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ADSORPTION PROPERTIES OF AL-PILLARED BENTONITE

Müjde ALTUNLU
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Supervisor: Prof. Dr. Saadet YAPAR

Bornova-İZMİR

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ÖZET

AL-TABAKALANDIRILMIŞ BENTONİTİN ADSORPSİYON ÖZELLİKLERİ

ALTUNLU, Müjde

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Saadet YAPAR

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Killer, hidroksi katyonları, iskelet yapısında bulunan silikat tabakaları arasına alarak yüksek adsorpsiyon özellikleri kazandırılmak üzere modifiye edilebilirler. Bu şekilde yapılan modifikasyonun asıl hedefi, yüksek adsorpsiyon kapasitesine sahip mikro gözenekli katılar oluşturmaktır.

Bu çalışma, seyreltilmiş kil süspansiyonu ve seyreltilmiş tabakalandırma çözeltisinin reaksiyonu ile geleneksel tabakalandırma metodlarına uygun olarak hazırlanmış Al- tabakalandırılmış killerin adsorpsiyon özelliklerini incelemiştir. Fenol ve 2-klorofenol, model çözelti olarak kullanılmıştır. Al-tabakalandırılmış killer, ham kilden sentezlenmiştir. Bu çalışmada, yapısal değişikliklerin adsorpsiyon özellikleri üzerine etkisinin çalışılması için, farklı OH^{-}/Al^{+3} ve Al^{+3}/kil

oranları kullanılarak adsorbanlar sentezlenmiştir. Bu sayede, OH^{-}/Al^{+3} ve Al^{+3}/kil oranı arttıkça adsorplanan fenol miktarının azaldığı sonucuna ulaşılmıştır. Diğer taraftan, 2-klorofenol model çözeltisinin adsorpsiyon özellikleri, maksimum fenol adsorpsiyonu gözlemlenen adsorban ile çalışılmıştır. Buradan bulunan sonuca göre, düşük çözelti denge derişimlerinde fenol ve 2-klorofenol için adsorplanan miktarlar aynı olmakla birlikte çözelti derişimi 60 mg/L'den yükseldikçe az da olsa bir değişim gözlenmektedir. Daha sonra, bu adsorpsiyon miktarları HDTMA bromür- bentonun adsorpsiyon miktarları ile karşılaştırılmıştır. Söz konusu adsorban, bentonun katyon değişim kapasitesinin %100'üne eşdeğer miktarlarda hekzadesiltrimetilamonyum bromür(HDTMA) kullanılarak elde edilmiştir. Bu çalışma, fenol adsorpsiyonun HDTMA-bentonlara göre OH^{-}/Al^{+3}=1.44 ve Al^{+3}/kil=1.8 olan Al-tabalandırılmış bentonitelerde yaklaşık 3 kat daha fazla olduğunu göstermiştir. Adsorbanın bu davranışı, yüksek mikro gözenekli yapıya sahip olduğunun bir göstergesidir. OH^{-}/Al^{+3}=1.44 ve Al^{+3}/kil=1.8 oranlarına sahip adsorban, sentezlenmiş olan diğer Al-tabakalı adsorbanlara göre fenol adsorpsiyonu en yüksek olan türüdür. Bütün bu adsorpsiyon çalışmalarının yanı sıra, adsorbanın iskelet yapısındaki değişikliklerin gözlenebilmesi için SEM, ham kilin kristal yapısına yüzey modifikasyonunun etkisini görebilmek için XRD analizleri ve kimyasal grup değişikliklerini gözlemleyebilmek için IR analizleri de yapılmıştır.

ABSTRACT

ADSORPTION PROPERTIES OF AL-PILLARED BENTONITE

ALTUNLU, Müjde

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Clays can be modified by introducing hydoxycations between the silicate layers to obtain high adsorption properties. The main target of this modification is to create microporous solids which have high adsorption capacity.

This study presents adsorption properties of Al-pillared bentonites which were prepared by the conventional methods of pillaring involving the mixing of dilute clay suspension with a dilute pillaring solution. Phenol and 2-chlorophenol solutions are used as a model pollutants. Al-pillared bentonites are synthesised from crude bentonites. The method is used in this thesis is that applying the different OH^-/Al^{3+} and Al^{3+}/clay ratios to the synthesised adsorbents. By this means, textural changes on

adsorption properties is studied. From these studies, it is concluded that while OH^-/Al^{3+} and Al^{3+}/clay ratios increase, adsorbed amount of phenol decrease. On the other hand, adsorption properties of 2-chlorophenol is studied with the adsorbent that has the maximum amount of phenol adsorption. From this point, the amounts adsorbed are nearly same for both of the phenol and 2-chlorophenol at low equilibrium concentrations. At high concentrations, exceeding from 60 mg/L, a slight difference is observed. These adsorption amounts are compared with the amounts adsorbed by hexadecyltrimetylammonium bromide(HDTMA)- bentonite. It was obtained through the modification of bentonite with HDTMA bromide, in an amount equilivalent to 100% of cation exchange capacity of the clay. The result of this study shows that the adsorbed amounts of phenol is appoximately three times higher in the case of Al-pillared bentonite having OH^-/Al^{3+}=1.44 and Al^{3+}/clay=1.8 than HDTMA-bentonites. This behaviour is a cursor of the high microporous structure of the adsorbent. The mentioned adsorbent (OH^-/Al^{3+}=1.44 and Al^{3+}/clay=1.8) has also the highest phenol adsorption amount than the others synthesised Al-pillared bentonites. Beside the adsorption studies, also the structure changes were indicated with SEM method, to see the effect of surface modification to the crystal structure of the crude clay, XRD analyses and to determine the chemical group changes IR analyses were done.

ACKNOWLEDGEMENT

I would like to thank my supervisor, Prof. Dr. Saadet YAPAR, for her kind personality,

I would also like to thank to my rukiye

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1.0 INTRODUCTION

Phenol and its derivatives are the primary pollutants due to their high toxic impact even at very low concentrations. The removal of phenol and the derivatives are an active area of research.

Pillared interlayered clays (PILCs) have attracted also increasing attention, particularly from industry since 1970s (Aourad et al., 2004), because of their modified physical and chemical properties.

Pillared bentonites are obtained by intercalating inorganic polycations between the silicate layers of clays, resulting in an increase of the basal spacings. The resulting materials have large surface and pore volumes, being suitable for applications as catalysts and adsorbents. (Riego et al., 1994). The adsorbing capacity of modified clays depends on not only surface area, but also mainly on micropore structure and surface components.

Especially, for water and soil treatment investigations, materials which have high adsorbing capacity is very important for beginning step. Pollution of groundwater by inorganic and organic chemicals is of serious environmental concern. Clay minerals play a key role for treatment processes and also for a decade, investigations are showed that pillared bentonites are the potential adsorbents, because of their unique polarity and pore distribution; their surface area, heat stability, and Lewis acidity are high (Wu et al., 2001).

Besides all mentioned developed properties, PILCs have not been commonly used as commercial scale because of pillaring process developed in laboratory is difficult (time consuming, temperature, agitation and adding control is needed) to extend to an industrial scale.

In this work, the adsorption properties of Al-pillared bentonites are studied by using the phenol and 2-chlorophenol as model pollutants. Al-pillared bentonites were prepared by the conventional method involving the mixing of a dilute clay suspension with dilute pillaring solution. During the synthesis of Al-pillared bentonite, parameters of OH^-/Al^{3+} and Al^{3+}/clay were changed and so it was observed the effect of this change on the structure and adsorption behavior of the adsorbents. The textural characteristics of the materials obtained were studied by XRD, IR and SEM Analyses. Adsorption behaviors were also observed by conducting the batch adsorption kinetic and isotherm studies.

If a comparison is done among all the synthesised Al-pillared bentonites, it is found that the adsorption amount is higher than the others in OH^-/Al^{3+}=1.44 and Al^{3+}/clay=1.8, which is named Sample 1 in this thesis. Adsorption amounts of the HDTMA-bentonite and crude bentonite are nearly same while Sample 1 is higher. On the other hand, phenol removal amount increases about four times when the crude bentonite subjected to the pillaring process as the Sample 1.

2.0 LITERATURE REVIEW

2.1 Adsorption

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

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

Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity.

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores

between adsorption surfaces. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

Adsorption mechanisms are generally categorized as physisoption (or physical adsorption) and chemisorption (or chemical adsorption). Physisorption is a weak attraction between between molecules of the solid and substance adsorbed. In this mechanism, the energy of interaction is largely due to van der Walls attractions, which include Keesom (dipol dipole), Debye (dipole-induced dipole) interactions. In chemisorption, a chemical reaction forms a chemical bond between the adsorbate and adsorbent in a monolayer on the surface. The adsorbate is joined to the adsorbent by covalent bond or forces of comparable strenght.

Adsorption takes place because of the presence of an intrinsic surface energy. When a material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules. The result of these forces is characterized as physical (or Van der Waals) adsorption, in contrast to the stronger chemical attractions associated with chemisorption. The surface area of a solid includes both the external surface and the internal surface of the pores.

Due to the weak bonds involved between gas molecules and the surface (less than 15 KJ/mole), adsorption is a reversible phenomenon (www.saf.chem.ox.ac.uk/instruments/BET/sorpoptprin). Gas physisorption is considered non-selective, thus filling the surface step by step (or layer by layer) depending on the available solid surface and the relative pressure. Filling the first layer enables the measurement of the surface area of the material, because the amount of gas adsorbed when the monolayer is saturated is proportional to the entire surface area of the sample. The complete adsorption/desorption analysis is called an adsorption isotherm. The six IUPAC standard adsorption isotherms are shown in Figure 2.1 below, they differ because the systems demonstrate different gas/solid interactions (www.saf.chem.ox.ac.uk/instruments/BET/sorpoptprin).

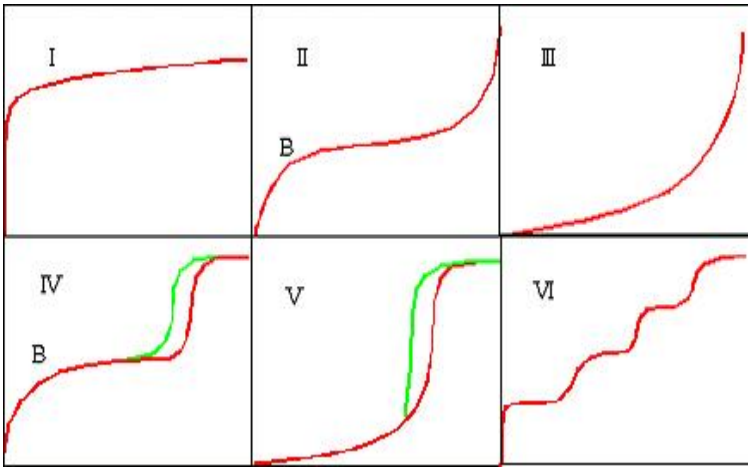

Figure 2.1 Six IUPAC standard adsorption isotherms
(http://saf.chem.ox.ac.uk/Instruments/BET/sorpoptprin.html)

The Type I isotherm is typical of microporous solids and chemisorption isotherms. Type II is shown by finely divided non-porous solids. Type III is typical of vapor adsorption (i.e. water vapor on hydrophobic materials). Type IV and V feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Finally, the rare type VI step-like isotherm is shown by nitrogen adsorbed on special carbon.

2.2 Porosity

Many solid and powder materials both natural (stones, soils, minerals, etc.) and manufactured (catalysts, cement, pharmaceuticals, metal oxides, ceramics, carbons, zeolites, clays etc.) contain a certain void volume of empty space. This is distributed within the solid mass in the form of pores, cavities, and cracks of various shapes and sizes. The total sum of the void volume is called the porosity.

The type and nature of porosity in natural materials depend on their formation (for instance rocks can be of igneous, sedimentary or metamorphic origin) while in man-made materials depend on their manufacturing and generally it can be controlled. Porosity strongly determines important physical properties of materials such as durability, mechanical strength, permeability and adsorption properties. The

knowledge of pore structure is an important step in characterizing materials, predicting their behavior.

The characterization of solids in terms of porosity consists in determining the following parameters:

Φ Pore size: Pore dimensions cover a very wide range. Pores are classified according to three main groups depending on the access size (www.saf.chem.ox.ac.uk/instruments/BET/sorpoptprin)

Micropores: less than 2 nm diameter

Mesopores: between 2 and 50 nm diameter

Macropores: larger than 50 nm diameter

Φ Specific pore volume and porosity: The internal void space in a porous material can be measured. It is generally expressed as a void volume (in cc or ml) divided by a mass unit (g).

Φ Pore size distribution: It is generally represented as the relative abundance of the pore volume (as a percentage or a derivative) as a function of the pore size.

Φ Bulk density: Bulk density (or envelope density) is calculated by the ratio between the dry sample mass and the external sample volume.

Φ Percentage porosity: The percentage porosity is represented by ratio between the total pore volume and the external (envelope) sample volume multiplied by 100.

Φ Specific surface area: The surface area of a solid material is the total surface of the sample that is in contact with the external environment. It is expressed as square meters per gram of dry sample. This parameter is strongly related to the pore size and the pore volume i.e. the larger the pore volume the larger the surface area and the smaller the pore size the higher the surface area. The surface area results from the contribution of the internal surface area of the pores plus the external surface area of the solid or the particles (in case of powders). Whenever a significant porosity is present, the fraction of the external surface area to the total surface area is small.

2.3. Adsorbent

A solid can be used as an adsorbent if it has a highly developed surface. Many natural and synthetic materials such as activated carbon, activated alumina, zeolite, clay, and synthetic resin have been used as adsorbents (Yılmaz, 2003).

Especially clays are commonly used adsorbents because of low price and can be easily modificate interlayer species. There are three major clay groups, as shown in Table 2.1

Table 2.1: Three major clay groups

NAME	CHEMICAL FORMULA
Montmorillonite	$Al_2(OH)_2Si_4O_{10}$
Illite	$K_{0-2}Al_4(Si_{6-8}Al_{0-2})O_{20}(OH)_4$
Kaolinite	$Al_2Si_2O_5(OH)_4$

2.3.1. Bentonite

Bentonite is a name given to particular clay that was originally found in Fort Benton, Eastern Wyoming. The name was given by W.C. Knight in 1898 (www.eytonsearth.org/bentonite-montmorillonite.php).

Previously, it was called Taylorite, which was named after William Taylor, who first began to draw attention to the clay deposits. In Figure 2.2 that is shown a microsphoto of bentonite mineral (www.eytonsearth.org/bentonite-montmorillonite.php).

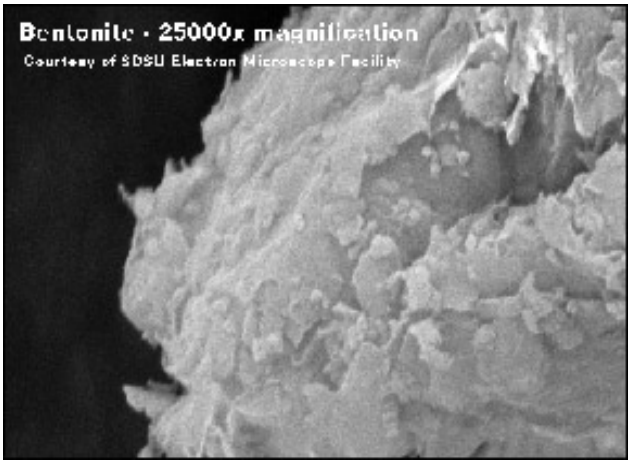

Figure 2.2: SEM photo of bentonite mineral

Bentonite is the name for the ore whose major constituent is the clay mineral, montmorillonite. As shown in Figure 2.3, montmorillonites are three-layer minerals consisting of two tetrahedral layers sandwiched around a central octahedral layer (www.eytonsearth.org/bentonite-montmorillonite.php).

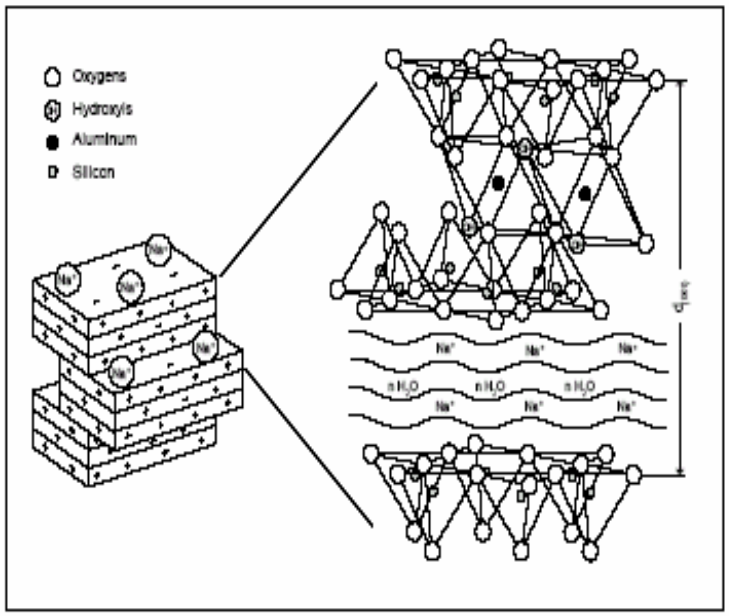

Figure 2.3 Crystalline structure of a Bentonite (Sodium Bentonite) showing interlamellar water layers.

The colour of bentonite ranges from white to light olive green, cream, yellow, earthy red, brown and sometimes sky blue when fresh but yellowing rapidly with exposure to air. When wet it is highly plastic and slippery. Bentonite feels and appears greasy or waxy.

There are two basic types of bentonite depending on whether they contain sodium or calcium in the crystal lattice.

2.3.1.1 Swelling Bentonites

Sodium bentonite contains sodium in the platy molecular structure; has strong swelling properties (ability to swell to many times its dry volume when wet) and possesses a high dry-bonding strength.

Sodium bentonite is most widely known to swell. It can absorb nearly 5 times its weight in water and full saturation may occupy a volume 12 to 15 times its dry built (http://www.cetco.pl/e/volclay.htm). The higher water absorption capacity of bentonite also makes it very plastic and resistant to fracturing or cracking.

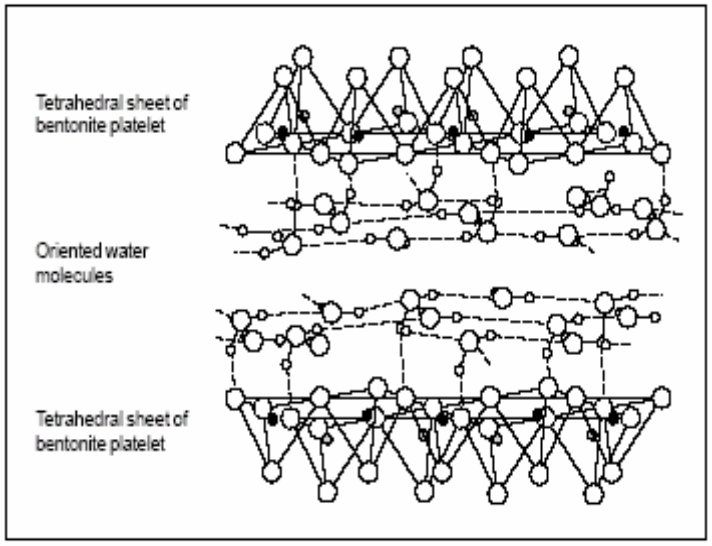

Figure 2.4 Configuration of the interlayer water system showing hydrogen binding to the adjacent clay surfaces when it swells (Grim, 1968)

2.3.1.2 Non-Swelling Bentonites

Calcium bentonite contains calcium in its structure; has a far lower capacity to swell when wet and usually exhibits greater adsorptive characteristics.

2.4. Modification of Clays

Clays can be modified by introducing hydroxycations between the layers to obtain microporous solids with catalytic or adsorption properties.

Intercalation of smectite clays via exchange of cations located in their interlayer space with hydroxymetal cations, followed by thermal treatment, is an effective way to modulate them in order to obtain adsorbents, catalyst supports or catalysts (Salerno and Mendioroz, 2002).

The metals commonly used are Al, Fe, Zr, Cr, Ti, and Ga, (Moreno et al., 1997b, Maes et al., 1997, Sychev et al., 2000, Bradley and Kydd, 1993). Today these materials called pillared clays (PILCs) are used in a wide range of catalysis reactions such as cracking (Brandt and Kydd, 1997; Gonzalez et al., 1999), alkylation (Vaugan et al., 1981), methanol conversion (Occelli at al., 1985), hydrotreatment (Shabtai and Fijal, 1986).

The material (bentonite) is always electrically unbalanced by substitutions, such as magnesium, iron, or calcium replacing aluminum or etc. This results in a charge deficiency resulting in a net negative charge of the particle that must be balanced externally by cations, which in turn are exchangeable. The quantity of cations required to create a net charge balance is called "the cation exchange capacity". The exchangeable cations are positioned but weakly held near the tetrahedral layers. The most prominent cations are sodium, calcium, magnesium, and potassium, respectively.

Using modification techniques, it can be increased the surface area of the bentonite. Increase in surface area causes increase in the adsorption capacity of the material. The exchangeability of these cations allows this material to remove heavy metals from water, an important consideration for wastewater treatment. Simultaneously, it removes cationic organics by ion exchange, resulting in an interaction with polymers. Its large swelling capacity, combined with ion exchange capacity, allows the material to form a floc with suspended solids that can be precipitated out of the water.

There are different ways to modify clay minerals: (1) adsorption, (2) ion exchange with inorganic cations and cationic complexes, (3) ion exchange with organic cations, (4) binding of inorganic and organic anions, mainly at the edges, (5) grafting of organic compounds, (6) reaction with acids, (7) pillaring by different types of poly (hydoxy metal)

cations, (8) interlamellar or intraparticle and interparticle polymerisation, (9) dehydoxylation and calcinations, (10) delamination and reaggregation of smectitic clay minerals, and (11) physical treatments such as lyophilisation, ultrasound, and plasma (Bergaya and Lagaly; 2001).

2.5. Phenol

Synonyms for phenol are hydroxybenzene, carbolic acid, phenic, phenic acid and phenyl alcohol. Chemical structure is shown in Figure 2.5**.**

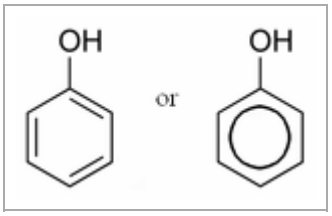

Figure 2.5. Chemical structure of phenol

Phenol can remain in the air, soil, and water for long periods of time if a large amount of it is released at one time, or if it is constantly released to the environment from a source. Small amounts of phenol do not remain in the air for longer than a day, in the soil for longer than 2 to 5 days, and in water for longer than 9 days (http://www.nsc.org/ehc/chemical/Phenol.htm).

Phenol is naturally occurring in some foods, in human and animal wastes(http://www.chemguide.co.uk/organicprops/phenol/background.html). Currently, the largest use of phenol is as an intermediate in the production of phenolic resins, which is used in the wood, adhesive construction, automotive and appliance industries. Phenol is also used in the production of synthetic fibers such as nylon and for epoxy resin precursors.

Phenol is obtained by fractional distillation of coal tar and by organic synthesis. By far, its largest single use is in manufacture of phenolic resins and plastics. Other uses include manufacture of explosives, fertilizers, paints, rubber, textiles, adhesives, drugs, paper, soap, wood preservatives, and photographic developers. When mixed with slaked lime and other reagents, phenol is an effective disinfectant for toilets, stables, cesspools, floors, and drains.

Phenol was once an important antiseptic and is still used as a preservative in injectables (http://www.atsdr.cdc.gov/mhmi/mmg115.html).

If phenol is absorbed into the body, it can cause headaches, dizziness, high blood pressure, heart effects, shallow breathing, wheezing, coughing, vomiting, stomach ulceration and eventually death. These health effects are the same whether absorption is due to eating contaminated food or drink, inhaling contaminated air or from skin absorption. Phenol and its compounds are not classifiable as to their

carcinogenicity to humans by the International Agency for Research on serious species of cancer (http://www.hpa.org.uk/chemicals/compendium/Phenol/background.htm).

After oxygeneration and oxygenation polimerization, phenol can form humic acid, which complicates soil and wastewater treatment. Phenol compounds are complex, poisonous to animals and toxic to water and soil at several ppm.

2.5.1. Physical and Chemical Properties of Phenol

Phenol is a colorless crystalline solid at room temperature with a typical sweet tarry odor. Its chemical formula is C_6H_5OH and its structure is that of a hydroxyl group (-OH) bonded to a phenyl ring; it is thus an aromatic compound. Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discoloured.

Phenol has a limited solubility in water (8.3 g/100 ml), but is completely miscible above 40 °C, as a liquid. It is slightly acidic: the phenol molecule has weak tendencies to lose the H^+ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion $C_6H_5O^-$ (http://en.allexperts.com/e/p/ph/phenol.htm). Compared to aliphatic alcohols, phenol shows much higher acidity.

Phenol is characterized by the influence of the hydoxyl group and the aromatic ring upon each other. The electronegative phenyl group imparts a slight acidity to the hydoxyl group. Therefore, phenol reacts with strong bases to form phenoxides, phenolates or phenates. Many of these salts, especially those of sodium and potassium, are soluble in water and all decompose readily in the presence of carbondioxide which releases the phenol.

Physical and Chemical properties of phenol are shown in Table 2.2.

You can taste and smell it at levels lower than those that are associated with harmful effects. Phenol evaporates more slowly than water, and a moderate amount can form a solution with water.

Table 2.2 Physical and chemical properties of Phenol

Phenol	
Systematic name	Phenol
Other names	hydroxybenzene, carbolic acid, phenic, phenic acid, phenyl alcohol
Chemical formula	C_6H_5OH
Smiles	OC1=CC=CC=C1
Molar mass (g/mol)	94.11
Apperance	White crystalline solid
CAS number	(108-95-2)
Density	1.07 g/cm3
Solubility in water	8.3 g/100 ml (20 °C)
Melting point	40.5 °C
Boling point	181.7 °C
Flash point (open cup)	85 °C
Acidity (pK_a)	9.95

2.6 Adsorption of Phenol on Pillared Clays

Pillared clays are a family of materials which currently receives considerable attention. These materials are obtained by intercalating inorganic polycations between the silicate layers of clays, resulting in an increase of the basal spacings (Riego et al., 1994).

Among the different pollutants of aquatic ecosystems, phenols are considered as priority pollutants since they are harmful to organisms even at ppb levels (Chapman et al., 1982). The removal of such compounds at such low levels constitutes a difficult problem. Among the methods employed are either destructive oxidation with ozone (Hoigne, 1985), hydrogen peroxide (Moza et al., 1988; Kochany and Bolton, 1992), and manganese oxides (Ulrich and Stone, 1989; Ukrainczyk and Mcbride, 1992), often assisted by light (Moza et al., 1988; Kochany and Bolton, 1992; Lipczynska-Kochany and Bolton, 1992) or adsorption into porous solids such as activated carbon (Speitel at al., 1989; Paprowicz, 1990); fly ash (Bishop et al., 1990) and clays, either natural or pillared (Mortland et al., 1986; Boyd et al., 1988; Ziekle and Pinnavaia, 1988; Srinivasan and Fogler; 1990; Michot and Pinnavaia, 1991; Wang, 1991; Kowalska et al., 1994).

3.0 EXPERIMENTAL STUDY

3.1 Materials Used

Basic materials used are; for preparing new featured adsorbents: Bentonite, for preparing pillaring solution: $AlCl_3$ and NaOH, for determining adsorption capacity of prepared adsorbent: Phenol and for second modification study of bentonite: Hexadecyltrimethyammonium bromide (HDTMA). All the reagents used are of analytical grade.

Bentonite obtained from Reşadiye, Tokat was washed with distilled water and seperated from impurities such as ironoxide and silica by differential sedimentation technique. The chemical analysis of the mineral is given in Table 3.1

Table 3.1 Chemical analysis of bentonite

Constituent	Value(%)
SiO_2	56.63
Al_2O_3	23.25
Fe_2O_3	4.41
Na_2O	2.85
MgO	1.77
K_2O	0.48
CaO	0.47
WL*	9.28

*Weight loss at 1000 °C

Phenol is supplied from Merck, which has the important name at its field of production of special chemicals. Specifications of phenol are shown at Table 3.2.

Table 3.2 Specifications of Phenol from the supplier

	Phenol
Formula	C_6H_6O
Molecular weight (g/mol)	94.1
Purity (%)	> 99.5
Melting point (°C)	> 40.5
Boiling point (°C)	180-182
Solubility (g/ml) at 20°C	77.5
pH (5%; water)	4.8-6.0
Nonvolatile portion (%)	< 0.05
Heavy metals (%)	< 0.001
Water (%)	< 0.5

3.2 Preparation of Al-pillared bentonite

Al-pillared bentonite has prepared in two steps: 1) preparation of pillaring solution and 2) intercalation of the Keggin ion onto bentonite.

3.2.1 Preparation of pillaring solution

In the first step Keggin Ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ was obtained from the reaction between 0.2 M $AlCl_3$ and 0.2 M NaOH. Reaction takes place by dropwise addition of an NaOH solution to a solution of $AlCl_3$ under the vigorous stirring. During the reaction; temperature and rate of addition were kept as constant. The temperature was 80 °C and rate of addition was 6 ml/min. The solution was allowed to age overnight (12-16 h) while being stirred and cooled to room temperature. Then the pH is measured with a pH-meter to control and to fix it at 3.6-4.0. The solution was stored at a dark black bottle at room temperature during the studies.

Keggin Ion is an oligomer prepared through the chemical reaction between $AlCl_3$ and NaOH. Specifications of Keggin Ion which are obtained from the literature studies are shown in Table 3.3.

Table 3.3 Specifications of Keggin Ion (GE at al., 1993)

	Keggin Ion
Formula	$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$
Molecular weight (g/mol)	1038.74

The pillaring reaction was carried out by using different Al^{3+}/clay and also different OH^-/Al^{3+} ratios, to study the effect of these ratios on the

structure of the pillared clay. During the synthesis, Al^{3+}/clay ratio was kept constant as 1.8 and/or 2.0 and/or 2.5, while OH^-/Al^{3+} ratios were changed as 1.44, 2.0, and 2.5 for each trial. The volumes of reactants at the starting pillaring solution (0.2 M $AlCl_3$ and 0.2 M NaOH) and the solution volume during the addition were adjusted to give the predetermined ratios. The amounts of OH^- and Al^{3+} used in the preparation of pillaring solution and OH^-/Al^{3+} and Al^{3+}/clay ratios of the clays are shown in Table 3.4.

Table 3.4 OH^-/Al^{3+} and Al^{3+}/clay ratios of Al-pillared clays

Sample	OH^-/Al^{3+}	Al^{3+}/clay	$n_{Al}{}^{3+}$ (mole)	$n_{OH}{}^-$ (mole)
1	1.44	1.8	0.100	0.144
2	2.00	1.8	0.045	0.090
3	2.50	1.8	0.032	0.080
4	1.44	2.5	0.100	0.144
5	2.00	2.5	0.045	0.090

Before the second step, there is an intermediate step which is called as Dispersion Preparation step. Dispersion of 2% (w/w) bentonite is prepared for the second step of intercalation. Since the bentonite is swelling type clay mineral, a vortex agitation and slow addition of solid to pure water was carried out to get a homogenous dispersion.

3.2.2 Intercalation of bentonite

In the second step, intercalation studies of adsorbent are performed by the reaction between 2% (w/w) of clay dispersion and pillaring solution with vigorous stirring. Again at this stage, temperature and rate of addition is controlled. Temperature is constant at 70 °C and rate of addition is approximately constant at 2 ml/min. After addition of bentonite is completed, the stirred mixture was allowed to age 70 °C for an additional 2 hours with continuous stirring. A color change from light yellow to white was observed during the reaction. The occurrence of the reaction could be followed by this color change. After the aging, the mixture was cooled to the room temperature.

The adsorbent washed seven times with the pure water to remove the unreacted impurities from the adsorbent structure. After each washing cycle, the pH and electrical conductivity values of filtered water was measured to decide the end of washing step. When electrical conductivity value is reached to the value which is less than 20 μsi, the washing is stopped.

After washing step, the clays were subjected to the FN-032 Sterilisator with dry air at 60°C for drying during 24-29 hours.

3.3 Characterization of Al-pillared Bentonite

3.3.1 XRD analysis

To see the effect of modification on basal spacing of bentonite, the samples was subjected the X-ray diffraction analysis by using a Rigaku D/Max-2200/PC diffraction spectrometer with Cu Kα radiation.

3.3.2 SEM Analyses

The crude bentonite and modified forms were subjected for SEM analysis to JEOL, JFM-6060 scanning electron microscope.

3.3.3 IR Analyses

The crude bentonite and modified clays were subjected to the IR-470 Shimadzu Spectrophotometer.

3.4 Adsorption of Phenol

The batch technique was used in the experiments conducted in two groups: kinetics and isotherm studies. The kinetic studies reveal that the equilibrium is established approximately in 150 minutes. A series of

isotherm experiments were also conducted by HDTMA-bentonite to compare the adsorption behavior of PILCs.

3.4.1 Adsorption kinetics

Kinetic studies are carried out using 200 ppm phenol solution. 0.2 gr of the sample is added to the phenol solution. These suspensions are shaken at 20 °C at different time intervals ranging from 30 min to 24 h.

At the end of time, the suspensions were centrifuged at 200 rpm to separate the solid and liquid phases. The supernatants were subjected to UV analyses to determine the final concentrations in JASCO 7000 UV spectrophotometer. The absorbances of the sample solutions and standards were measured at 269 nm. The amount adsorbed was determined from the difference between initial and final concentrations. From the concentration of the supernatants the adsorbed quantities were determined using the mass balance equation:

$$Q = (C_0 - C) * V / m$$

where Q (mg/g) is the adsorbed amount per gram of clay at time t for kinetic studies and at equilibrium for isotherm studies, C_0 (mg/L) is the initial phenol concentration, C (mg/L) is the phenol concentration at time t for kinetic studies or equilibrium concentration for isotherm studies, V (L) and m (g) represent the solution concentration and the amount of adsorbent used, respectively. Standart solutions were prepared at a concentration range from 10 to 60 ppm.

3.4.2 Adsorption isotherms

Adsorption isotherm studies were carried out as the same methods as Chapter 3.4.1. in a concentration range 0- 200 ppm at 20°C.

4. RESULTS AND DISCUSSION

4.1. pH Control

pH change is very important on the structure of the synthesized clay. It has to be kept constant and controlled during the formation of oligomer solution and intercalation. However, the pH value in the formation of the oligomer solution is high, there will be polimerisation in the oligomer solution and the final product of the reaction is not achieved.

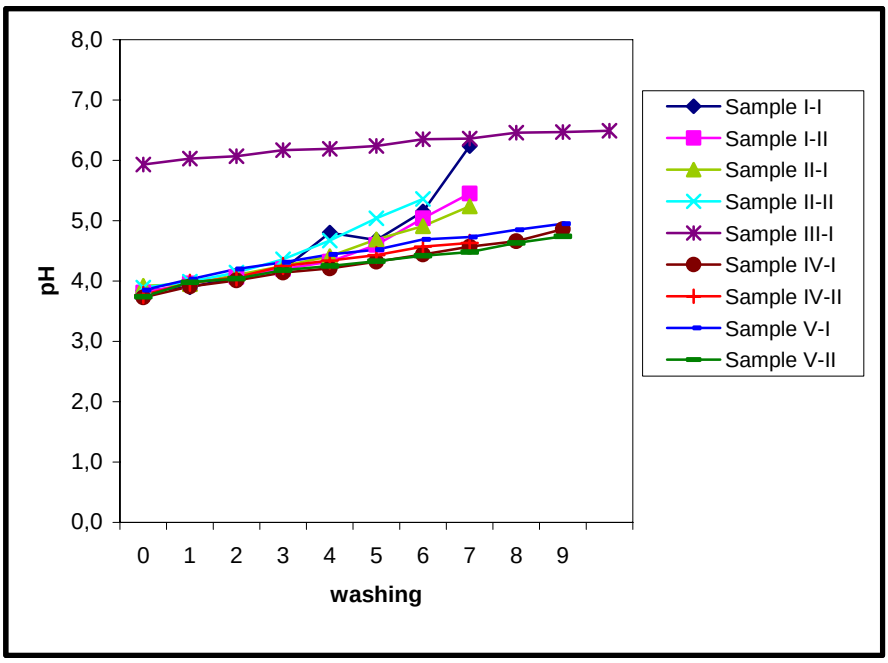

Figure 4.1 pH change during washing.

On the other hand, the clay structure changes to the undesired form when the pH is also high during the intercalation step. Therefore the pHs of the pillaring solution and the filtrate were measured carefully. pHs, in the washing step, are proved that during the reactions, intercalation and preparation of oligomer solution, is not changed and values are recorded. The data obtained are shown in Figures 4.1 and 4.2. Also, conductivity measurements are done to seperate non-clay minerals and excess salts.

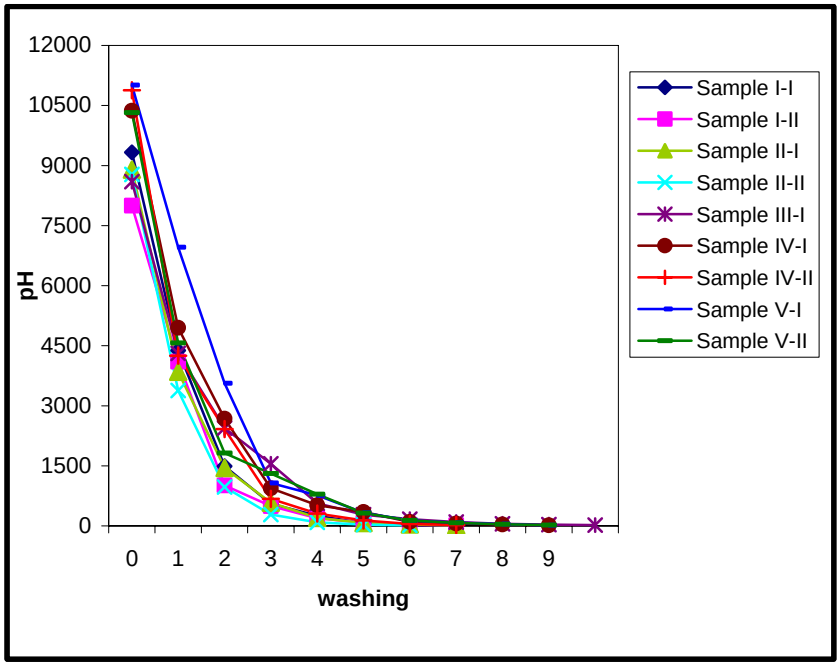

Figure 4.2 Conductivity change during washing.

4.2. Characterization of Adsorbents

4.2.1. XRD Analysis

To see the effect of surface modification to the crystal structure of the crude clay, the samples were subjected to XRD analyses. The changes in basal spacing of the samples was measured by X-ray diffraction method. XRD pattern of crude bentonite is shown in the Figure 4.3. Due to the results of XRD analysis in Figure 4.3, it is shown that the crude bentonite consists of montmorillonite- 15A, montmorillonite- 14A and beidellite-12A.

The XRD patterns of the samples are given in the Figure 4.4, 4.5, 4.6, 4.7 and 4.8 for all synthesised Al-pillared adsorbent species.

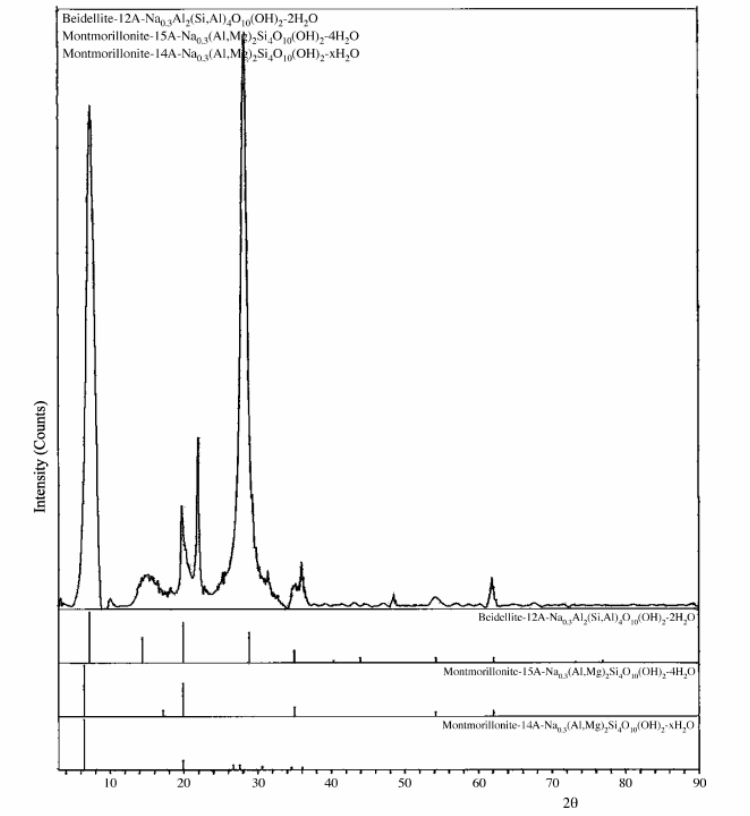

Figure 4.3 XRD pattern of crude bentonite

It was measured that the basal spacing (d_{001}) of crude bentonite is 11.94 Å at the 2θ of 7.4. The XRD traces of the pillared samples between the angles of 0° and 10° are shown in Figure 4.9.

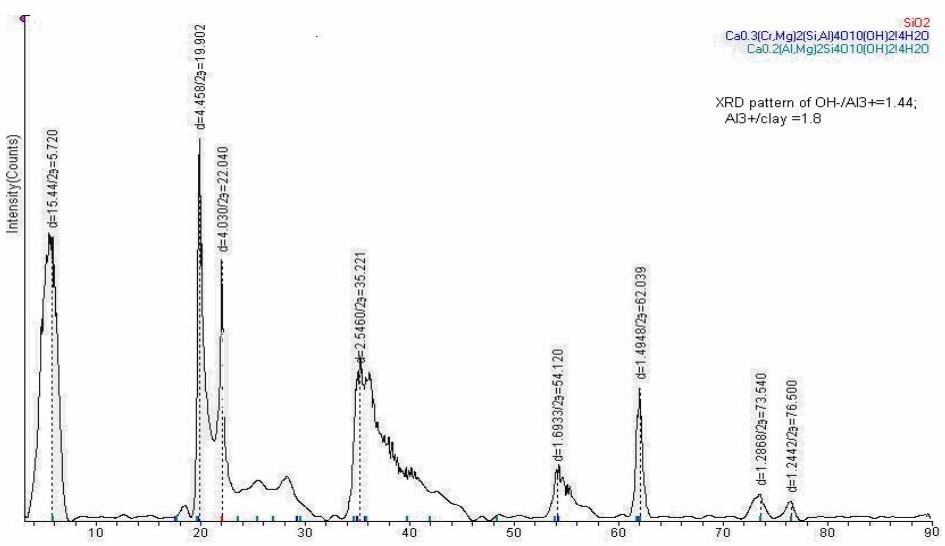

Figure 4.4 XRD pattern of Sample 1.

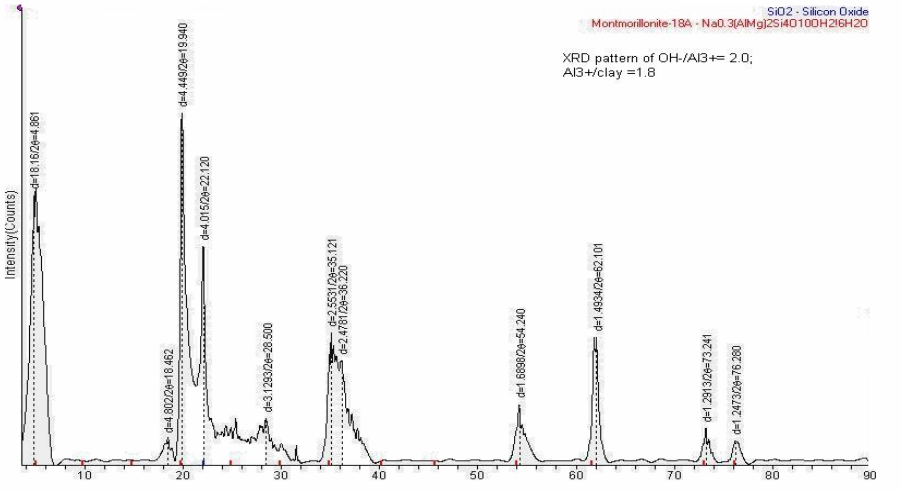

Figure 4.5 XRD pattern of Sample 2.

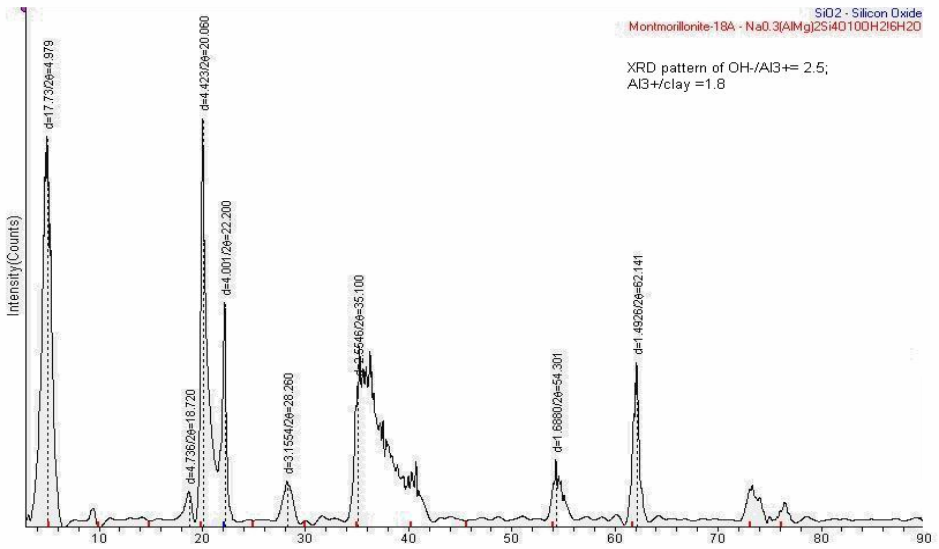

Figure 4.6 XRD pattern of Sample 3.

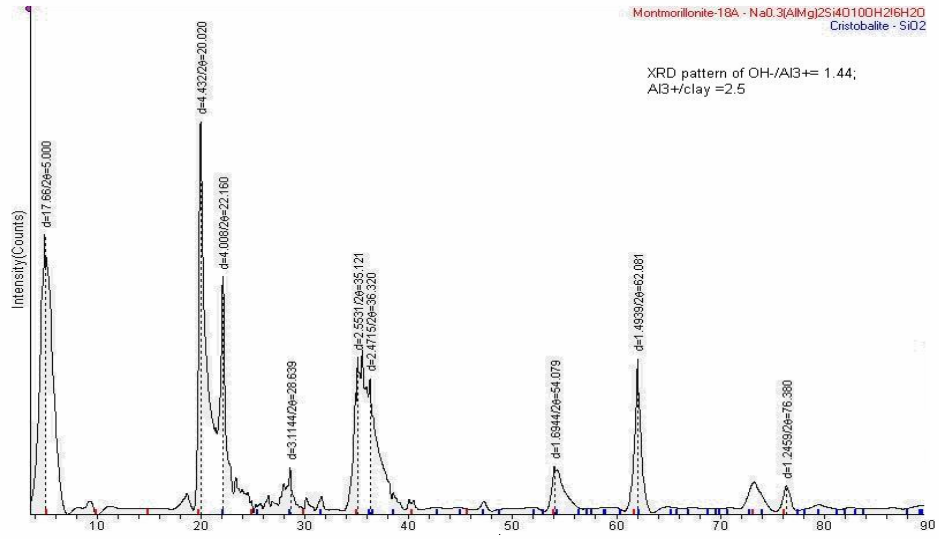

Figure 4.7 XRD pattern of Sample 4.

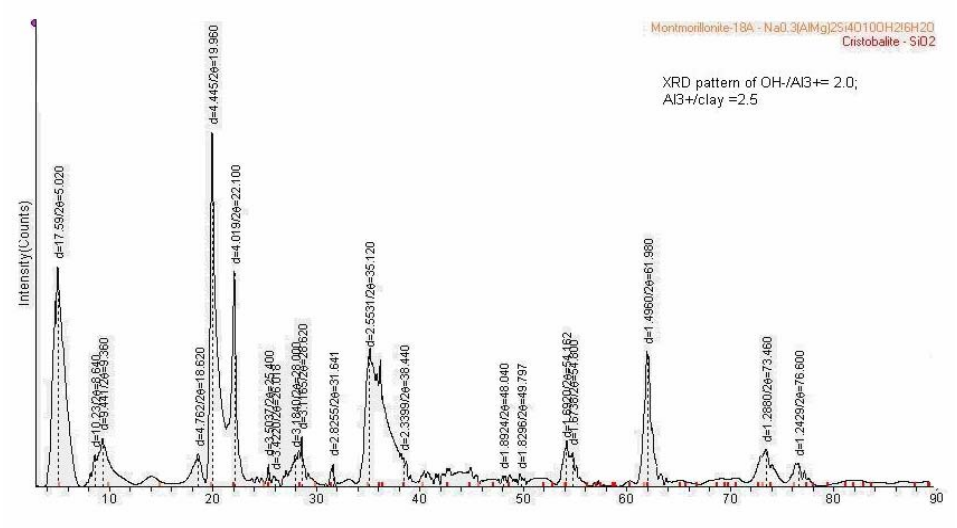

Figure 4.8 XRD pattern of Sample 5.

XRD measurements of crude and Al-pillared clays show the expansion of the interlamellar space of the clay by location of the Keggin Ions between the silicate layers. This is the conclusion of the expansion in interlayer spacing was affected by the surface coverage.

Beside crude bentonite, in this study also bentonite modified with HDTMA and Al- pillared clays XRD analysis have been measured and measurements are showed in the Table 4.1.

As shown at the Table 4.1, basal spacings of crude, Al-pillared bentonite and also modified bentonite with HDTMA are given along with the expansion in interlayer distance.

Table 4.1 Basal spacings (d_{001}) (Å) and expansion in interlayer distance upon modification

sample	OH^-/Al^{3+}	Al^{3+}/clay	d_{001}(Å)	d_{001}-9,6 (Å)	2θ
crude bentonite	-	-	11.94		7.4
HDTMA	-	-	18.03	8.43	
1	1.44	1.8	15.44	5.84	5.72
2	2.0	1.8	18.16	8.56	4.861
3	2.5	1.8	17.73	8.13	4.979
4	1.44	2.5	17.66	8.06	5.00
5	2.0	2.5	17.59	7.99	5.02

Due to the XRD measurements which are shown in Table 4.1, it can be observed that an increase of $OH^-/Al^{3+}$and Al^{3+}/clay causes a decrease in basal spacings, however, Sample 1 is an exception because of the lowest value of the basal spacing it has. Also, the increase in basal spacing is maximum in the case of sample 2. This information is in contrast to that the most homogeneous structure between the Al-pillared samples is sample 3. For sample 2, a 8.56Å increase in basal spacing shows the maximum increase, between the other species, before the delamination occurs.

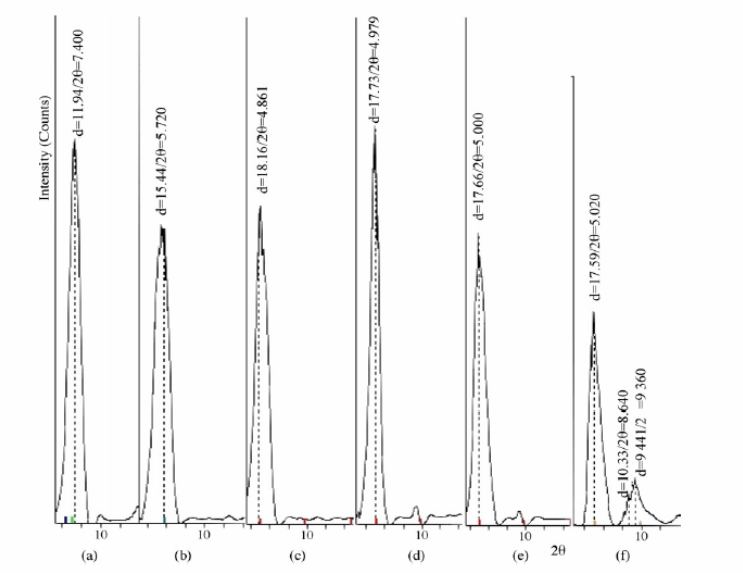

Figure 4.9 Comparison of XRD traces between the angles 0° and 10°: (a) crude bentonite, (b) Sample 1, (c) Sample 2, (d) Sample 3, (e) Sample 4, (f) Sample 5

If a comparison is done between the XRD traces of the crude bentonite and the pillared ones from Figure 4.9, it can be easily seen that there is a shift to lower angles, 2Θ. Also, there is an intensity decrease in the order sample 3 > sample 2 > sample 1 > sample 4 > sample 5. Beside these informations, there is no significant changes in the width of the peaks is easily seen from the Figure 4.9. Sample 3 has the sharpest and the most intensive peak, which suggest that the intercalation process is homogeneous (Sanchez and Montes, 1997). The less intense and broader peaks suggest that a fraction of clay remained unpillared (Gonzales et al, 1992) and/or delamination has occurred (Katdare et al, 1999). On the other

hand, the results of XRD analyses suggest partial delamination and Sample 4 and 5 have a relatively high degree of delamination.

Basal spacing of crude bentonite is measured as 11.94 Å. This measurement indicates that in the crude bentonite structure there is inorganic cations, mainly Na^+, in hydrated state in the interlayer state occur. Increase in basal spacings with HDTMA modification is higher than Al-pillaring method.

Basal spacing values are in between the thickness of the silicate layer (9.6 Å), and the spacing of the bentonite having Na^+ ions in the interlayer space with one moleculer water layer (12.5 Å). To proof that, in Table 3.1 the chemical composition of bentonite is given. As shown in the table, the inorganic exchangeable cations between the silicate layers are composed of mainly Na^+. Calculated d_{001}-9.6 values are also shown in the Table 4.1. These values show pore height of the adsorbent.

4.2.2 IR Analyses

The IR Spectra of crude and Al-pillared bentonite are given in Figure 4.10, 4.11, 4.12, 4.13 and 4.14. The chemical changes of the crude bentonite and Al-pillared bentonite can be easily seen from these Figures. In the Figures y axis shows absorbance and x axis shows the wavelenght in cm^{-1}. Figure 4.10 shows the IR spectra of the crude bentonite.

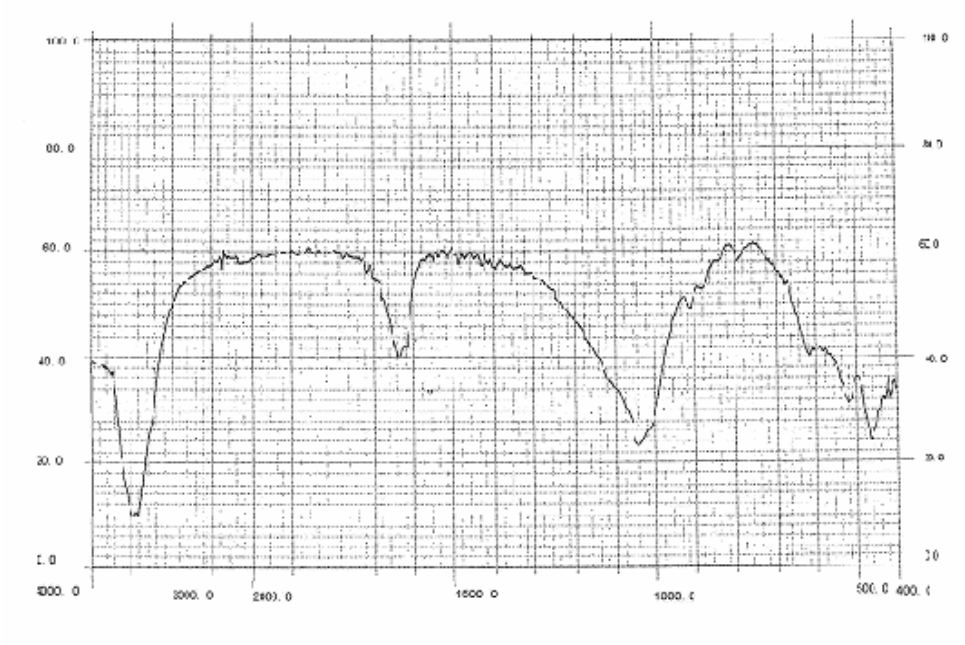

Figure 4.10 IR Spectra of Crude Bentonite

The observed characteristics from the crude bentonite IR spectra is the special chemical species exist at 3630 cm^{-1}, 3450 cm^{-1} and 1640 cm^{-1} correspond to stretching of O-H in crystal structure. This feature mean that the streching of O-H in the adsorped water and deformation vibration of water, respectively.

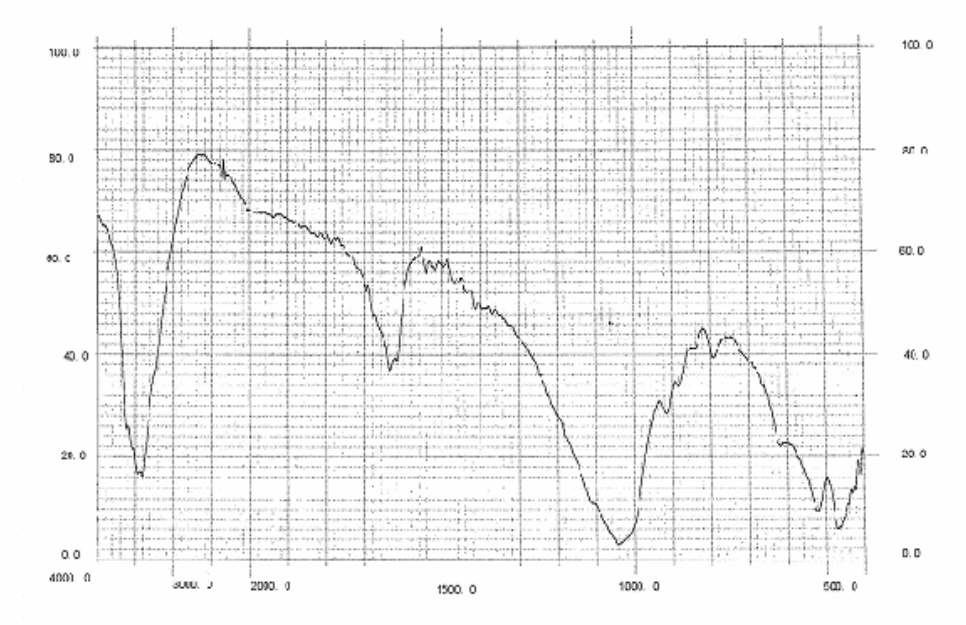

Figure 4.11 IR Spectra of Sample 1.

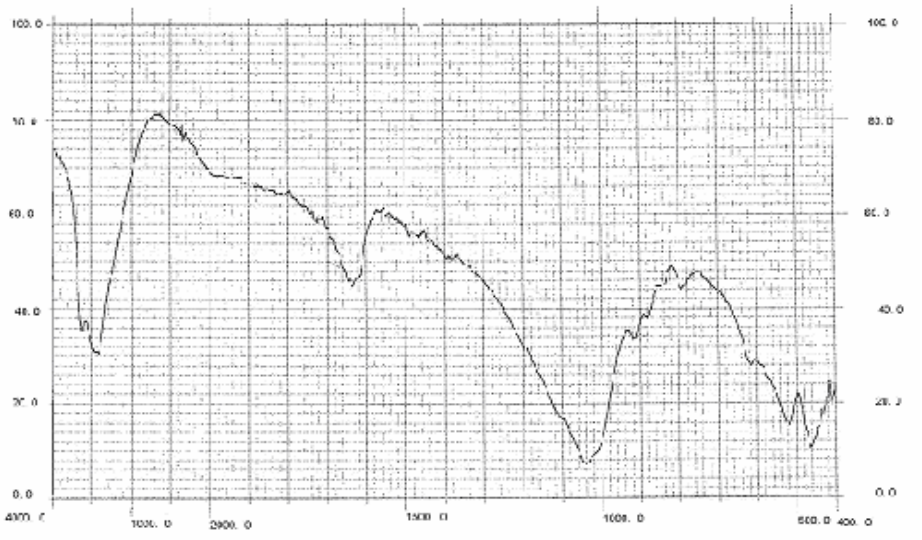

Figure 4.12 IR Spectra of Sample 2.

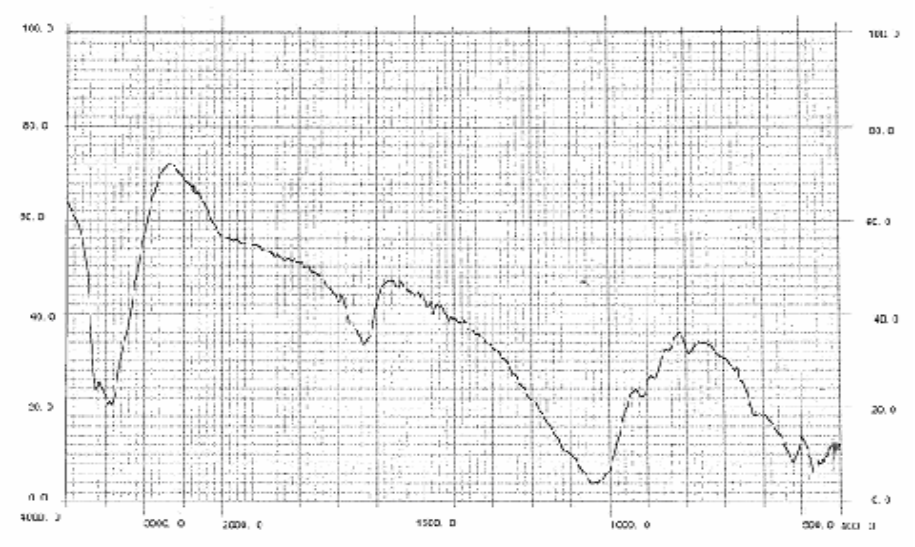

Figure 4.13 IR Spectra of Sample 3.

From the Figure 4.11, 4.12 and 4.13 which present the different characteristic bands, for the Al-pillared adsorbents Al^{3+}/clay=1.8, confirm that all the samples differ little or more as the structural mean. The bending at 3630 cm^{-1} ,3450 cm^{-1} and also 1640 cm^{-1} is much more dominant in height and the smallest in width at Sample 1. From this point, it is observed that the height of the band decreases when the Al^{3+}/clay =1.8 is constant and OH^{-}/Al^{3+} increases. However, the width of the band increases when the Al^{3+}/clay =1.8 is constant and OH^{-}/Al^{3+} increases. Adsorption bands are not differs so much for these samples in the case of the Al^{3+}/clay=1.8 when OH^{-}/Al^{3+}. The characteristics are so similar maybe only the intensity, width and height are different and these difference can be seen in the figures.

There is bending at 1040-1060 cm^{-1}. The adsorption band in the mentioned wavelenght indicates the Si-O stretcing and differs from the crude bentonite structure. There is an intensity decrease occur for Sample 1,2,3. This part is related to the crystal structure of the synthesised adsorbent. The differences observed in this band indicates that the structure takes the Keggin ion, so this proves that the Keggin ion joins the structure. Also the slope of the band increases when the OH^{-}/Al^{3+} ratios icreases. The height of the mentioned band is highest in the Sample 1. Another difference is around 600-400 cm^{-1}.

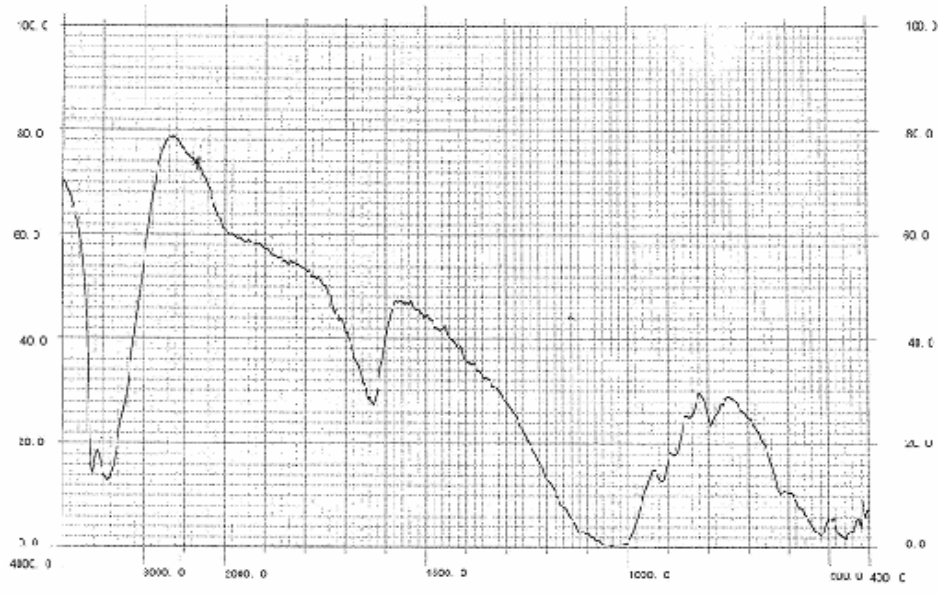

Figure 4.14 IR Spectra of Sample 4.

If a comparison is done between Sample 1 and Sample 4, it is concluded that the bending at 3630 cm^{-1}, 3450 cm^{-1} and 1640 cm^{-1} is higher than sample 4 but sample 4 has higher in width than sample 1. On the other hand, the band at 1040-1060 cm^{-1} is nearly zero absorbance in sample 4 and the width of the absorbance of this band is higher than sample 1. These observations show that the different structure of adsorbents are formed also when the OH^-/Al^{3+} is constant and Al^{3+}/clay increases.

4.2.3 SEM Analyses

SEM images of the crude, HDTMA and Al-pillared bentonite are given in the Figure below.

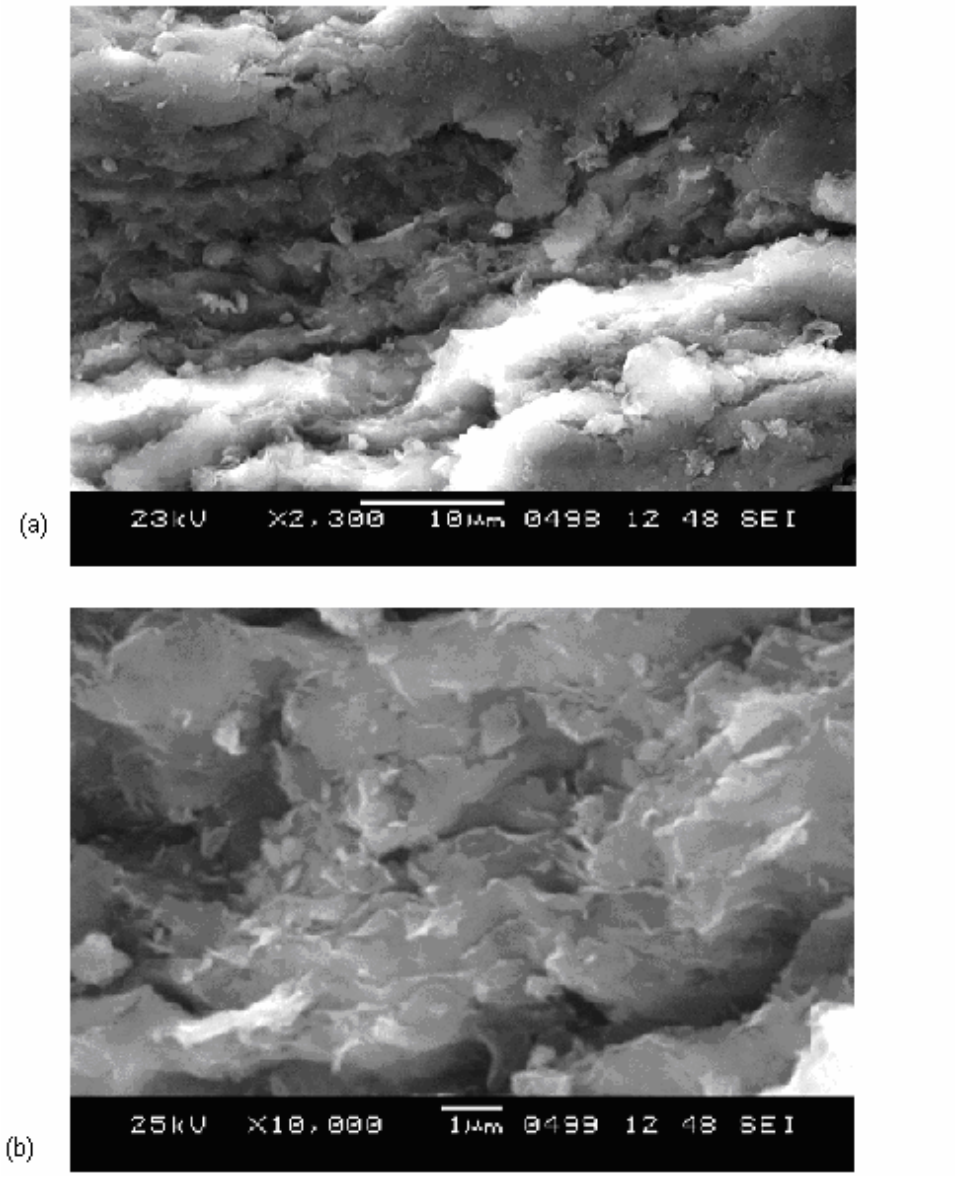

Figure 4. 15 SEM Images of crude bentonite (a) X 2.300 (b) X 10.000.

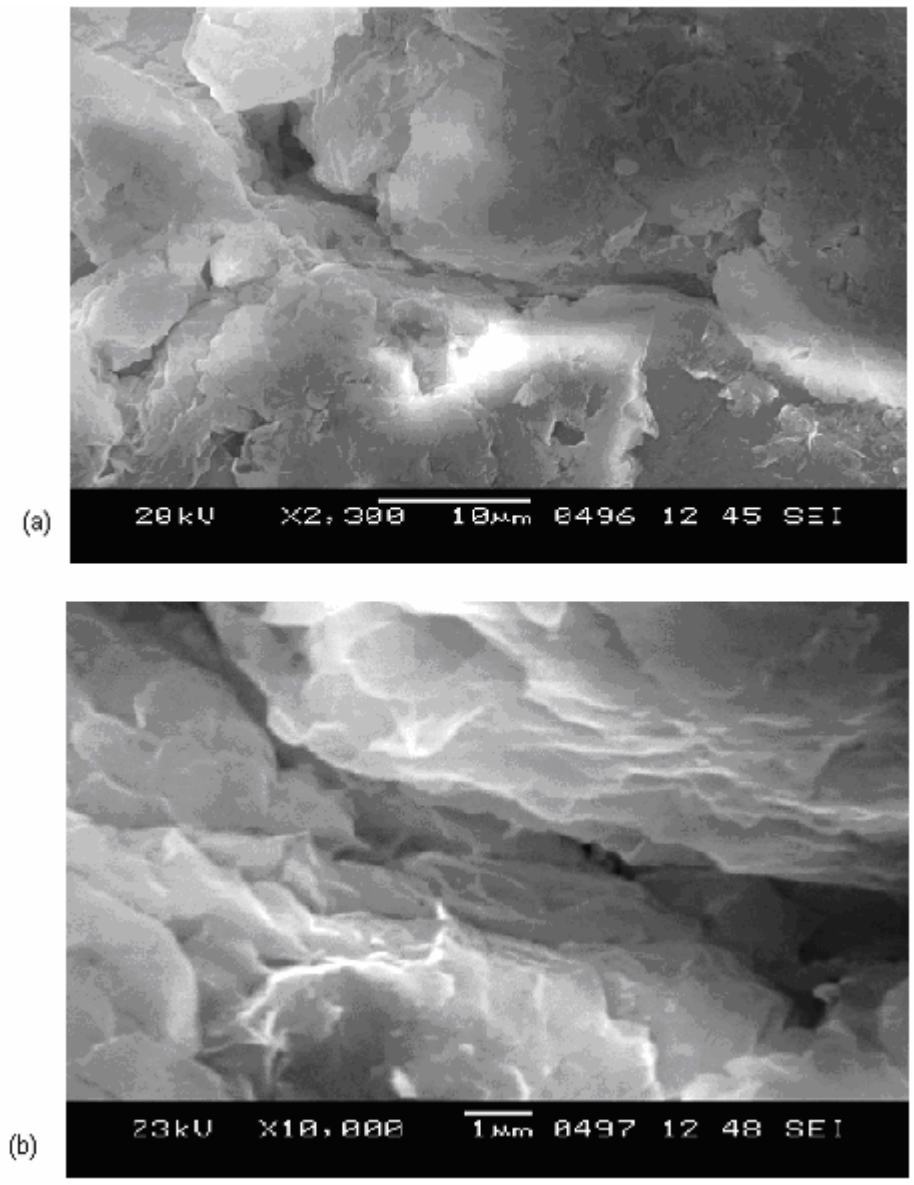

Figure 4. 16 SEM Images of HDTMA- bentonite (a) X 2.300 (b) X 10.000.

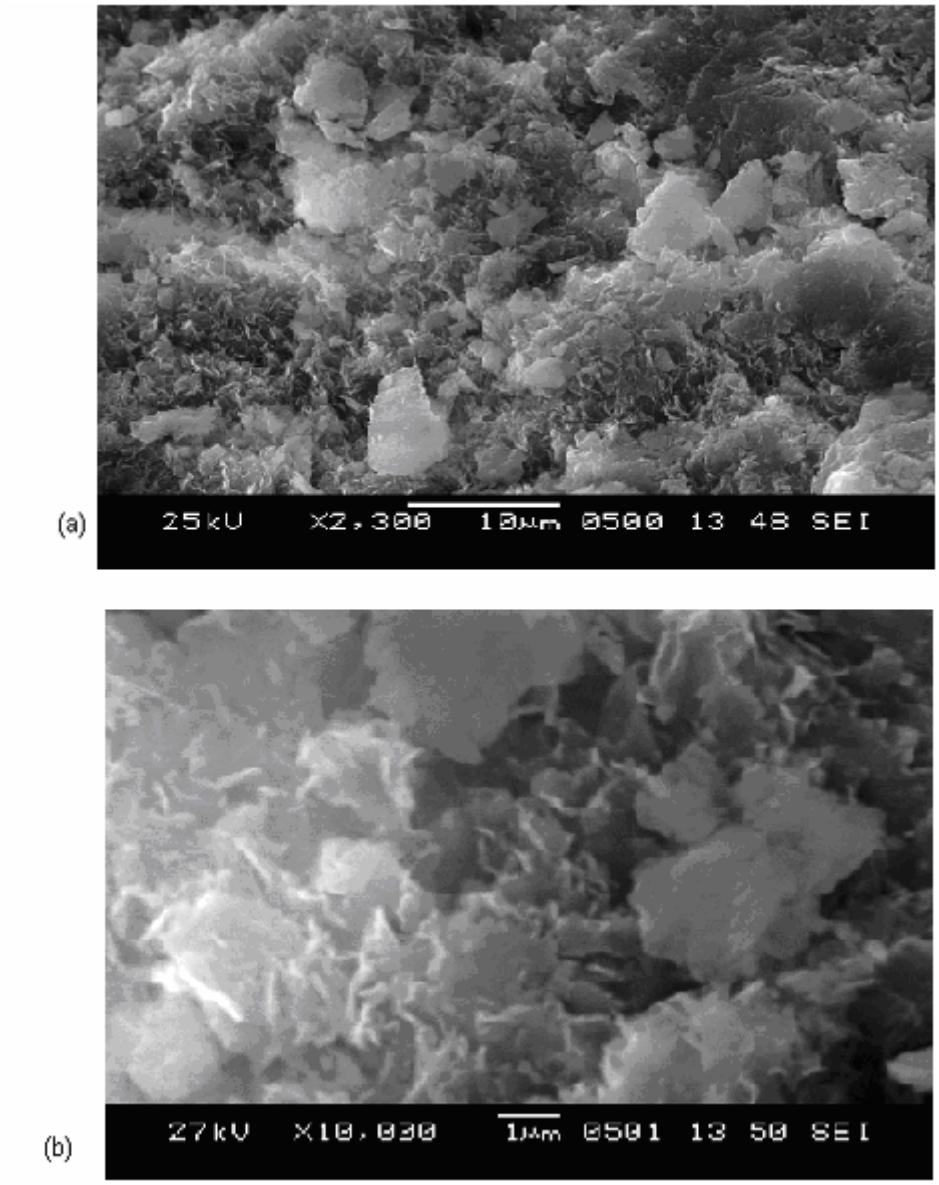

Figure 4. 17 SEM Images of Al-pillared bentonite (a) X 2.300 (b) X 10.000.

From the images, it can be seen that the crude bentonite has homogeneous structure and it is seemed as the leaf and this leaf-like structure has curly margins.

In the case of HDTMA-bentonite, a curved homogeneous structure is formed with the small spaces between the individual particles. The leaf like structure with curly margins is also observed on the surfaces of these curved structures. Al-pillared bentonite has a sponge like appearance with smaller size of the particles. Leaf like structure is completely disappeared and more porous structure is formed. Although the individual mineral has curly margins, a discontinuity suggesting the breakdown of the leaf like structure is formed. In addition to the formation of the micropores, the breakdown of the leaf like continuous structure causes an additional increase in surface area. According to the investigations which are reported by Danis et al., 1998 and Zielke and Pinnava, 1988 the adsorption of the phenolic compounds depends on the pore structure and surface composition of the adsorbent. Therefore, the observed structural changes will positively affect the adsorbed amounts.

4.2.4 Adsorption Behaviour

In Figure 4.18, it is shown that the change in adsorbed amounts with time. The time required to reach the plateau increases with decreasing

OH^-/Al^{3+} and Al^{3+}/clay ratios and the equilibrium is established within 24h.

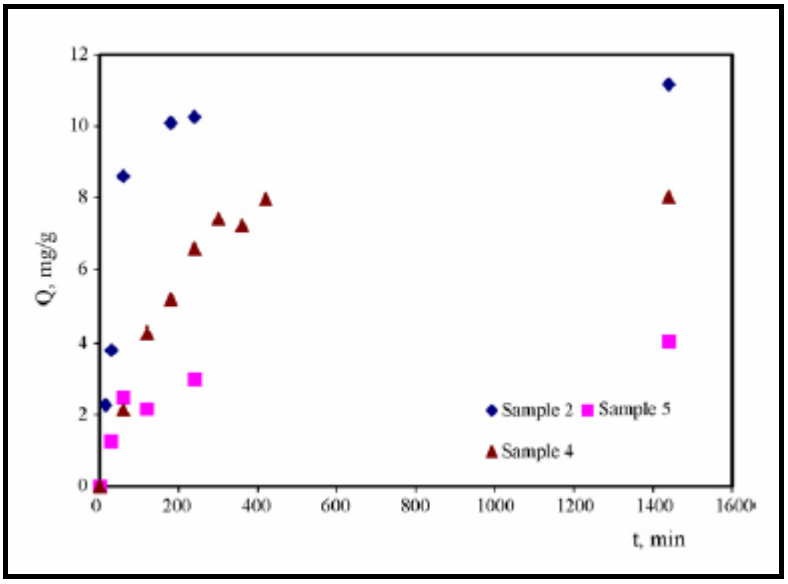

Figure 4. 18 The change in adsorbed amounts with the time.

Adsorbed amounts increase when OH^-/Al^{3+} ratio decreases. From the graph, it is shown that the Sample 2 adsorbs the greater amounts than Sample 4 and Sample 5.

In the Figure 4.19, adsorption isotherms of crude bentonite, HDTMA- bentonite and Sample 1 are shown. Sample 1 has the maximum phenol removal capacity between the other pillared adsorbents. As seen from the Figure 4.19, the adsorbed amounts of the pillared bentonites is much more higher than the crude and HDTMA bentonite.

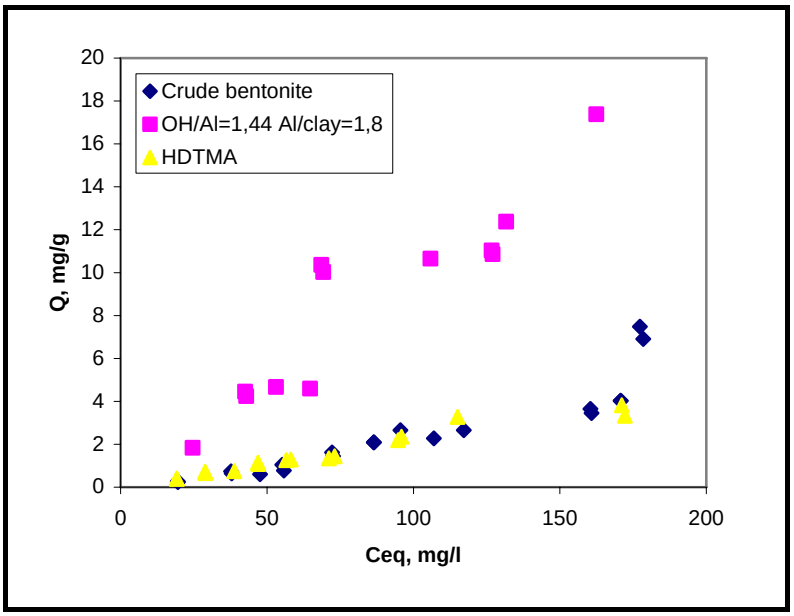

Figure 4. 19 Adsorption isotherms of crude bentonite, Sample 1 and HDTMA .

Based on the Al^{3+}/clay ratios, the results of isotherm studies are divided in two groups and all these groups are presented in Figure 4.20. Except Al^{3+}/clay ratios, the shape of the isotherms placing in two groups is quite different. In the first group isotherms(Al^{3+}/clay=1.8), there is a region at which the adsorbed amount increases very slowly and the two regions at which the adsorbed amount increases very rapid. The rate of increase is approximately same at these two regions placing at the beginning and end of the isotherms. Although a continuous increase is observed in the second group isotherms, the increase in adsorbed amounts is very slow at he beginning and then a relatively sharp increase is observed.

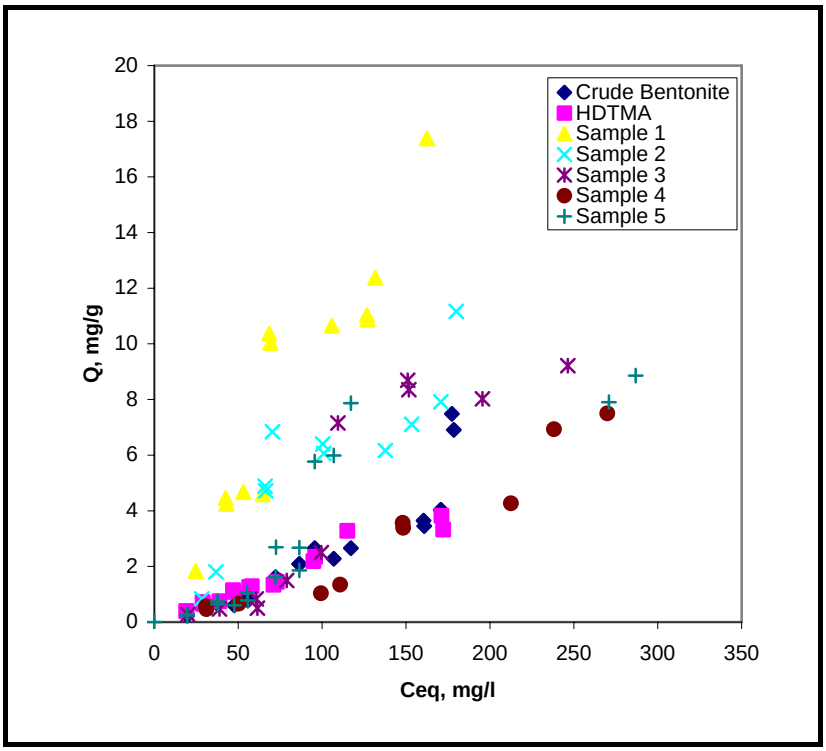

Figure 4. 20 Adsorption isotherms of crude, HDTMA bentonites and Sample 1,2,3,4,5.

The adsorbed amounts decrease with increasing OH^-/Al^{3+} ratio and the difference at the concentrations exceeding 60 mg/L becomes significant for both cases. In addition of this information, also the shape of the isotherms depend on the OH^-/Al^{3+} and Al^{3+}/clay ratios used. In contrary of this observation, the difference between adsorbed amounts is always considerable in the case of increasing Al^{3+}/clay ratios for the same OH^-/Al^{3+} ratio and the decrease in adsorbed amounts has also higher order of magnitude. When it is assumed that all the aluminum cations was in the form of polyoxyhydoxy aluminum catios, the Al^{3+}/clay ratios (1.8 and 2.5) correspond to 3 and 43% stoichiometric excess amounts. From the

Table 3.4 in the Part 3.2.1, it is shown that the amount of aluminum used in the preparation of pillaring solution decreases with increasing OH^-/Al^{3+} ratios for the same Al^{3+}/clay ratios. The decrease in the amount of Al^{3+} causes a decrease in the number of polyoxyhydoxy aluminum cations and also an increase in the number of free Al^{3+} species. Al^{3+} is called as the limiting reactant in the reaction due to the reaction stoichiometry. During the pillaring reaction, the adsorption of other Al species is also possible (Schoonheydt et al.,1993) due to it is actually an ion exchange process and the more active sites on the surface is being occupied and hence the microporosity will probably increase in the case of high excess amounts. As mentioned in Part 4.2.1, XRD analyses suggest the partial delamination and it is observed that samples 4 and 5 have a relatively high degree of delamination due to the XRD analyses. All these clues show the formation of different structure. Different structure of adsorbents causes the different sorbate-surface interactions and therefore different mechanism of adsorption. This idea can be supported by the adsorption isotherm figures. Surface structure similarities of the crude and Al-pillared bentonites show the similar adsorption mechanisms. Phenol is adsorbed on crude bentonite by two mechanisms. These are: the hydrogen bonding between oxygen atoms of silicate layer and hydoxyl groups of phenol and election donor-acceptor mechanism taking place between the basic surface oxygens and aromatic ring of phenol molecule (Banat et al, 2000). The other Al species and also the intercalated polyoxyhydoxy aluminum cations is important parameters for adsorption mechanisms.

Table 4.2. % phenol removal values of the each species.

	% phenol removal
Organo bentonite	**4.5**
OH/Al=1.44 Al/Clay=1.8	**16**
OH/Al=2.00 Al/Clay=1.8	**7.5**
OH/Al=2.5 Al/Clay=1.8	**3.5**
OH/Al=1.44 Al/Clay=2.5	**2.5**
OH/Al=2.00 Al/Clay=2.5	**1.5**

From the Table 4.2, % phenol removal of the crude, HDTMA and pillared bentonites are shown. Phenol removal capacity decreases, as the OH^-/Al^{3+} and also Al^{3+}/clay increases. Percentage of phenol removal for the organo bentonite is 4,5 and this amount increases with the applying of the crude bentonite to pillaring untill the OH^-/Al^{3+} is reached 2.0, and also phenol removal is maximum at the Sample 1. In other words, phenol removal amount increases about four times when the crude bentonite applying the pillaring process as the OH^-/Al^{3+}=1.44 Al^{3+}/clay=1.8.

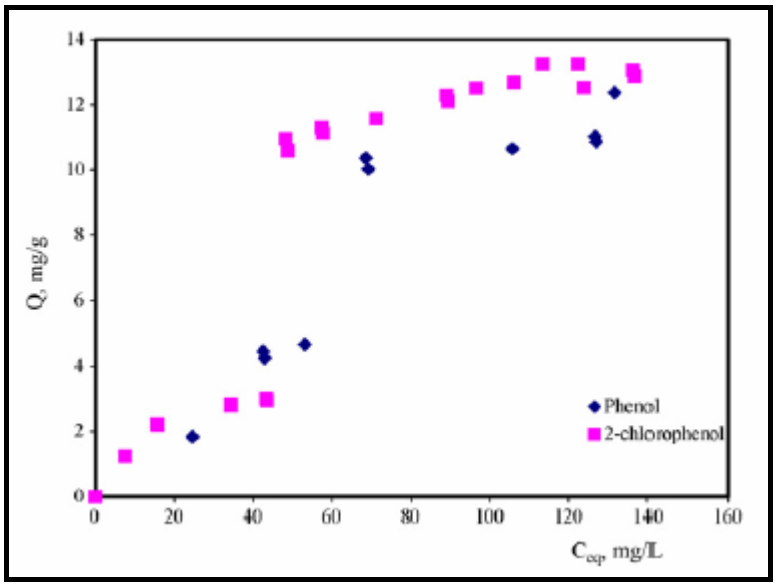

Figure 4. 21 Adsorption isotherms of 2-chlorophenol and phenol on Sample 1.

From now on, it is summerised the adsorption amounts and isotherms of the synthesised Al-pillared clays. At the light of these informations, the maximum adsorbed amount observed in Sample 1. Since the highest phenol removal capacity is obtained from Sample 1, is studied that the 2-chlorophenol adsorption on this adsorbent. From Figure 4.21, it is shown that the adsorption amounts are very close each other for both adsorbates to the equilibrium concentration of 60 mg/l and higher than this concentration levels, there is a small difference occurs.

5.0 CONCLUSIONS

A time consumer but efficient preparation of Al-pillared clays shows that it is possible to prepare pillared clays from concentrated clay suspensions with high adsorption capacity.

In this study, modifying the adsorbent surface with different OH^-/Al^{3+} and Al^{3+}/clay ratios, effect of this changes to the clay structure and phenol adsorption capacity of adsorbent are investigated.

pH control is very sensitive point because of the chemical characterisation of phenol. In addition of this information, also during the pillaring reaction controlling temperature, time and rate of addition is very important parameters because these parameters affect the adsorbent structure and define the adsorbent characteristics.

The basal spacing values are greater than crude bentonite and also increases when OH^-/Al^{3+} and Al^{3+}/clay changes. This value is maximum in the Sample 2 with the 8.56Å increase in basal spacing before delamination occurs. The structural changes occuring as a result of the use of different ratios cause different adsorption mechanisms. Beside the OH^-/Al^{3+} ratio, the amount of the aluminum used in the preparation of the pillaring solution is a parameter affecting the adsorption capacity of adsorbent.

IR spectra of the crude bentonite and the pilared clays prove the coverage of surface by Al molecules since the bends corresponding to these molecules could be observed.

From SEM analysis of the crude and pillared bentonite differences and modification effects could be easily seen. Crude bentonite has homogeneous structure and it is seemed as the leaf and this leaf-like structure has curly margins. In the case of Al-pillared bentonite, it has a sponge like appearance with smaller size of the particles. Leaf like structure is completely disappeared and more porous structure is formed.

Equilibrium is reached at least 24 hours of adsorption. Based on the Al^{3+}/clay ratios, the results of isotherm studies are divided in two groups. For two of this groups, the time required to reach the plateau increases with decreasing OH^-/Al^{3+} and Al^{3+}/clay ratios. Adsorbed amounts increase when OH^-/Al^{3+} ratio decreases. Maximum adsorption is observed in Sample 1. This sample of Al-pillared bentonite has the high adsorption capacity and different shape of the isotherm than HDTMA modified bentonite.

As a result of this study, it has been found that the bentonite modified with OH^-/Al^{3+}=1.44 and Al^{3+}/clay=1.8 has the maximum phenol adsorption capacity, at about 16% phenol removal capacity, and is applicable in removing phenol and its derivatives from aqueous phase.

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CIRRICULUM VITAE

Mujde ALTUNLU was born in Hatay, Antakya in September 21, 1981. She is a citizien of Turkish Republic. She graduated from the Department of Chemical Enginerring of Gazi University in 2004. She started her career in DYO Printing Ink Inc., which is the member of Yasar Holding, in March 21, 2005 as R&D Engineer. She is still working for this ink manufacturing company at the same position.