.00	5.00	71.0
1	0.03	0.28	0.01	0.05	0.60		2.00
2	0.03	0.11	0.01	0.00	0.20	Below detection limit	1.50
3	0.03	0.17	0.00	0.00	0.15		2.00
4	0.03	0.06	0.02	0.00	0.05		2.25
5	0.03	0.17	0.02	0.00	0.15		2.00
6	0.03	0.11	0.02	0.00	0.15		2.00

Table 3a. Concentrations of Heavy Metals after Adsorption from Solutions of Mixed Salts (5 ppm)

Time, h	Concentration, ppm					
	Cu ²⁺	Ni ²⁺	Cd ²⁺	Zn ²⁺	Fe ³⁺	Pb ⁴⁺
Initial	6.38	7.00	8.00	7.00	6.45	7.50
1	0.26	5.83	6.71	6.49	2.10	6.75
2	3.97	6.28	6.93	6.47	0.95	6.25
3	5.00	6.22	6.91	6.43	0.85	6.25
4	4.97	6.06	6.86	6.33	0.55	6.25
5	5.09	5.94	6.69	6.23	1.10	6.00
6	5.09	6.06	6.97	6.19	1.30	6.00

Table 3b. Concentrations of Heavy Metals after Adsorption from Solutions of Mixed Salts (20ppm)

Time, h	Concentration, ppm					
	Cu ²⁺	Ni ²⁺	Cd ²⁺	Zn ²⁺	Fe ³⁺	Pb ⁴⁺
Initial	21.88	22.63	19.49	13.14	18.68	24.52
1	15.72	20.32	17.57	12.59	10.05	20.24
2	20.00	20.70	17.51	12.49	13.22	21.90
3	19.88	20.70	18.07	12.43	16.54	21.43
4	19.79	20.48	18.59	12.26	17.41	21.43
5	19.59	20.59	18.82	12.19	17.56	21.43
6	19.74	20.59	17.81	12.04	17.66	21.19

Discussion

Modification with Oxides

BET isotherms of the raw clays **1** and **4** showed a big difference in porous structures of kaolin and montmorillonite. BET isotherm of **4** is typical for non-porous materials. This result agrees with literature data on raw kaolin as a non-porous material [66]. In contrast to kaolin, BET isotherm of montmorillonite **1** is typical for mesoporous structures. It is close to type IV and has profound hysteresis, indicating relatively high pore volume.

Modification of both clays with ferric oxide resulted in significant increase of their surface areas and pore volumes at relatively small amount of introduced oxide. Total amount of introduced ferric oxide was higher in the case of montmorillonite compared to kaolin. Table 1 data, along with data for BET isotherm of sample **2**, are in good agreement with literature [49, 67-69] and prove a significant increase of montmorillonite porosity after modification. BET isotherm of sample **2** belongs to mixed II+IV type with the gradual slope increase in the range $P/P_0=0.1-0.4$. This shape is characteristic for wide pore size distribution. Shape of the pores is cylindrical as one can see from hysteresis of type H1 in accordance with IUPAC classification [70]. One can define the modification of **1** by ferric oxide as pillaring.

For kaolin, development of porous structure was also clearly indicated by BET isotherms. Its isotherm shows a profound hysteresis loop for sample **5**, while practically no hysteresis was observed in raw clays **4**. This result was unexpected as this clay is non-expandable. However, similar methodology of kaolinite treatment has been reported [66]. Exfoliation of raw kaolinite led to increase of total surface area. Micropores, probably not detectable by nitrogen BET, were reported in this work after treatment of the clay with 3-chloropropyltriethoxysilane with calcination at moderate temperature. Development of porous

structure in kaolin was also reported in several recent publications [71, 72]. Surface charge of kaolin particles strongly depends on pH and ionic strength of the solution. At low pH, one can expect positive charging of the particles' edges and negative charging of the faces. Treatment of kaolin with ferric salt in alkaline media probably leads initially to adsorption of hydrated ionic iron species such as $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$, etc. At high pH, edges gain negative charge [73] and electrostatic forces should facilitate adsorption of positive ferric ionic species to the edges of the particles. Results of this experiment prove the ability of kaolin to form mesoporous structure in spite of its non-expandable properties. In contrast to sample **2**, the shape of hysteresis in the isotherm of sample **5** has mixed H1-H3 type showing presence of both cylindrical and slit pores.

While modification with ferric oxide increased both total BET surface area and porosity of montmorillonite, silica modification unexpectedly reduced them (Table 1). It should be noted that the total amount of introduced silica was much higher than ferric oxide for both clays. Modification of montmorillonite by silica using TEOS and a surfactant as a gallery template was reported earlier. Li et al. [1] defined the products as silica-pillared clays. In their work, such a material was identified as silica-clay composite. Unfortunately in both reports amounts of reacted TEOS were not presented. Considering high amount of TEOS incorporated into the structure of clay, we suggest that obtained material is rather composite than simply pillared clay. The silica component of this composite might be responsible for reduced porosity due to partial filling of the interlayer space with formed silica. In the case of kaolin, BET isotherm of sample **6** has stepwise shape (type VI) that indicates formation of two monolayers and proves bimodal pore size distribution. The product has low porosity formed mainly by micropores. A possible explanation of this result is formation of silica from TEOS

independently from kaolin particles. Thus, this method was not effective in modification of kaolin.

Immobilization of Ligand

Raw kaolin **4** displayed very low immobilization capacity on organic molecules due to its almost non-porous structure. A small amount of the TMS-EDTA was probably immobilized on external surface of clay particles. If we take into account the volume of a single molecule of TMS-EDTA (386.18 Å³, calculated using Spartan '06 software), the total pore volume in kaolin (Table 1) is almost three fold lower than the total volume of immobilized molecules. In contrast, high porosity of montmorillonite should enable immobilization of TMS-EDTA in mesopores.

However, in spite of such significant structural differences, ligand loading on sample **1** is not very different from the loading on sample **4**. It is evident that even in the case of expandable clay, steric hindrances still restrict accessibility of potential immobilization sites in the interlayer space to large molecules of TMS-EDTA.

Total amount of immobilized ligand was strongly affected by modification of clay either by ferric oxide or by silica. Thus, introduction of 40% of Fe₂O₃ to kaolin, and 42% to montmorillonite increased immobilization capacity of these clays by 298% and 385%, respectively (Figure 6). Such a notable effect might be referred to disappearance of steric hindrances that makes almost all interlayer space accessible for TMS-EDTA.

In the case of silica-modified clays, total specific loading of TMS-EDTA increased by a factor of over 25 in comparison to raw clay (Figure 6). Such an effect cannot be explained by increase of specific surface area. It is worth mentioning that TMS-EDTA loading density to **3**

and **6** is higher than to mesoporous silica gel itself [64]. Possibly, a significant part of TMS-EDTA was grafted in micropores, which surface area cannot be calculated using BET method.

Characterization

Comparison of IR spectra of raw sample **1** and organomodified clay **7** clearly prove presence of organic molecules in the material. Thermal analysis of **7** showed total weight losses of about 23% wt up to 700 °C. If we assume scission of the ligand molecule on Si-C bond, this amount is in good agreement with the total weight loading of TMS-EDTA.

DSC pattern of silica-modified montmorillonite shows three well-defined endothermic peaks that might be attributed to multistep decomposition of immobilized ligand. There are no literature data on thermal behavior of TMS-EDTA. The temperature of the first peak is very close to the decomposition temperature of EDTA (237-245 °C). Thermal destruction of EDTA is a multistep process involving initial cleavage of C-N bonds and followed by decarboxylation of acidic carboxyl groups [74]. In addition, the second and the third peaks are in the region of decomposition of most of hybrid organic/inorganic materials and might be attributed to Si-C bond cleavage. Thus, thermal decomposition of immobilized ligand is a complex three-step process. Alternatively, multiple peaks might be originated from multiphase nature of the obtained material where TMS-EDTA molecules might be immobilized on both silica and clay surfaces.

Adsorption of Heavy Metals

High loading of chelated ligands disclose the procedure to the design of effective adsorbents for environmental protection. Adsorption of heavy metal on clays is well known technology of water clean-up [75-78]. However, natural clays can adsorb metal cations only on ion exchanging sites $\equiv\text{Si-O-}$ or $\equiv\text{Al-O-}$ on the clay surfaces. The complexes of metals with

these sites are not stable, and metal adsorption is reversible. In addition, clay surfaces are protonated at low pH, which makes positive charge and prevents adsorption of metal cations [6]. More stable complexes can be formed with organic chelate ligands (Figure 7).

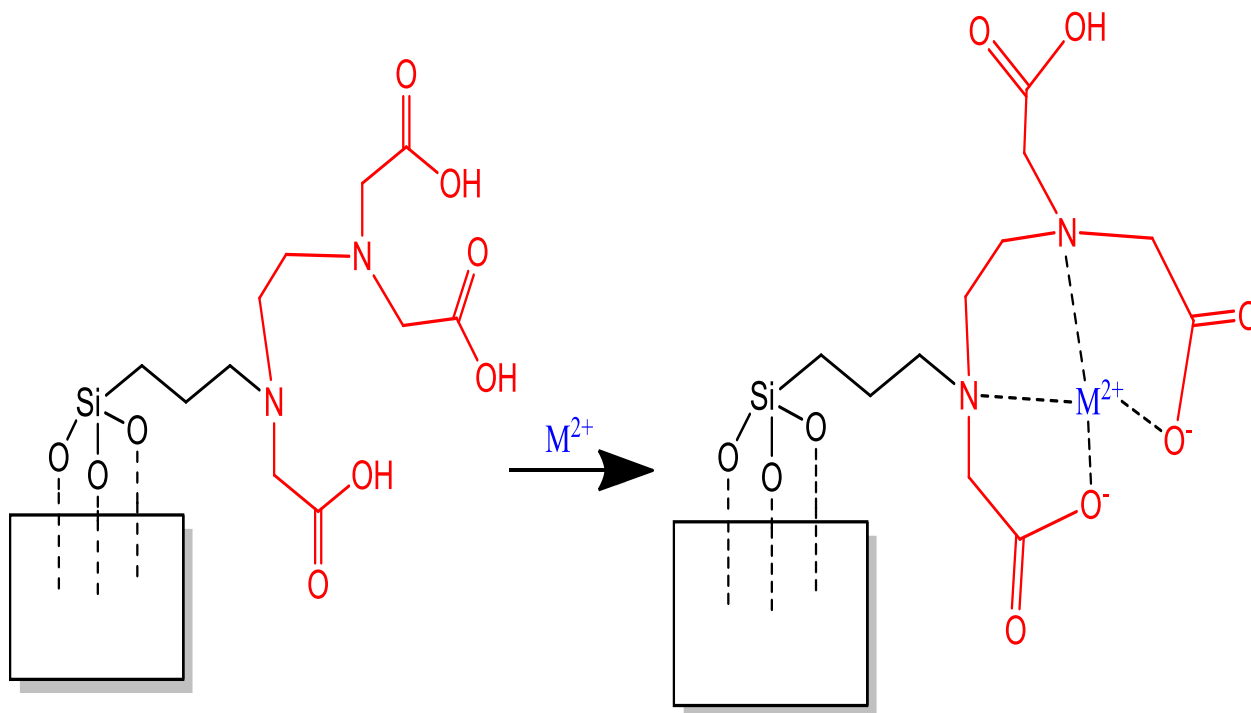


Figure 7. Adsorption of Heavy Metals by Organoclay

In particular, $\log K$ for complexes of Zn^{2+} , Cd^{2+} , Ni^{2+} and Cu^{2+} with EDTA are 16.5, 16.6, 18.6, and 18.8, respectively. Cations Fe^{3+} form much more stable complexes with EDTA ($\log K = 25.7$). For comparison, the range of $\log K$ for the reaction of metal cations, with cation-exchanging sites on montmorillonite surface are very low. Thus, for negatively charged sites their values are in the range 2.37-2.56. For neutral surface OH^- groups they are still lower [78].

We studied adsorption of four divalent cations (Zn^{2+} , Cd^{2+} , Ni^{2+} , and Cu^{2+}), one trivalent (Fe^{3+}), and one tetravalent (Pb^{4+}) heavy metals on sample **7** from solutions of single salts and their mixture. Table 2 lists results of column adsorption of individual heavy metals from aqueous solutions. One can see that effectiveness of modified clay as an adsorbent with all single heavy metals is pretty high. Concentrations of metals in eluents after adsorption were 0.1-4.3% of initial concentrations. Table 3a and Table 3b also list results of column adsorption of mixture of heavy metal from aqueous solutions of 5 ppm and 20 ppm respectively.

Compounds containing Pb^{4+} do not belong to common contaminants of environment. One of the sources of Pb^{4+} in soil was tetraethyl lead $Pb(C_2H_5)_4$ used in the past as an antiknock additive to fuels. At present time, this additive is not used in most countries in the world. Lead (IV) tetraacetate is hydrolyzed in neutral aqueous solution and can be dissolved only in acidic media. Normally, clays do not adsorb metal cations effectively at low pH; however, organoclay **7** displayed high adsorption capacity on this metal even in presence of acid (Appendices I-K).

Industrial wastewaters usually contain mixed contaminants. For estimation of adsorption selectivity, clean-up of an acidic mixture of heavy metal salts was conducted on the column filled with **7** (Figure 5). Analysis of eluent samples showed a preferable adsorption of Fe^{3+} cations that is in agreement with literature data on the stability of metal complexes with EDTA.

Conclusion

Highly porous materials were obtained by modification of montmorillonite and kaolin with ferric oxide. The modified clays contain both micropores and mesopores. Modification of clays with silica led to mixed silica-clay composites with relatively lower porosity. An

interesting characteristic of such composites is extremely high loading capacity for chelating of ligand N-[3- (trimethoxysilyl)propyl]ethylenediaminetriacetic acid trisodium salt. Obtained organoclay based on silica modified montmorillonite was successfully used for adsorption of heavy metal cations from individual and mixed solutions of their salts.

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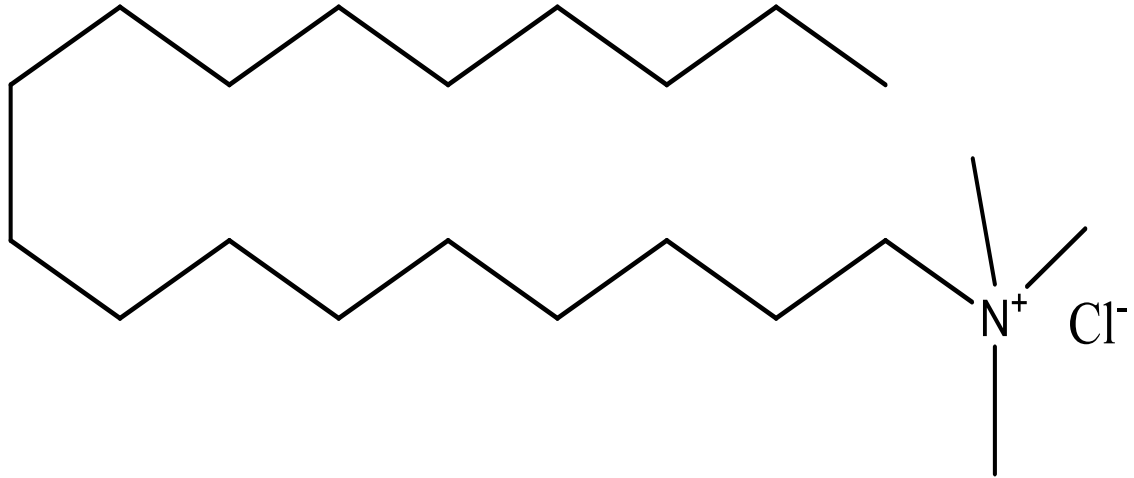
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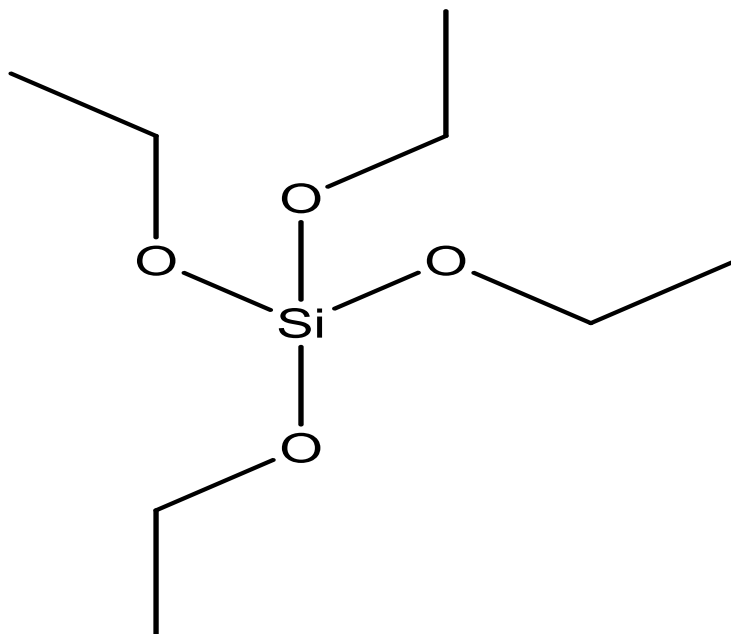
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APPENDICES

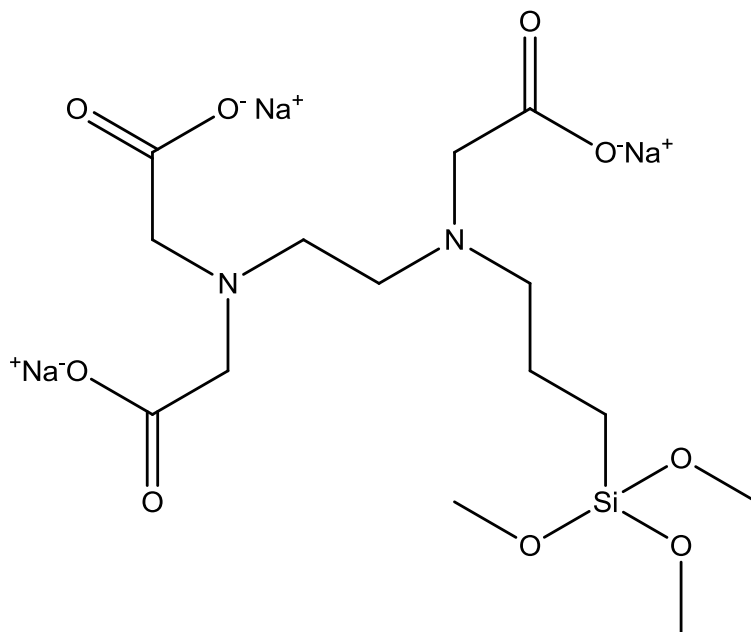
Appendix A: Trimethylstearylammonium Chloride (The surfactant)



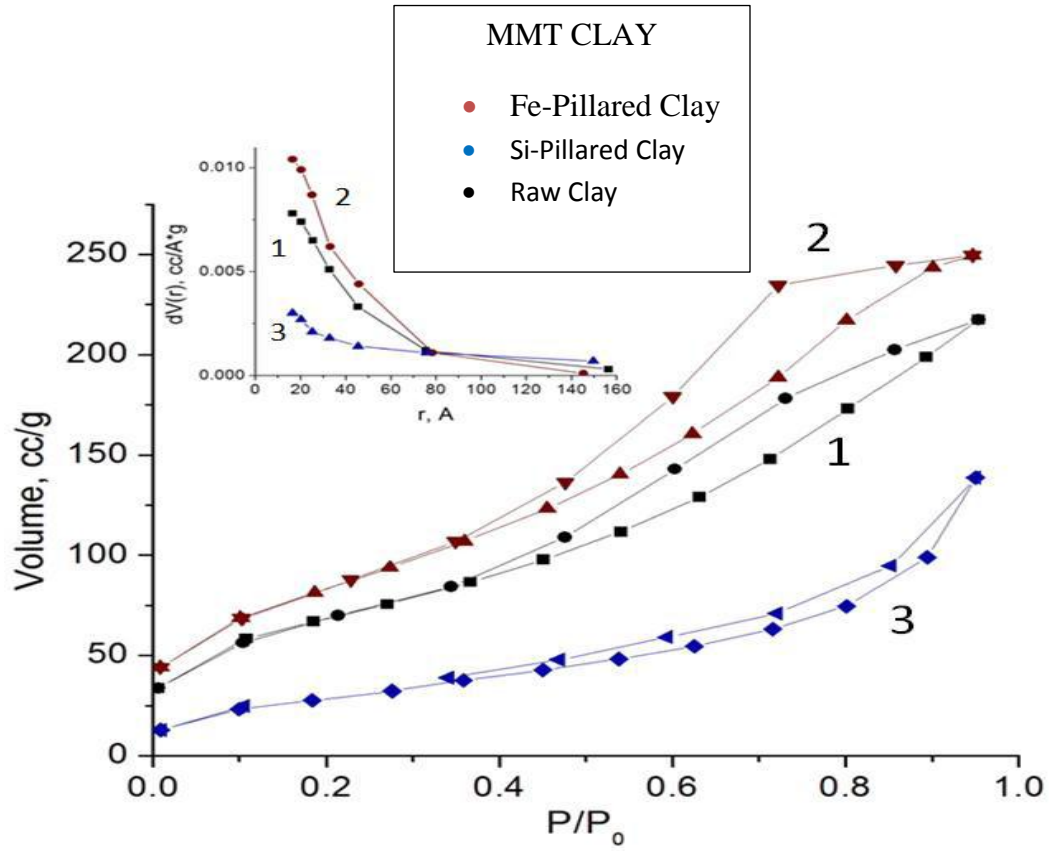
Appendix B: Tetraethoxysilane (The Precursor)



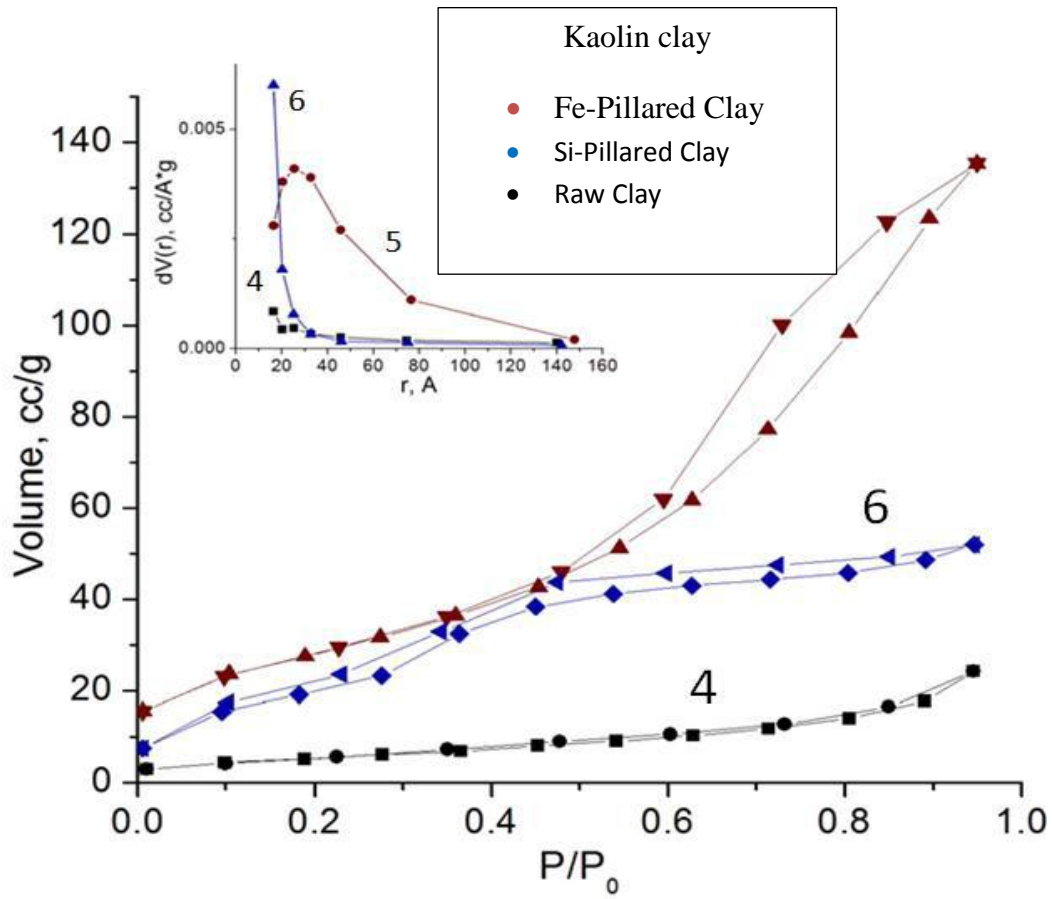
Appendix C: TMS-EDTA, Chelated Ligand



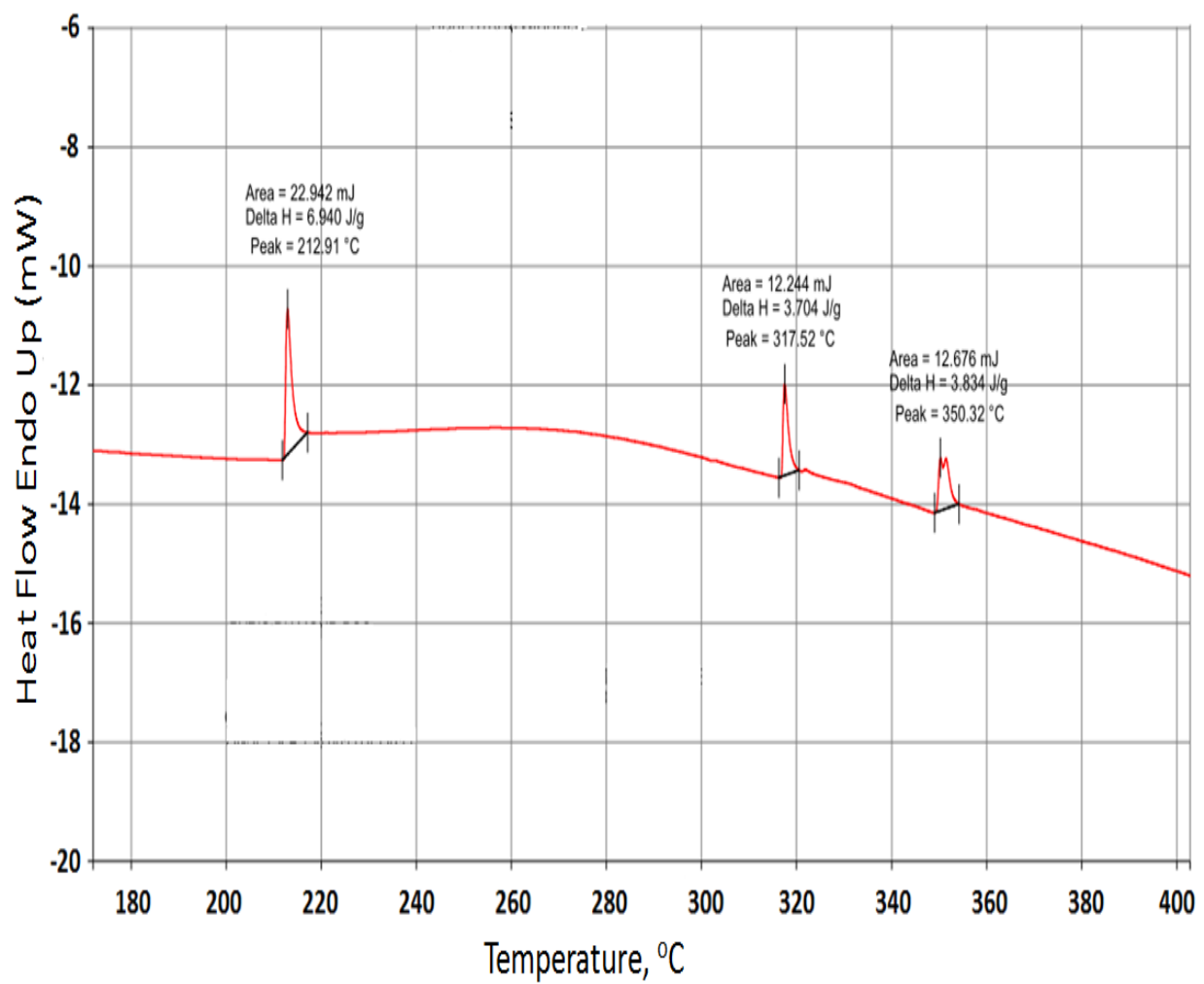
Appendix D: Structural Characteristics of MMT Pillared Clay



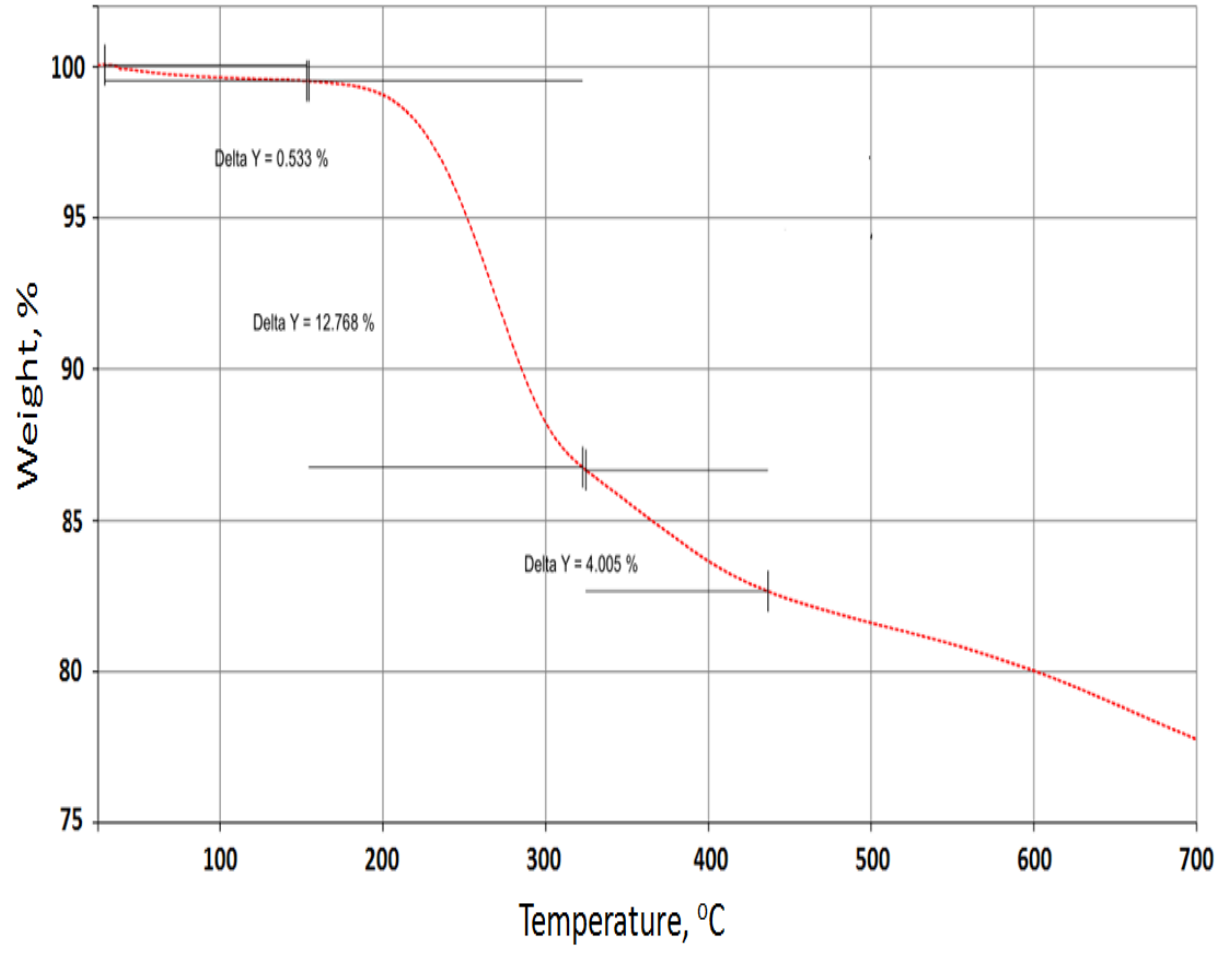
Appendix E: Structural Characteristics of Kaolin Pillared Clay



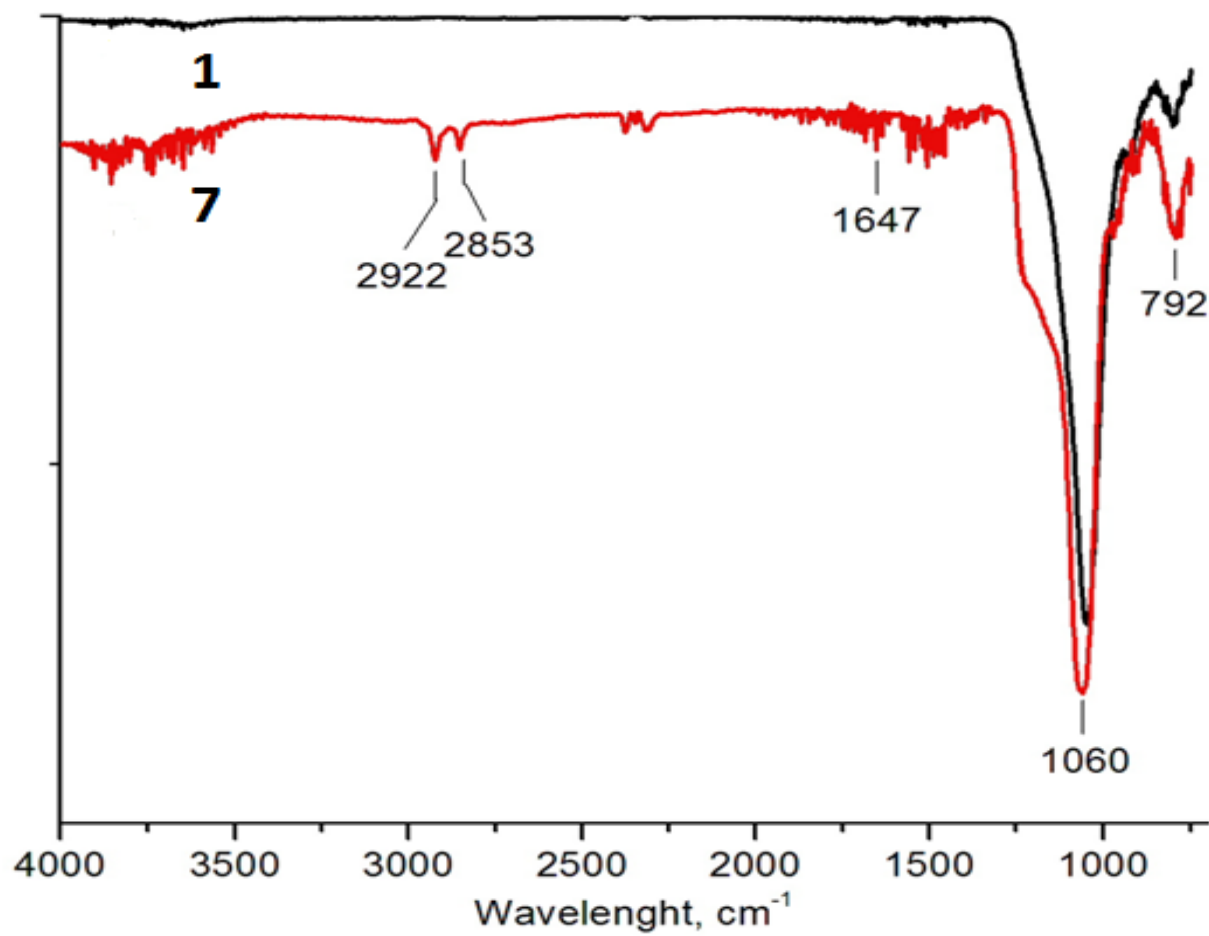
Appendix F: DSC Analysis



Appendix G: TGA Analysis

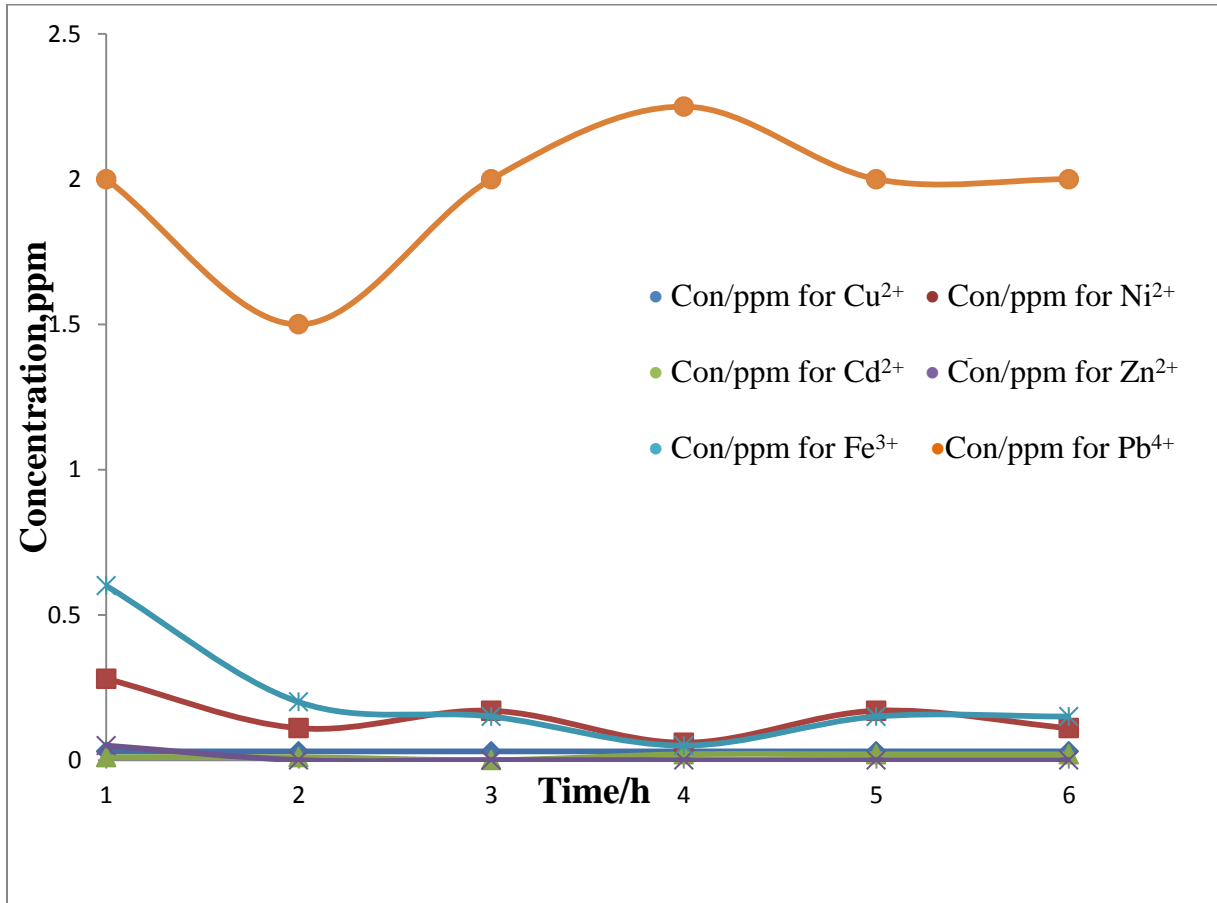


Appendix H: FT-IR Spectra of Organoclay

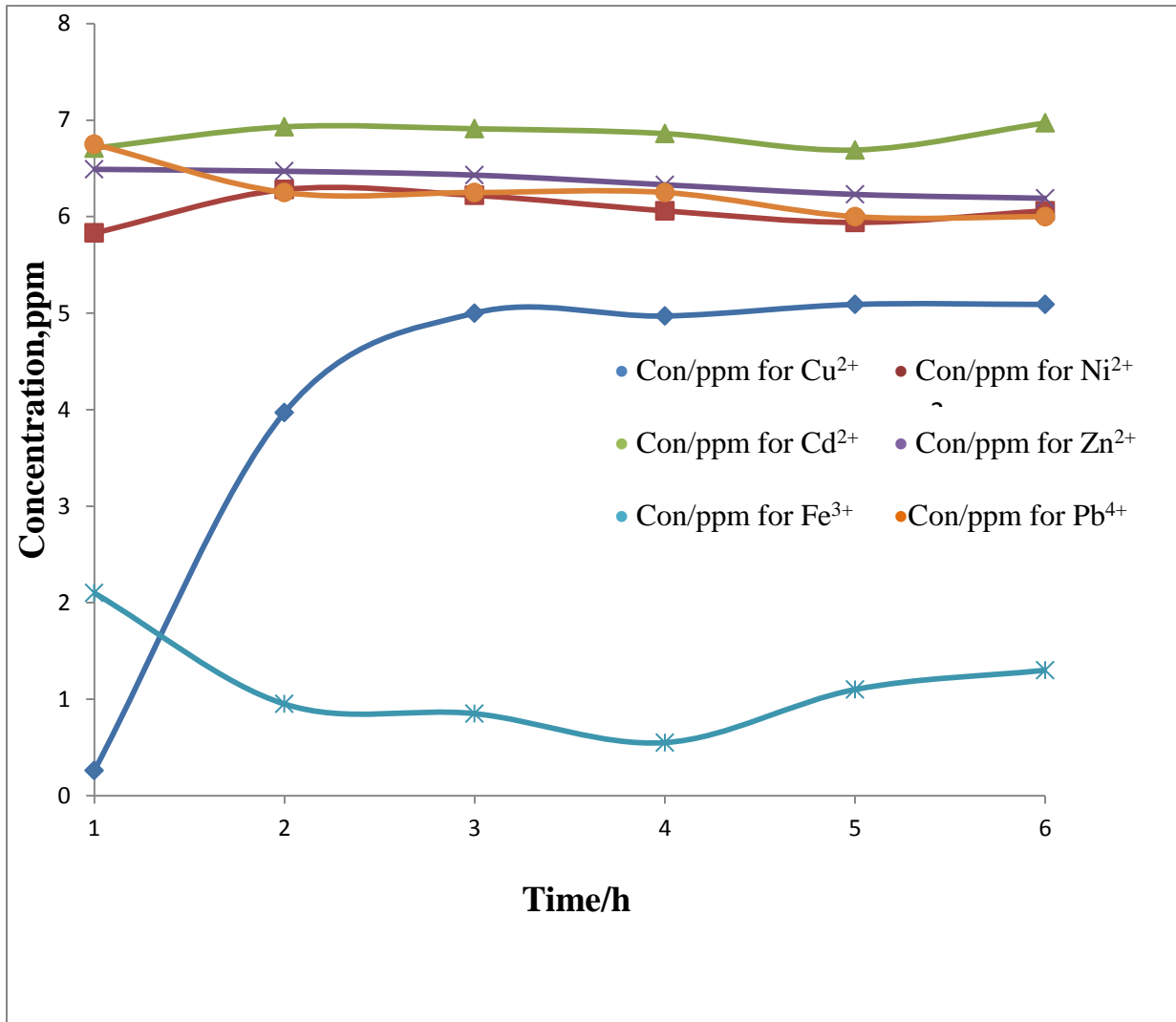


AAS RESULTS

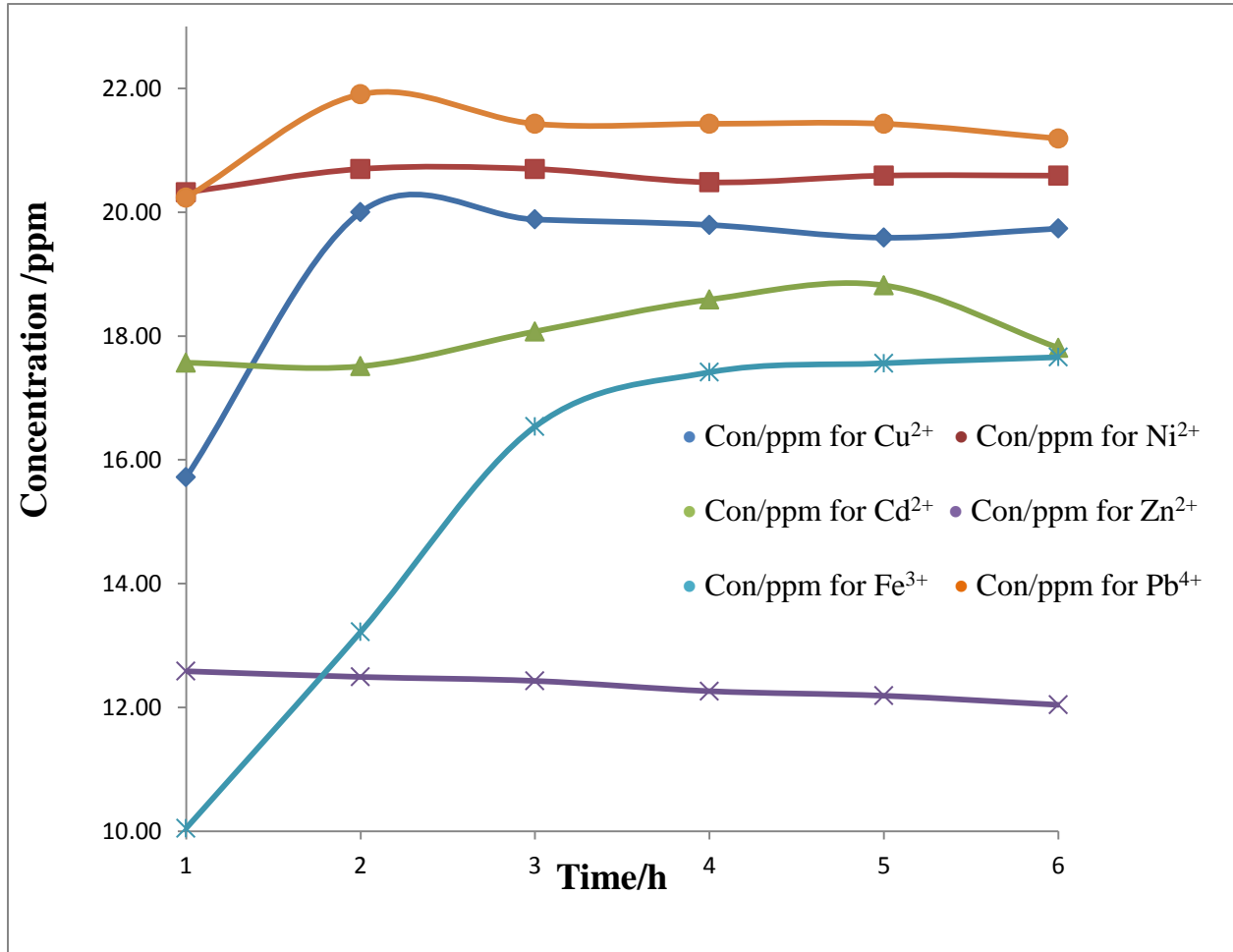
Appendix I: Initial Concentration of 5 ppm for all Single Salt and 71 ppm for Pb^{4+} Salt



Appendix J: Initial Concentration of 5 ppm (Mixture of Six Salts)



Appendix K: Initial Concentration of 20 ppm (Mixture of Six Salts)



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 ‘Modified Organoclay containing Chelating Ligand for
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 science*. Research Paper, ETSU, Johnson City, TN,
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