ADSORPTION OF SOME HERBICIDES ONTO ORGANO-CLAYS FROM AQUEOUS SOLUTION

by

Yoldaş SEKİ

December, 2002
İZMİR

ADSORPTION OF SOME HERBICIDES ONTO ORGANO-CLAYS FROM AQUEOUS SOLUTION

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We certify that we have read the thesis, entitled **"ADSORPTION OF SOME HERBICIDES ONTO ORGANO-CLAYS FROM AQUEOUS SOLUTION"** completed by **Yoldaş SEKİ** under supervision of **Prof. Dr. Kadir YURDAKOÇ** and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Clay samples were compared with modified clay samples for the sorption of 1,1'-dimethyl – 4, 4' bipyridillium dichloride (paraquat, cationic herbicide) from water by measuring the adsorption isotherms and fitting the data to Langmuir and Freundlich equation. Bentonite, illite and sepiolite were chosen as clay samples and DB, NB, DI, NI, DS and NS as organo-clays. Specific surface area, pore size distribution and monolayer volume values of the samples were determined at 77 K with B.E.T method showing a decrease in the order of natural samples dodecylammonium and nonylammonium clays respectively. X-Ray powder diffraction analysis of the samples and the effects of modifying agents on the layer structure of clays were also investigated. After modification, an increase in d_{001} values was observed except sepiolite. Organic matter contents of modified samples were determined as the percentage of H, C, N. C_m (adsorption capacity) ranged from 0.382 mmol/g for DS up to 2.229 mmol/g for NI. $Kd_{0,3}$ (distribution coefficient) values increase from 0.177 for DS up to 0.843 for NI. The organic carbon partition coefficients (K_{oc}) and K_f values were also calculated and the highest values were found for NI. The batch experiment indicates that illite and nonylammonium illite (NI) are the most effective adsorbents among the clay samples and modified clay samples respectively. Although paraquat herbicide is a cationic herbicide, modification of illite and bentonite with nonylammonium ion increased the adsorption capacities of the samples in the order being DS < S < NS < DB < B < DI < NB < I < NI. In this study, it was proved that paraquat can be removed from aqueous solution by using organo-modified clays especially nonylammonium illite and bentonite instead of natural clays. Nonylammonium illite can also be used as an effective oral adsorbent in the case of paraquat poisoning.

Keywords : paraquat, adsorption, clay, organo-clay, removal

ÖZET

Paraquat herbisitinin sudan uzaklaştırılaması için, kil örnekleri ile modifiye kil örneklerinin sulu çözeltiden adsorpsiyon isothermleri, ölçülmüş sonuçlar, Langmuir ve Freundlich denklemlerine uygunlukları açısından karşılaştırılmıştır. Bentonit, illit, sepiyolit doğal kil örnekler olarak seçilen, DB, NB, DI, NI, DS, NS ise organo-kil örnekleri olarak değerlendirilmiştir. Örneklerin özgül yüzey alanları ve gözenek boyut dağılımları 77 K'de N_2 gazı adsorpsiyonu ve desorpsiyon izotermlerinden hesaplanmıştır. Veriler değerlendirildiğinde genel olarak doğal killer, nonil modifiyeli killer ve dodesil modifiyeli killer sırasında bir azalma belirlenmiştir. Tüm örneklerin X ışını toz kırınımı analizleri (XRD) yaptırılarak modifiye ajanların kilin tabakalı yapasına olan etkisi incelenmiştir. Modifikasyondan sonra d_{001} değerlerinde sepiyolit hariç bir artış gözlenmiştir. Örneklerin, organik madde içerikleri element analiz cihazıyla incelenerek %H, %C ve %N değerleri bulunmuştur. Adsorpsiyon kapasiteleri (C_m) DS için olan 0,382 mmol/g aralığı ile NI için olan 2,229 mmol/g aralığı arasında değişmektedir. Dağılma katsayıları ($Kd_{0,3}$) DS değeri olan 0,177 den 0,843 olan NI değerine kadar artmaktadır. Koc ve K_f değerleri hesaplanmış ve NI için en yüksek değerler bulunmuştur. Yapılan deneyler sonucunda kil örnekleri içerisinde illite organo-killer arasında da NI en etkili adsorplayıcı olarak belirlenmiştir. Paraquat katyonik bir herbisit olmasına karşın doğal örnekleri nonil amonyum iyonu ile modifiye etmek adsorpsiyon kapasitesini arttırmıştır. Sıralama da şu şekilde verilebilir. DS < S < NS < DB < B < DI < NB < I < NI. Bu çalışmayla suya kontamine olmuş paraquat herbisitini çözeltiden uzaklaştırmak için killerin yerine nonil amonyum klorür ile modifiye edilmiş killerin, daha etkili bir adsorplayıcı olarak kullanılabileceği gösterilmiştir. Ayrıca NI'in paraquat zehirlenmelerinde etkili bir oral adsorplayıcı olarak kullanılabileceği sonucuna varılmıştır.

Anahtar sözcükler : paraquat, adsorpsiyon, kil, organo-kil

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Chapter 1

INTRODUCTION

1. The Adsorption – Desorption Process

1.1 Introduction to Molecular Adsorption

The adsorption of molecules on to a surface is a necessary prerequisite to any surface mediated chemical process. For example, in the case of a surface catalysed reaction it is possible to break down the whole continuously-cycling process into the following five basic steps:

1. Diffusion of reactants to the active surface
2. Adsorption of one or more reactants onto the surface
3. Surface reaction
4. Desorption of products from the surface
5. Diffusion of products away from the surface

The above scheme not only emphasises the importance of the adsorption process but also its reverse - namely desorption. It is these two processes which are considered in this Section.

1.1.1. Some Notes on Terminology:

Substrate is frequently used to describe the solid surface onto which adsorption can occur; the substrate is also occasionally referred to as the adsorbent.

Adsorbate is the general term for the atomic or molecular species which are adsorbed (or are capable of being adsorbed) onto the substrate.

Adsorbent is a material that can adsorb a chemical or contaminant out of solution

Adsorption is the process in which a molecule becomes adsorbed onto a surface of another phase (note: to be distinguished from absorption that is used when describing uptake into the bulk of a solid or liquid phase)

Coverage is a measure of the extent of adsorption of a species onto a surface. Usually denoted by the lower case Greek "theta", q

Exposure is a measure of the amount of gas which as surface has seen; more specifically, it is the product of the pressure and time of exposure (normal unit is the Langmuir, where 1 L = 10^{-6} Torr s).

1.1.2. How do Molecules Bond to Surfaces?

There are two principal modes of adsorption of molecules on surfaces:

1- Physical Adsorption (Physisorption)
2- Chemical Adsorption (Chemisorption)

Physical Adsorption: the only bonding is by weak van der Waals - type forces. There is no significant redistribution of electron density in either the molecule or at the substrate surface.

Chemical Adsorption: a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character. In Table 1 typical characteristics of adsorption processes are shown.

Table 1.1 Typical Characteristics of Adsorption Process

Properties	**Chemisorption**	**Physisorption**
Temperature Range (over which adsorption occurs)	Virtually unlimited (but a given molecule may effectively adsorb only over a small range)	Near or below the condensation point of the gas (e.g. Xe < 100 K, CO_2 < 200 K)
Adsorption Enthalpy	Wide range (related to the chemical bond strength) – typically 40 - 800 kJ mol^{-1}	Related to factors like molecular mass and polarity but typically 5-40 kJ mol^{-1} (i.e. ~ heat of liquefaction)
Crystallographic Specificity (variation between different surface planes of the same crystal)	Marked variation between crystal planes	Virtually independent of surface atomic geometry
Nature of Adsorption	Often dissociative may be irreversible	Non-dissociative Reversible
Saturation Uptake	Limited to one monolayer	Multilayer uptake possible
Kinetics of Adsorption	Very variable - often an activated process	Fast - since it is a non-activated process

The most definitive method for establishing the formation of a chemical bond between the adsorbing molecule and the substrate (i.e. chemisorption) is to use an appropriate spectroscopic technique IR to observe the vibration frequency of the substrate/adsorbate bond.

1.1.3. Adsorption Isotherms

Adsorption isotherms describe the equilibrium conditions for an adsorbate (that which is adsorbing) onto the surface of an adsorbent. Usually the amount of material adsorbed is some complex function of the concentration of the adsorbate. Many theories and models have been developed to describe different types of isotherms. Some of them are Langmuir isotherm, Freundlich isotherm, B.E.T. isotherm...

1.1.3.1. Langmuir Isotherm

One of the simplest and most widely used isotherms is the Langmuir isotherm that was originally derived from adsorption kinetics by equating the rates of adsorption and desorption onto a flat surface.

The Langmuir equation is based on the following assumptions:

1- Adsorption of adsorbate molecules takes place at well-defined adsorption sites and each site can contain only one molecule.

2- The surface is homogeneous; the energy of adsorption is equal for all adsorption sites.

Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid.

As with all chemical equilibria, the position of equilibrium will depend upon a number of factors:

1. The relative stability of the adsorbed and gas phase species involved
2. The temperature of the system (both the gas and surface)
3. The pressure of the gas above the surface

In general, factor (2) and (3) exert opposite effects on the concentration of adsorbed species. We can say that the surface coverage may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

We may derive the Langmuir isotherm by treating the adsorption process as we would any other equilibrium process - except in this case the equilibrium is between the gas phase molecules (M), together with vacant surface sites, and the species adsorbed on the surface. Thus, for a non-dissociative (molecular) adsorption process we consider the adsorption to be represented by the following chemical equation:

$$S - * + M_{(g)} \rightleftarrows S - M$$

S - *, represents a vacant surface site

In writing this equation we are making an inherent assumption that there are a fixed number of localised surface sites present on the surface.

We may now define an equilibrium constant (K) in terms of the concentrations of "reactants" and "products"

$$\mathbf{K = \frac{[S - M]}{[S - *]\,[M]}}$$

We may also note that:

- [S - M] is proportional to the surface coverage of adsorbed molecules, i.e. proportional to θ
- [S - *] is proportional to the number of vacant sites, i.e. proportional to $(1-\theta)$
- [M] is proportional to the pressure of gas , P

Hence, it is also possible to define another equilibrium constant, b, as given below:

$$\mathbf{b = \frac{\theta}{(1-\theta)\,P}}$$

Rearrangement then gives the following expression for the surface coverage

$$\mathbf{\theta = \frac{bP}{1+bP}}$$

This is the usual form of expressing the Langmuir Isotherm.

As with all chemical reactions, the equilibrium constant, b, is both temperature-dependent and related to the Gibbs free energy and hence to the enthalpy change for the process.

1.1.3.2. Freundlich Isotherm

$$C_{i,s} = K_d C_{i,w}^{\,n}$$

$C_{i,w}$ = concentration of solute in water (mg/L)

$C_{i,s}$ = Concentration of solute in solid material (mg/kg)

This is an empirically derived model, and has limited theoretical foundation; Kd = Distribution constant (L/kg); n = exponential term of water concentration

The linear form of Freundlich equation is;

$$\log (C_{i,s}) = \log K_d + n \log C_{i,w}$$

The mechanism of sorption is mixed between fixed sites and a pseudo-partition process; many layers of fixed sites exist all with different enthalpies no mechanism can be deduced from this relation. The Fruendlich isotherm is an empirical relation.

1.1.3.3. The BET Isotherm

Derivation of the Langmuir isotherm expression was based on the idea of coverage of the surface with single layers of adsorbent. Isotherm curves for adsorption rather than flatten out after initial stage of adsorption suggest a secondary adsorption stage. S. Brunauer, P. H. Emmett, and E. Teller have worked out a description of this process, and expression for the corresponding adsorption isotherm, known as the BET isotherm. (Gordon M. BARROW, 1996)

The adsorption process can be described as adsorbed molecules on the surface sites and attachment of molecules to sites where occupied by adsorbed molecules.

In order to represent x for P/P^0 the expression for the BET isotherm is

$$\frac{V}{V_m} = \frac{c\,x}{(1-x)\,(1-x+cx)}$$

If we take the reciprocal of each side of the equation and multiply both sites by V_m and by $x/(1-x)$, it will be

$$\frac{x}{1-x}\,\frac{1}{V} = \frac{1}{cV_m} + \frac{(c-1)x}{c\,V_m}$$

If we plot left side of the equation against x, it will give a straight line. The values of the intercept on the $x = 0$ axis and that of the slope can be calculated to obtain the V_m and c values.

1.2 The Desorption Process

An adsorbed species present on a surface at low temperatures may remain almost indefinitely in that state. As the temperature of the substrate is increased, however, there will come a point at which the thermal energy of the adsorbed species is such that one of several things may occur:

1. A molecular species may decompose to yield either gas phase products or other surface species.
2. An atomic adsorbate may react with the substrate to yield a specific surface compound, or diffuse into the bulk of the underlying solid.
3. The species may desorb from the surface and return into the gas phase.

The last of these options is the desorption process. In the absence of decomposition the desorbing species will generally be the same as that originally adsorbed but this is not necessarily always the case.

(An example where it is not found in the adsorption of some alkali metals on metallic substrates exhibiting a high work function where, at low coverage, the desorbing species is the alkali metal ion as opposed to the neutral atom. Other examples would include certain isomerisation reactions.)

Chapter 2

CLAYS

2. Introduction to clays

2.1. Description of the clay

Clay has two definitions. According to the clay mineralogist, a clay mineral is a layer silicate mineral (also called a phyllosilicate) or other mineral which imparts plasticity and which hardens upon drying or firing. (Guggenheim and Martin 1995)

The word "clay" is also used to refer to a particle size in a soil or sediment. The term is used in the U.S. and by the International Society of Soil Science for a rock or mineral particle in the soil having a diameter less than 0.002 mm (2 microns), whereas sedimentologists classify particles smaller than 0.004 mm as clay.

In practice, "clay" is used to refer to the fine-grained, mineral fraction of earth material, and can include clay silicates as defined above, oxide-hydroxide minerals, such as goethite, hematite, manganese oxides, and some zeolites.

Clay is used as a rock term and also as a particle – size term in the mechanical analysis of sedimentary rock, soils, etc. As a rock term it is difficult to define precisely, because of the wide variety of materials that have been called clays. In general the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. By plasticity is meant the property of the moistened material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed. Chemical analyses of clays show them to be composed essentially of silica, alumina and water frequently with appreciable quantities of iron, alkali alkaline earths. (Ralph E. Grim, 1968)

In most cases clay finest as a cheap filler have been used in polymer composites including rubbers, plastics, coatings and paints, etc. (Jing Cao Dai et al. 1999)

2.1.1 General Features

2.1.1.1 Classification of Clay Minerals

I. Amorphous

- Allophane group

II. Crystalline

A. Two – layer type (sheet structure composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)

1. Equidimensional

- Kaolinite group
- Kaolinite, nacrite, etc.

2. Elongate

- Halloysite group

B. Three- layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)

1. Expanding lattice

a. Equidimensional

- Montmorillonite group
- Montmorillonite, saucinite, etc.
- Vermiculite

b. Elongate

- Montmorillonite group
- Nontronite, saponite, hectorite

2. Nonexpanding lattice

- Illite group

C. Regular mixed – layer types (ordered stacking of alternate layers of different types)

- Chlorite group

D. Chain structure types (hornblende – like chains of silica tetrahedrons linked together by octahedral groups of oxygen and hydroxyls containing Al and Mg atoms)

- Attapulgite
- Sepiolite
- Palygorskite

2.1.1.2 Structure of the Clay Minerals

Two structural units are involved in the atomic lattice of most of the clay minerals (Ralph & Grim, 1968). The first unit is built of silica tetrahedrons. In tetrahedrons silicon atom is equidistant from four oxygen, or hydroxyl to balance the structure (As shown in Fig 2.1). Silicon atom is at the centre. Silica tetrahedral groups form hexagonal network. Silicon ion shares its charge equally between the four oxygen ions, leaving each oxygen with an excess charge of negative one. We now have the orthosilicate anion, which could at least theoretically be neutralised by four protons (hydrogen ions). This anion tends to react readily with alkali and alkali earth ions. The SiO_4^{4-} anion does have another option open to satisfy the charges

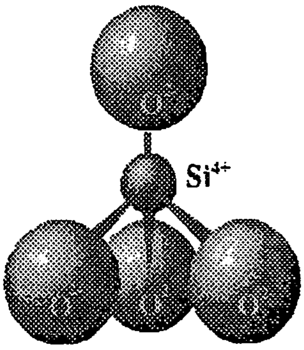


Figure 2.1 Silica tetrahedral units

The second unit is built of two sheets of closely packed oxygens or hydroxyls in which aluminium, iron, or magnesium atoms embedded magnesium, aluminium or iron atoms in octahedral co-ordination. When magnesium is present, all the positions are filled to balance the structure (Ralph, & Grim 1968). When aluminium is present, two- thirds of the suitable positions are filled to balance the structure as shown in Fig 2.2. Within the phyllosilicate mineral structure the aluminium ion is "more comfortable" in an octahedral co-ordination. The aluminium/oxygen radius ratio is 0.41. Aluminium might be said to share +0.5 of its charge with each of the surrounding oxygen ions, leaving each oxygen ion with a negative 1.5 charge.

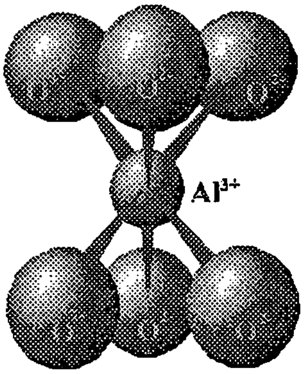


Figure 2.2 Octahedral unit

This excess negative charge on the oxygen ions needs to be balanced and the charge can at least be partially balance if each oxygen ion is bonded with two aluminium ions. Once again, this could theoretically happen by the three face oxygen ions, the two edge oxygen ions, or the single corner oxygen ion bonding with two Al ions. In this case aluminium is slightly less electropositive than is silicon and is able to approach close enough that corner oxygen ions can be shared. In a matrix of these octahedral units each oxygen will be bonded to two aluminium ions, leaving it with a remaining -1 charge. The charge can be satisfied by attaching a proton (hydrogen ion) and when this type of structure is continued in three dimensions we have the mineral Gibbsite. As shown in Fig. 2.3

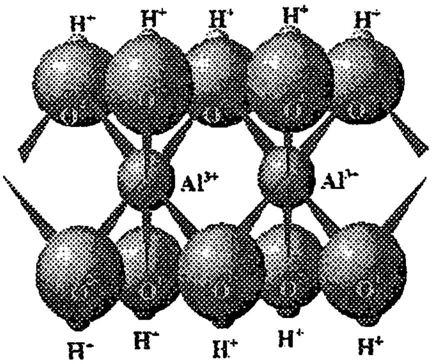


Figure 2.3 Structure of the Gibbsite

We have another option for balancing the remaining -1 charge on the oxygen ions. Remember we left a sheet of silicon tetrahedral units with apical oxygen ions having an unbalanced charge? The two sheets can be brought together with the apical oxygen ions of the tetrahedral layer also being in the octahedral layer. As a result, the charge on these oxygen ions is balanced by bonding to one silicon ion and two aluminium ions. This is the basic structure of our first phyllosilicate mineral, KAOLINITE. As shown in Figure 2.4

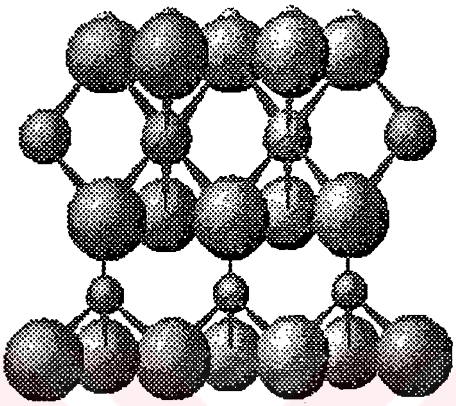


Figure 2.4 Structure of the Kaolinite

We can say that kaolinite which is constructed of a layer of silicon tetrahedral units and a layer of octahedral units is called a 1:1 clay mineral. Thus, kaolinite is a 1:1 nonexpanding clay mineral. Because there is a tendency for hydrogen bonds to form between micelles. While individual hydrogen bonds are very low energy, the bonding energy is additive and the sum of the many hydrogen bonds between micelle results in the micelles being very strongly bonded together and nearly impossible to separate. Thus, we speak of kaolinite as being a nonexpanding.

Now, since we replaced the hydrogen ion on one layer of octahedral oxygen ions by a silicon ion it is only logical that the remainder of the hydrogen ions can be similarly replaced. Indeed, this can be done as shown in Fig 2.5. and another class of clay minerals is thereby introduced. By the same logic as above, we have now formed the basic structure of 2:1 clay minerals. These minerals consist of two silicon tetrahedral layers and one aluminium octahedral layer. For example, Montmorillonite.

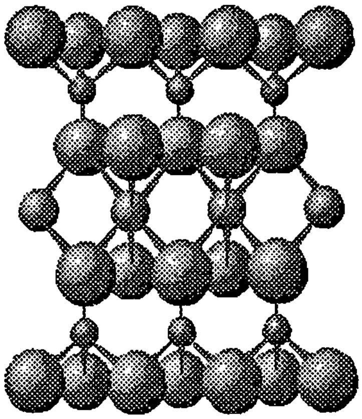


Figure. 2.5 Structure of 2:1 clay minerals

There is one more type of mineral. In certain situations we find that a 2:1 clay mineral has been crystallised in an environment containing an excess of aluminium. Under these conditions an extra aluminium octahedral layer (Gibbsite) will form between the micelles as illustrated at above. This formation is not random, but will be found as a complete layer in each intermicelle space. Minerals having this characteristic constitute what is known as the CHLORITE group. The aluminium (Gibbsite) layer has the effect of binding the micelles tightly, and this group of minerals is also nonexpanding. Those with this view will usually call the chlorites 2:1:1 minerals. Others feel that the gibbsite layer in an integral part of the micelle, and will usually refer to the chlorites as 2:2 minerals.

Bentonite that is also known as montmorillonite derives from deposits of weathered volcanic ash. It often contains substantial amounts of magnesium and a wide variety of rare trace minerals. It is one of the most effective natural intestinal detoxifying agents available and has been recognised as such for centuries by native peoples around the world. Bentonite also selectively adsorbs an interesting variety of organic materials. Once hydrated (combined with water), bentonite has an enormous surface area. A single quart bottle can represent a total surface area of 960 square yards or 12 American football fields. Bentonite is made of a great number of tiny platelets, with negative electrical charges on their flat surfaces and positive charges on their edges. The application areas of bentonites vary depending on the kinds and amounts of its constituents such as smectites (which are the major clay minerals, other clay minerals) and non-clay minerals (Önal et al., 2001 Murray, 1991; Grim et al., 1978). When bentonite absorbs water and swells, it is stretched open like a highly porous sponge; the toxins are drawn into these spaces by electrical attraction and bound fast. Bentonite can absorb pathogenic viruses, aflatoxin (a mold), and pesticides and herbicides including Paraquat and Roundup. The clay is eventually eliminated from the body with the toxins bound to its multiple surfaces.

Montmorillonite are dioctahedral smectites in which isomorphous substitution occurs. Aluminium and sometimes iron substitutes for silicon in the tetrahedral layer and iron or magnesium for aluminium in the octahedral layer (Newman, 1987). As a result of the isomorphous substitutions, crystalline order is reduced and structural imperfections arise (Ray L. Frost et al. 1996)

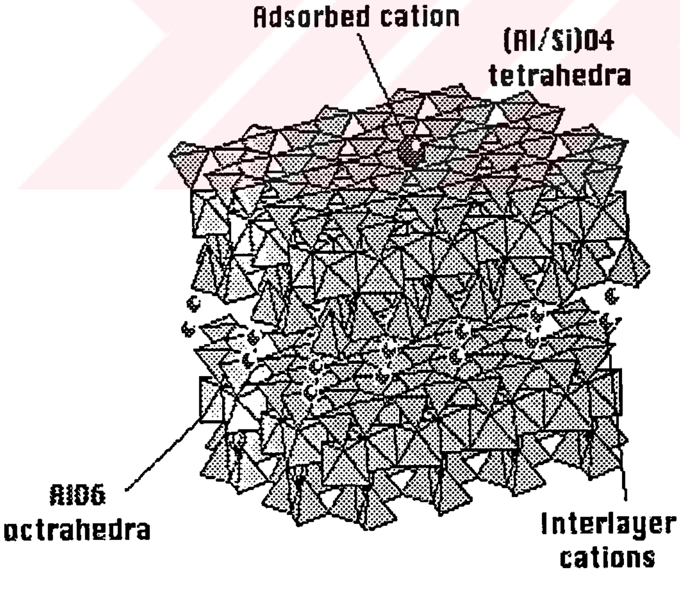


Figure 2.6 The structure of Montmorillonite

2.1.1.3 Formation of Clays

Clays and clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. Most clay minerals form where rocks are in contact with water, air, or steam. Examples of these situations include weathering boulders on a hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water, and rocks in contact with water heated by magma (molten rock). All of these environments may cause the formation of clay minerals from pre-existing minerals. Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits.

2.1.1.4. Ion Exchange with Clays

The exchange reaction is stoichometric and thereby differs from simple sorption. This distinction, however, is sometimes difficult to apply since nearly every ion – exchange processes is accompanied by sorption or desorption (Ralph E. Grim 1968). The heat evolved in the course of an ion exchange reaction is usually rather small, 2± kcal/mole (Helfferick, 1962). Ion exchange that is appropriate for Mass Conservation Law is a reversible. Ion exchange rate is affected ionic diffusion rate, temperature, concentration, and transmittance. Order of capable adsorption for cations is $H^{+}>Al^{+3}>Ba^{+2}>Sr^{+2}>Ca^{+2}>Mg^{+2}>NH^{4+}>Na^{+}>Li^{+}$. Alkylammonium ions and quaternary ammonium ions can be replaced with some other ions which exist on the surface or interlayer. Often, the clay mineral has to be modified by ion exchange with organic cations when used as absorbent for a pesticide (El- Nahhal et al., 1999, Bojomueller, 2000).

2.1.1.5. Cation-exchange Capacity

We can define cation exchange capacity as the total amount of positively charged cations that can exchange. The property of exchange capacity is measured in terms of miliequivalents per gram or more frequently per 100 g. Exchange capacity is determined at neutrality, that is pH 7 (Ralph E. Grim, 1968). Clay and organic matter particles act as giant anions, being covered over their surfaces with net negative charges. Cations are attracts to the surface and exchange takes place. Cation – exchange capacity of some clay minerals is shown in Table 2.1

Table 2.1 CEC values of the some samples

Clay Mineral	CEC (milliequivalents per 100 g, pH =7)
Kaolinite	3-15
Halloysite. $2H_2O$	5-10
Halloysite. $4H_2O$	40-50
Smectite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Sepiolite	3-15

The cationic exchange capacity and the nature of the compensating cation play major roles in the interactions of organics with the solid surface of clays. (Pusino et al., 1995, Draoui et al., 1999). Ion exchange with alkylammonium ions is a well-known method to make clay minerals and clays dispersible in organic solvents and to render the compatible with hydrophobic materials in compounding process (Bergaya & Lagaly et al.,)

2.2. Differential Thermal Analysis

It measures the difference in temperature between a sample and a thermally inert reference as the temperature is raised. The plot of this differential provides information on exothermic and endothermic reactions taking place in the sample. Temperatures for phase transitions, melting points, crystallisation can all be determined by using it. In the case of the clay minerals, differential thermal analyses show characteristic endothermic reactions due to the dehydration and to loss of crystal structure, and exothermic reactions due to the formation of new phases at elevated temperatures (Ralph E. Grim 1968).

2.3. Thermogravimetric Analysis

It measures changes in weight of a sample with increasing temperature. Moisture content and presence of volatile species can be determined with this technique. In this method, the loss in weight of the metarial upon heating to higher and higher temperature is recorded and plotted against the temperature.

2.4. Surface Area Determination

Specific surface area of powders can be determined using nitrogen (alternatively krypton) adsorption. The specific surface area plays an important role in determining soil physical and chemical properties and therefore has a great influence on processes related to soil conversation, fertility and pollution. (İnel & Tümsek, 1999)

2.5. XRD Analysis

XRD data were used to determine 1- whether the clay structure is altered by the organic modification process. 2- the surface thermal stability of the coating and where (outer surface, interlayer or both the organic species are located. (Song & Sandi).

Chapter 3

ORGANO-CLAYS

3. General Properties of Organo-clays

Clay minerals consist of silicate layers in which isomorphous substitution occurs. Aluminium and sometimes iron substitutes for silicon in the tetrahedral layer and iron or magnesium for aluminium in the octahedral layer (Newman, 1987). As a result of the isomorphous substitutions, clays possess a negative charge compensated by inorganic cations such as Ca^{+2}, K^{+}, Na^{+} on their surfaces forming a hydrophilic environment. The interlayer space is available to host polar organic molecules (Mortland, M. M., 1970) or organic cations that may substitute the original inorganic ones (Lagaly, 1994, Lagaly, 1969, Socias & Viciana, 1998) when clay samples modified with organic substances, organo-clays form. There are a lot of processes to modify clay minerals: ion exchange with organic cations, ion exchange with inorganic cations and cationic complexes, adsorption, grafting of organic compounds. (Bergaya & Lagaly, 2001). A range of cationic surfactant mainly primary and quaternary alkylammonium has been used to render different organoclays (Mortland, 1986, Jaynes, 1991, Jaynes, 1991, Hermosin, 1992, Zhang, 1993, Dentel, 1995, Hermosin 1995, Socias- Viciana 1998). As organic cations exchange for metal ions on the mineral surfaces, the metal cations are released into solution. The organic cations may also enter into ion-exchange reactions with exchangeable cations between the layers (Covan & White, 1958, Theng et al., 1967, Theng, 1974, Akçay, 2000). At the end of this process there will be swelling. The degree of interlamellar swelling and the dispersibility are influenced by the migration of interlayer but also octahedral cations (Muller et al.,). The Organo- clay is especially used to remove neutral organic contaminants because of hydrophobic environment. The use of organo-clays provided photoprotection reduced volatilisation, maintaining the herbicidal activity in the soil surface in laboratory and field experiments. Largest adsorption also resulted in optimal reduction of photodecomposition and volatilisation.

3.1 Classification of Organo- clays

Organo- clays have been grouped in two general type organophilic clays and adsorptive (Boyd et al., 1991). This classification is in terms of their sorptive mechanism and sorptive properties. Organophilic clays are synthesised addition of quaternary ammonium cations including large alkyl hydrocarbon R groups. The synthesis results in the formation of paraffin – like organic phase, which is fixed on the mineral surface and interlayer. Such organic phases act as partition media for organic contaminants, with the extent of sorption inversely related to the water solubility of organic contaminants (Zhao, 1998). When small quaternary ammonium cations are used it can be defined adsorptive organo- clays. In these organic organo-clays, the organic cations act as nonhydrated pillars that prop open the clay layers exposing the abundant siloxane surface area. (Zhao, 1998).

Two mechanisms have been offered to reveal the sorption of organic substances in clay – water systems. The first one contains ion- exchange, protonation, hydrogen bonding, coordination/ion dipole reactions with clays. The second mechanism can be described as partition process containing nonpolar interactions between organic matter and neutral organic contaminants. Neutral organic substance sorption increases as clay organic matter content increases. Organo-clays have recently been revealed as good adsorbent for polar pesticides in water (Hermosin and Cornejo, 1992, Bottero et al., 1994, Hermosin et al., 1995, Sanchez Caamzano & Sanchez – Martin, 1994, Vinmond- Laboudigue et al., 1996, Zhao et al., 1996, Pantani et al., 1997, Carrizosa M.J., 2000).

As example one of the procedures of preparation of organo-clays was as follow:

1) Weigh 50 mg of the previously pretreated clay in a series of bottles containing 50 mL distilled water.

2) Put the amount of cationic surfactant from the calculation by the formula given below to replace 100 % of the CEC.

Conc. of Surfactant (g/l) = 0.93 (meq. /g) x Conc. of Clay (g/l) x MW of HDTMA (364.460 (g/mole) x (mole/eq.) x (eq./103meq.)

3) Mix well overnight, centrifuge or let settle to separate the phases, remove the supernatant, and wash the suspension with distilled water to remove any extra surfactants, and then freeze dry.

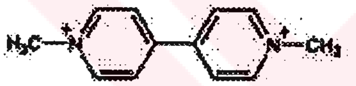
The surface of the clay mineral montmorillonite was modified from hydrophilic to hydrophobic by pre-adsorbing it with organic cations.

Chapter 4

PROPERTIES OF PARAQUAT

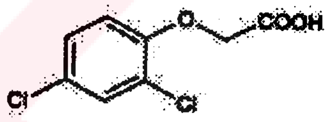
4.1. Paraquat and Some Derivatives

Primary use of Paraquat is as herbicide and here are the molecular structures of paraquat and some derivatives



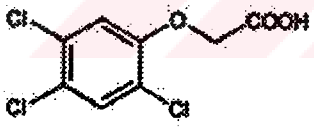
Paraquat

1,1'-Dimethyl-4,4'-bipyridinium



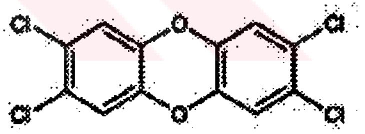
2,4-D

2,4-Dichlorophenoxy acetic acid



2,4,5-T

2,4,5- Trichlorophenoxy acetic acid



TCDD

2,3,6,7-tetrachlorodibenzodioxin

Figure 4.1 The structure of Paraquat and some derivatives

2,4-D is used as herbicide and also to increase latex output of old rubber trees. 2,4,5-T and TCDD are used formerly as herbicide.

4.2. The Properties of Paraquat

Paraquat is widely used in agriculture as a non-selective and useful herbicide (Tinco et al., 1993). Paraquat is a quaternary nitrogen herbicide widely used for broadleaf weed control. It is a quick-acting, nonselective compound that destroys green plant tissue on contact and by translocation within the plant. It has been employed for killing marijuana in the U.S. and in Mexico. It is also used as a crop desiccant and defoliant, and as an aquatic herbicide. Paraquat exerts its herbicidal activity by interfering with intracellular electron transfer system, inhibiting reduction of NADP to NADPH during photosynthesis when superoxide, singlet oxygen, hydroxyl and peroxide radicals are formed in plants (Lewis & Nemery, 1995). This process eventually leads to the destruction of lipid cell membranes by polymerisation of unsaturated lipid compounds (Sandy et al., 1986). The physical properties of paraquat are shown in Table 4.1

Table 4.1 Physical properties of Paraquat

Molecular Formula	$C_{12}H_{14}Cl_2N_2$
Appearance	white powder
Boiling Point	175-180°C(decomposes)
Density (g/ cm^3)	1,25
Water Solubility	High
Stability	In acid and neutral solutions
Volatility	Nonvolatile

The bipyridinium derivative diquat and paraquat are widely used general non selective weed killers. Both are quite toxic for man and warm - blooded animals. Owing to their cationic nature, bipyridinium herbicides are prone to sorption interactions and their displacement from the bonding sites of an organic matrix requires special conditions, mostly achieved by refluxing with strong sulphuric or hydrochloric acid (Tekel & Kovacicova, 1993). Once paraquat enters the soil environment it is rapidly and strongly bound to clay minerals and organic matter and deactivated. (Riley et al., 1976; Ricketts, 1999). In agricultural applications, pesticides, which are often used with surfactants as dispersing or wetting agents, are distributed on plants and soils. (Esumi et al., 1998). These substances are leached through the soil and contaminated to groundwater. Therefore to immobilise it is of great importance for human and animal health. It was reported that herbicides were unlikely to give rise to serious health problems when properly used. (Swan, 1969; Howard, 1980; Nakumuro, 2000). Pesticides and their metabolites have been reported in drinking water, agricultural water and aquatic organisms since 1945 (Martinez et al., 1983; Chiron et al, 1993; Gonzalez- Pradas, 1997). Sorption on solid substrates, such as clay or activated carbon, is one of the methods, which has been used for removing pesticides from water. (Terriere et al., 1966; Grzenda, et al., 1966,Gonzalez- Pradas, 1997).

The specific aims of this study are as below;

1- Investigate the modification of the clays with long chain organic cations to remove divalent herbicide paraquat from water.

2- Understand the adsorption process of paraquat in some natural clay samples and organo- clays by using batch experiment

3- Enhance the adsorption capacities of clays to remove paraquat herbicide from water

4- Find suitable oral adsorbent for paraquat poisoning.

Chapter 5

MATERIAL AND METHOD

5.1 Clays and Herbicide

Bentonite used as adsorbent for this study is from a mining resource of Edirne , containing calcium as exchange ion. Natural sepiolite was purchased from Eskişehir. Illite was supplied by MTA (General Directorate of Mineral Research & Exploration Centre). The cation exchange capacity (CEC) equivalents of illite, bentonite and sepiolite samples determined according to the ammonium acetate saturation method (Akcay, G., & Yurdakoç, M. K., 2000). The properties of the natural clays are summarised in Table 5.1

Table 5.1 The properties of clay samples

Sample	CEC (meg/100g clay)	B.E.T Specific Surface Area (m^2 /g)	d_{001} Å
Bentonite	97	73	7.629
Illite	49	200	10.106
Sepiolite	82	292	12.561

The herbicide paraquat (methylviolegen dichloride or N, N'- dimethyl – gamma, gamma' – bipyridylium dichloride) is a powder (crystalline) solid with a boiling point of 175- 180 ° C (decomposes), density of 1.25 g/cm^3, high water solubility, being stable, incompatible with strong oxidising agents. It is also very toxic by inhalation, ingestion if adsorbed through skin. It was purchased from Aldrich Co. and structural formula is shown in Figure 5.1.

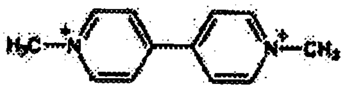


Figure 5.1 Structural Formula of Paraquat

Paraquat was used without further modification or purification. The pretreatment procedure for natural clays was as follow;

The appropriate amount of natural clay weighted mixed with pure water in a beaker. Let stand overnight so that large particles settle. Liquid phase was poured out and clay suspension was filtrated and then dried at 55 ° C for 24 h.

5.2. Organo – clay

First of all, amine salts were prepared by mixing dodecylamine and nonylamine with 0.05 M HCI solution. The reaction is

$R\text{-}NH_2 + HCl \longrightarrow RNH_3^+ Cl^-$

The hydrogen ion concentration was 20 percent in excess of the stoichometric amount for the complete conversion of the amine to the salt form.

The modified clays were prepared from clay samples by addition of dodecylamine and nonylamine salts. They were added as solid greater than mass equivalent to the CEC of the clay. The mixtures were exposed to stirring for 24 h at 25 ° C and then centrifuged to separate the phases. Supernatant was decanted and the remaining clay suspension was washed with ethanol/water (50:50) and pure water until chloride free determined by an $AgNO_3$ test. These modified samples were dried at 50 °C. Dried organo-clay was ground in agate mortars.

The amount of amine salt used in preparation dodecylillite;

CEC of illite = 49 meg / 100 g clay

$$\text{The amount of amine salt per 100g clay} = \frac{\text{1 meg org. cation x (CEC +5) x F.w of salt}}{\text{F.w of org. Cat.}}$$

$$= 186.37\ \text{x}10^{-3}\ \text{x}\ (49+5)\ \text{x}\ \frac{221.82}{186.37}$$

$$= 11.978\ \text{g / 100g clay}$$

For 10 g clay 10 x 11.978 /100 = 1.1978 g / 10 g clay

For Nonylillite;

$144.28\ \text{x}10^{-3}\ \text{x}\ (49+5)\ 179.23/144.28 = 9.678$ g

For 10 g clay 10x 9.678 /100 = 0.9678 g NI

The amounts of amine salt used in this experiment are shown in Table 5.2. The properties of modified clays are summarised in Table 5.3

Table 5.2 The amount of amine salt used in modification process.

Amine Salt	Sepiolite (10g)	İllite (10 g)	Bentonite (10g)
Nonylammonium Chloride	1.5593 g	0.9678 g	1.7923 g
Dodecylammonium chloride	1.9298 g	1.1978 g	2.2182 g

The organic carbon content % OC, % N and % H results were determined with Elementer Analysensysteme GmbH, Institute Für Chemie, (Chemnitz Technical University Germany). The results are given in Table 5.3

Table 5.3 The properties of modified samples

Sample	Saturating Cation	% OC	d_{001} Å	% N	%H
Bentonite	Dodecylammonium	16.825	18.059	1.428	3.298
	Nonylammmonium	6.994	13.689	0.583	1.250
Sepiolite	Dodecylammonium	13.104	12.471	0.941	1.425
	Nonylammmonium	1.899	12.096	0.018	2.958
Illite	Dodecylammonium	6.409	18.392	0.580	2.614
	Nonylammmonium	3.557	14.482	0.400	1.847

5.3. Surface Characterisation of the Samples

5.3.1. Surface Area Measurements

B.E.T method was applied to determine the surface area after N_2 adsorption at 77 K (with Sorptomatic 1990, Chemnitz Technical University, Germany). Samples were subjected to preheating procedure of 2h in vacuum at 130 °C before the N_2 adsorption and then applied N_2 gas adsorption at 77 K. Adsorption and desorption isotherms are shown in Figure 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 5.10 for B, DB, NB, I, DI, NI, S, DS, NS respectively. Pore size distribution data according to the Dollimore- Heal Method. are given in Table 5.4, 5,5, 5.6, 5.7, 5.8, 5.9, 5.10, 5.11, 5.12 for B, DB, NB, I, DI, NI, S, DS, NS respectively. Surface area, monolayer volume of the samples are shown in Table 5.13

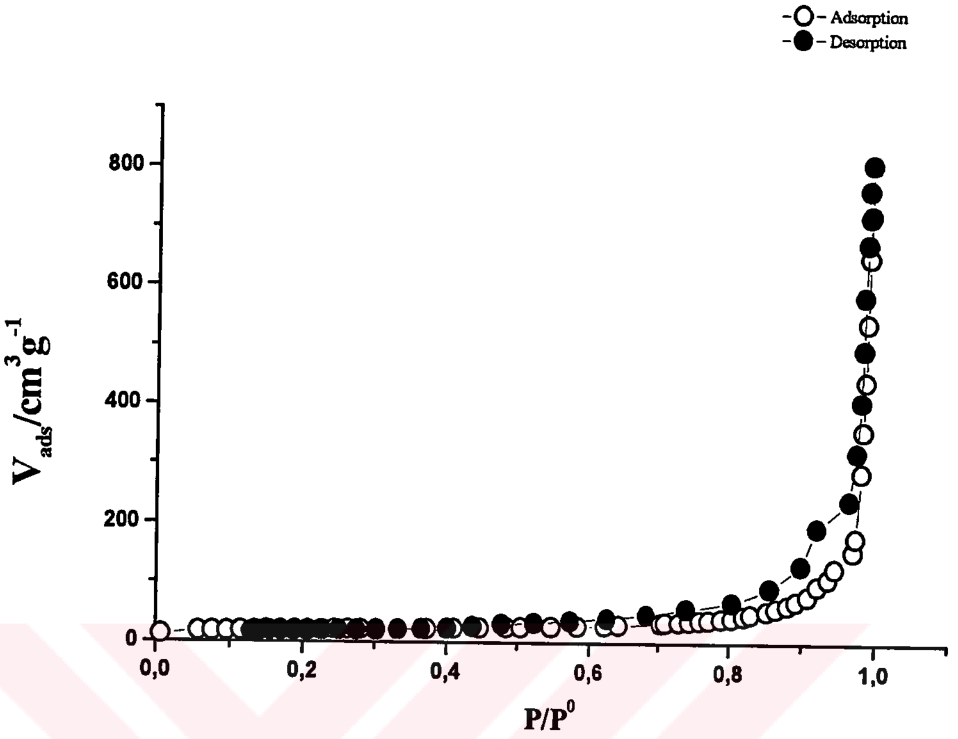


Figure 5.2 Adsorption – Desorption Isotherms for Bentonite

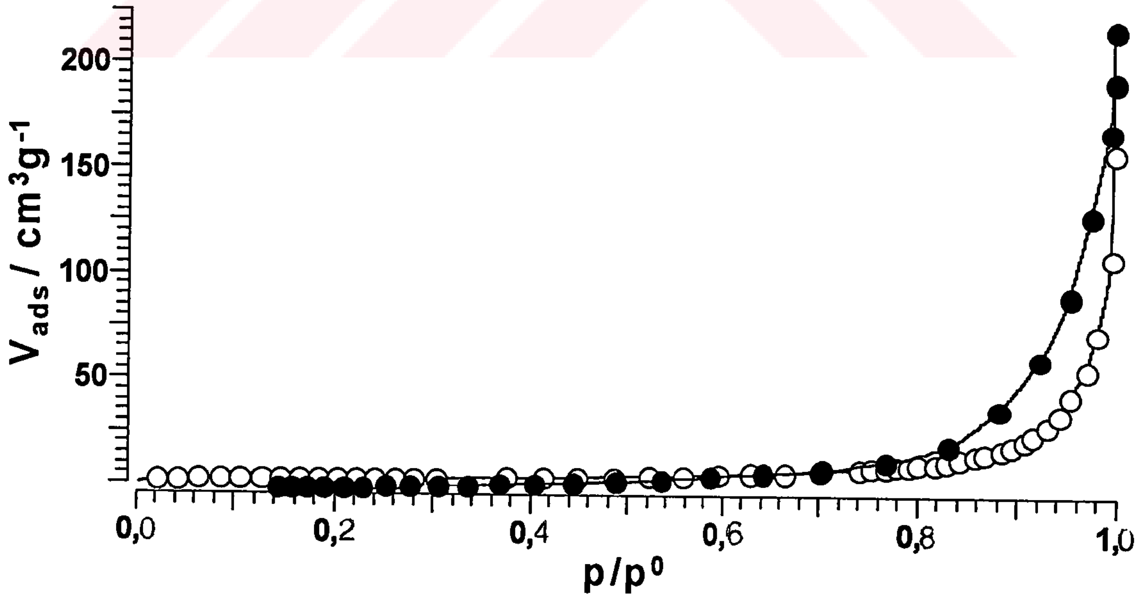


Figure 5.3 N_2 Adsorption – Desorption Isotherms for DB

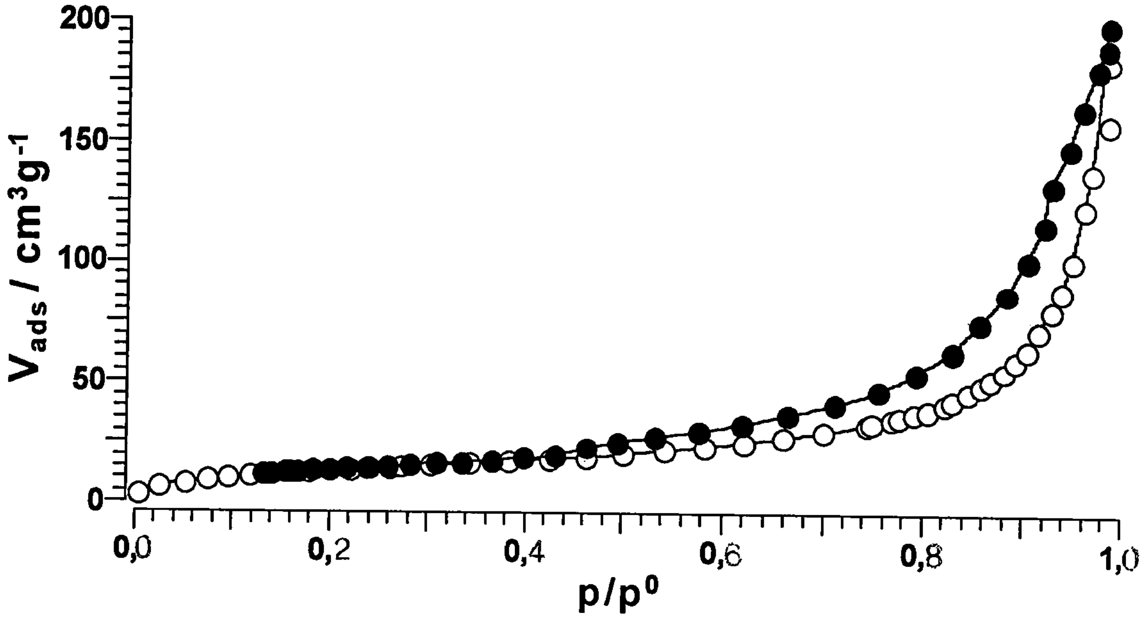


Figure 5.4 N_2 Adsorption – Desorption Isotherms for NB

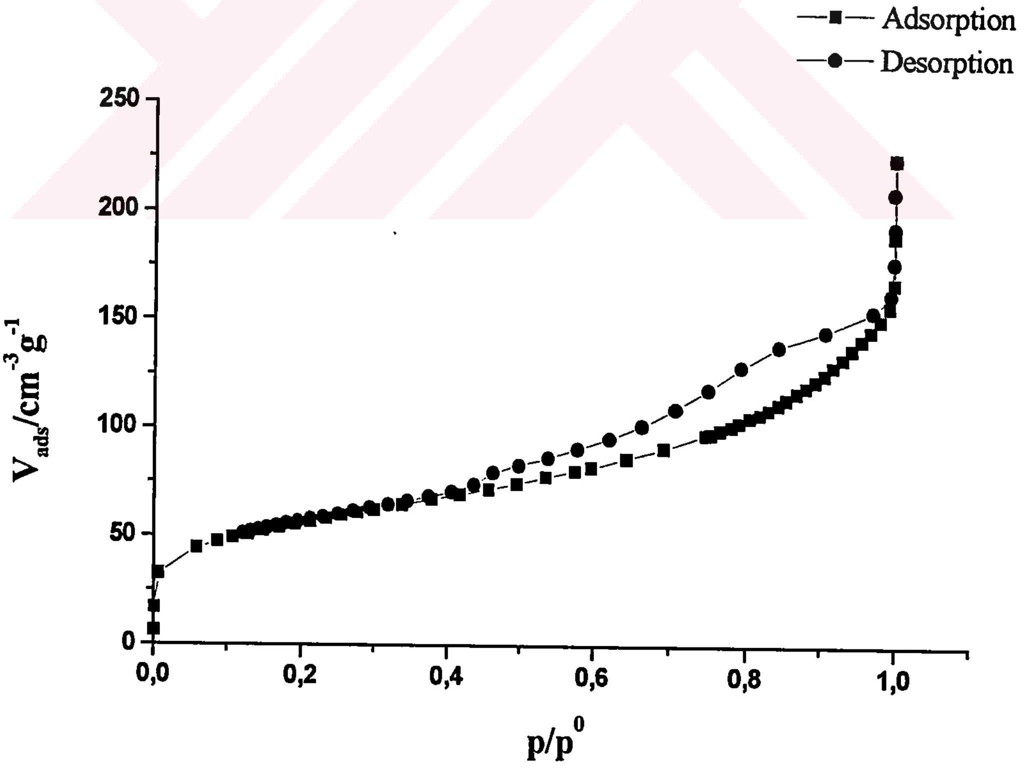


Figure 5.5 N_2 Adsorption – Desorption Isotherms for I

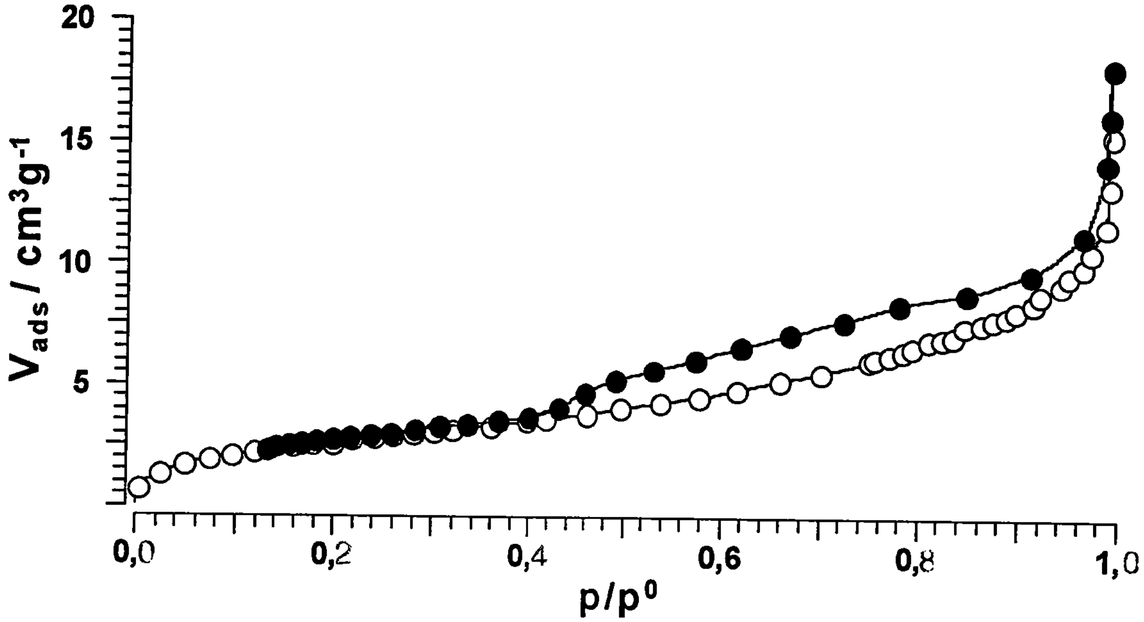


Figure 5.6 N_2 Adsorption – Desorption Isotherms for DI

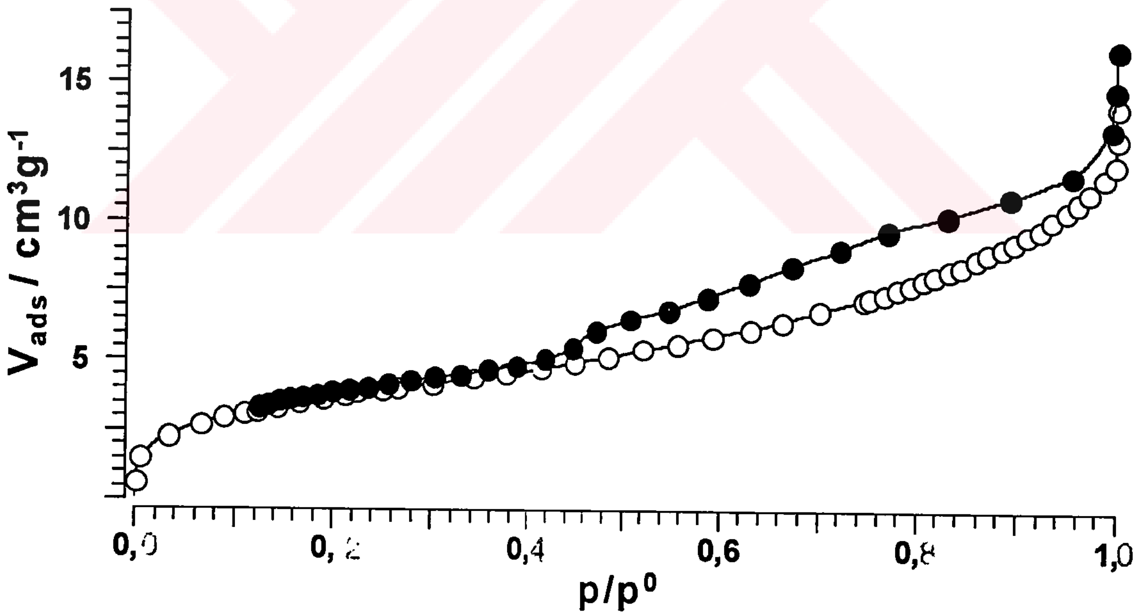


Figure 5.7 N_2 Adsorption – Desorption Isotherms for NI

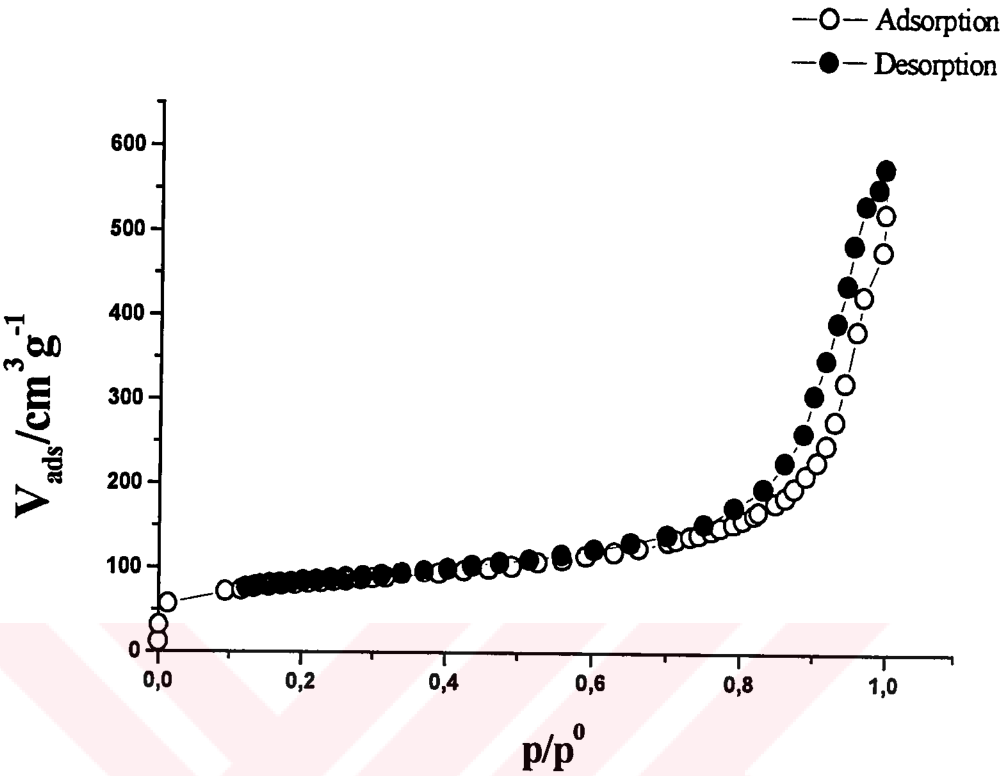


Figure 5.8 N_2 Adsorption – Desorption Isotherms for Sepiolite

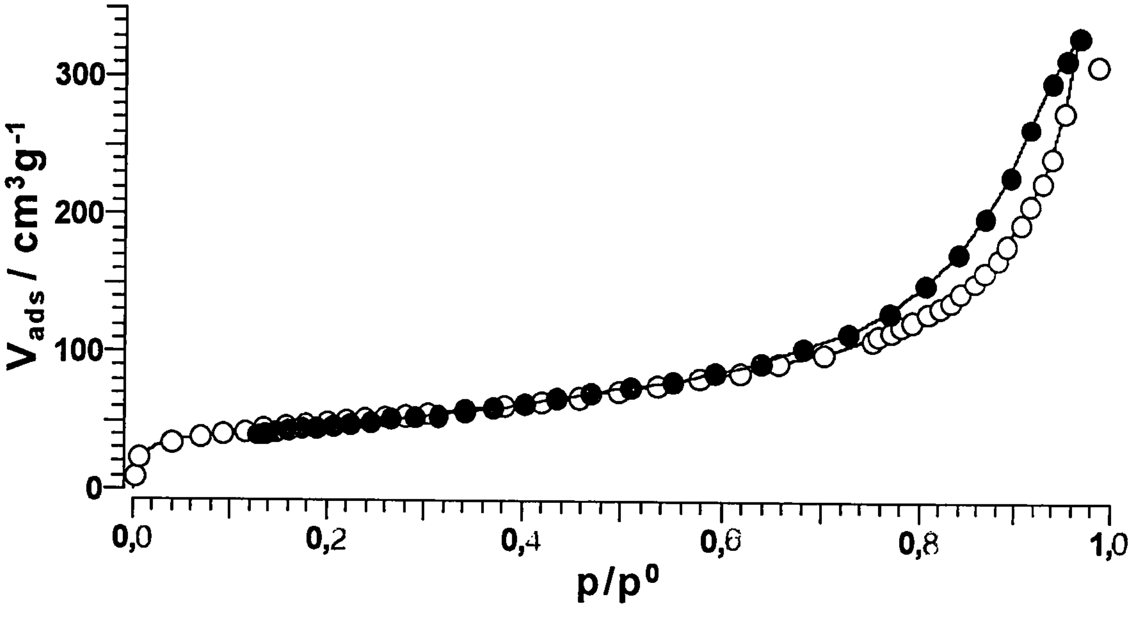


Figure 5.9 N_2 Adsorption – Desorption Isotherms for DS

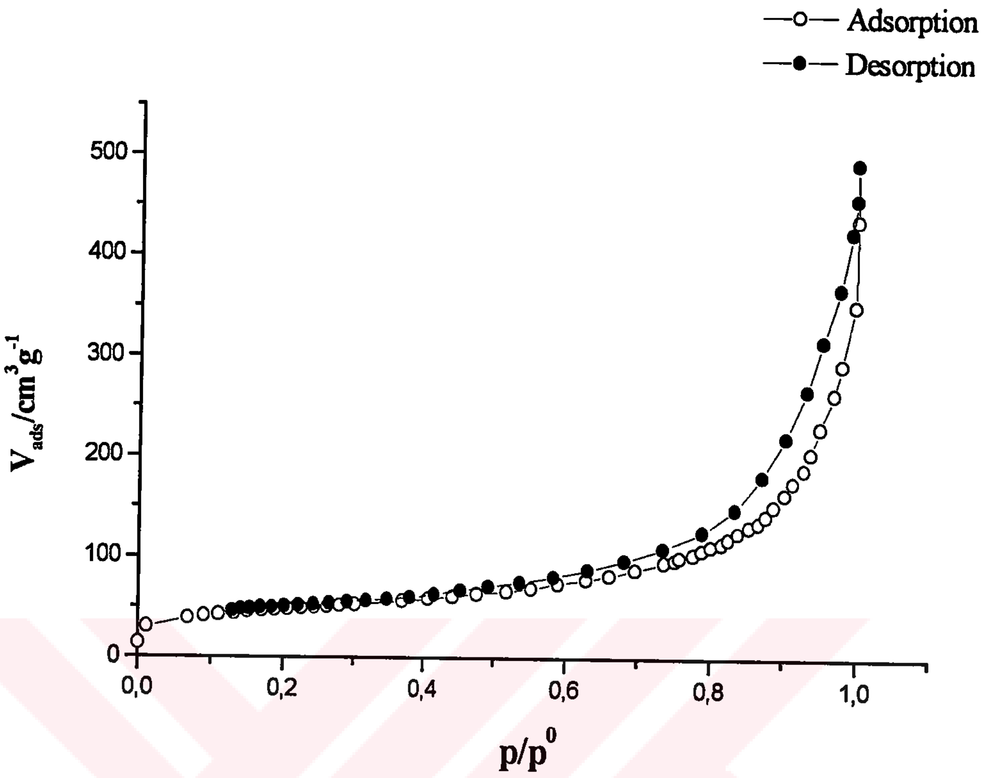


Figure 5.10 N_2 Adsorption – Desorption Isotherms for NS

Table 5.4 Pore Size Distribution Data for Bentonite

From	To	V	V%	A	A%
nm	Nm	cm³/g	%	m²/g	%
0	3	0.0000	0.00	0.000	0.00
3	6	0.0188	1.47	19.152	15.62
6	10	0.0239	1.86	12.673	10.34
10	20	0.1036	8.09	27.648	22.55
20	100	0.4700	36.69	44.530	36.32
100	400	0.6647	51.89	18.591	15.17
400	600	0.0000	0.00	0.000	0.00
600	2000	0.0000	0.00	0.000	0.00

Table 5.5 Pore Size Distribution Data for DB

From	To	V	V%	A	A%
nm	Nm	cm³/g	%	m²/g	%
0	3	0.0000	0.00	0.000	0.00
3	6	0.0015	0.41	1.228	3.03
6	10	0.0071	1.97	3.338	8.23
10	20	0.0575	16.03	15.559	38.35
20	100	0.1787	49.81	18.211	44.89
100	400	0.1140	31.78	2.235	5.51
400	600	0.0000	0.00	0.000	0.00
600	2000	0.0000	0.00	0000	0.00

Table 5.6 Pore Size Distribution Data for NB

From	To	V	V%	A	A%
nm	Nm	cm³/g	%	m²/g	%
0	3	0.0000	0.00	0.000	0.00
3	6	0.0269	8.30	25.305	29.82
6	10	0.0293	9.04	14.704	17.33
10	20	0.0847	26.13	23.745	27.98
20	100	0.1670	51.50	20.483	24.14
100	400	0.0163	5.02	0.616	0.73
400	600	0.0000	0.00	0.000	0.00
600	2000	0.0000	0.00	0.000	0.00

Table 5.7 Pore Size Distribution Data for Illite

From	To	V	V%	A	A%
nm	nm	cm³/g	%	m²/g	%
0	2	0.0000	0.00	0.000	0.00
2	10	0.1507	47.94	127.060	89.75
10	25	0.0401	12.75	12.080	8.53
25	2000	0.1236	39.31	2.433	1.72

Table 5.8 Pore Size Distribution Data for DI

From	To	V	V%	A	A%
nm	nm	cm³/g	%	M²/g	%
0	3	0.0059	2.06	9.402	7.67
3	6	0.0841	29.37	82.247	67.12
6	10	0.0334	11.69	17.831	14.55
10	20	0.0187	6.52	5.262	4.29
20	100	0.0631	22.05	5.690	4.64
100	400	0.0810	28.31	2.106	1.72
400	600	0.0000	0.00	0.000	0.00
600	2000	0.0000	0.00	0.000	0.00

Table 5.9 Pore Size Distribution Data for NI

From	To	V	V%	A	A%
nm	nm	cm³/g	%	m²/g	%
0	3	0.0086	3.54	13.725	10.81
3	6	0.0840	34.68	81.252	64.00
6	10	0.0407	16.81	21.834	17.20
10	20	0.0212	8.74	6.295	4.96
20	100	0.0313	12.92	3.202	2.52
100	400	0.0235	9.70	0.464	0.37
400	600	0.0112	4.62	0.093	0.07
600	2000	0.0218	8.99	0.092	0.07

Table 5.10 Pore Size Distribution Data for Sepiolite

From	To	V	V%	A	A%
nm	nm	cm³/g	%	m²/g	%
0	3	0.0013	0.15	1.788	0.98
3	6	0.0329	3.93	30.361	16.58
6	10	0.0616	7.35	29.959	16.36
10	20	0.2347	28.03	62.168	33.94
20	100	0.4559	54.45	57.770	31.54
100	400	0.0494	5.89	1.089	0.60
400	600	0.0016	0.20	0.016	0.01
600	2000	0.0000	0.00	0.000	0.00

Table 5.11 Pore Size Distribution Data for DS

From	To	V	V%	A	A%
nm	nm	cm³/g	%	m²/g	%
0	3	0.0075	1.45	11.538	6.24
3	6	0.0545	10.55	50.436	27.27
6	10	0.0853	16.52	43.188	23.35
10	20	0.1920	37.16	54.512	29.47
20	100	0.1774	34.33	25.284	13.67
100	400	0.0000	0.00	0.000	0.00
400	600	0.0000	0.00	0.000	0.00
600	2000	0.0000	0.00	0.000	0.00

Table 5.12 Pore Size Distribution Data for NS

From	To	V	V%	A	A%
nm	nm	cm³/g	%	m²/g	%
0	2	0.0000	0.00	0.000	0.00
2	10	0.0989	13.25	67.322	44.61
10	25	0.2217	29.69	56.192	37.24
25	2000	0.4261	57.07	27.400	18.16

Table 5.13 The properties of the samples and modified samples

Sample	Monolayer Volume (cm^3/g)	Surface Area m^2/g
Bentonite	16.67	73
DB	2.42	10
NB	11.54	50
Illite	46.06	200
DI	22.89	100
NI	31.25	136
Sepiolite	67.07	292
DS	40.97	178
NS	39.34	171

5.3.2. X Ray Diffraction Analysis of the Samples

The basal spacing of the smectites is the distance between two consecutive layers within the unit cell. (Corrizosa et al. 2000). The basal spacing of the clays and modified clays were measured by using PTS 3000 (for 2θ = 3-10°), Seifert Kooperation Ahrensburg; HZG 4 (for 2θ = 8-63°), Freiberger Präzisionsmechanik GmbH (Chemnitz Technical University/ Germany). The results were given in Figure 5.11, 5.12, 5.13, 5.14, 5.15, 5.16, 5.17, 5.18, 5.19 for Bentonite, DB, NB, Illite, DI, NI, Sepiolite, DS, NS respectively. Basal Spacing values of samples and modified samples were presented in Table 5.1 and Table 5.3 respectively.

5.3.3 Thermogravimetric Analysis of the Samples

Thermogravimetric Analysis data of clay samples and modified samples are shown in Figures 5.20, 5.21, 5.22, 5.23, 5.24, 5.25, 5.26, 5.27, 5.28 for Bentonite, DB, NB, Illite, DI, NI, Sepiolite, DS, NS respectively.

5. 3. 4 Adsorption from Solution Experiments: Determination of Equilibrium Concentration

Adsorption isotherms of clays and organo- clays were determined by using batch equilibrium method. 0.1 g of clay and modified clays were weighted into 50 mL of flasks filled with 20 mL aqueous solution of herbicide paraquat whose concentration were between 100 and 1200 μM. The suspensions were shaken 24 hours at room temperature and centrifuged at 4000 rpm for 15 min at the same temperature. Liquid phases were taken and equilibrium concentration was determined by calibration curves after measuring their absorbance values by using SHIMADZU UV – 1601 model UV- spectrophotometer at 258 nm. Difference between initial concentration and equilibrium concentration is equal to portion adsorbed.

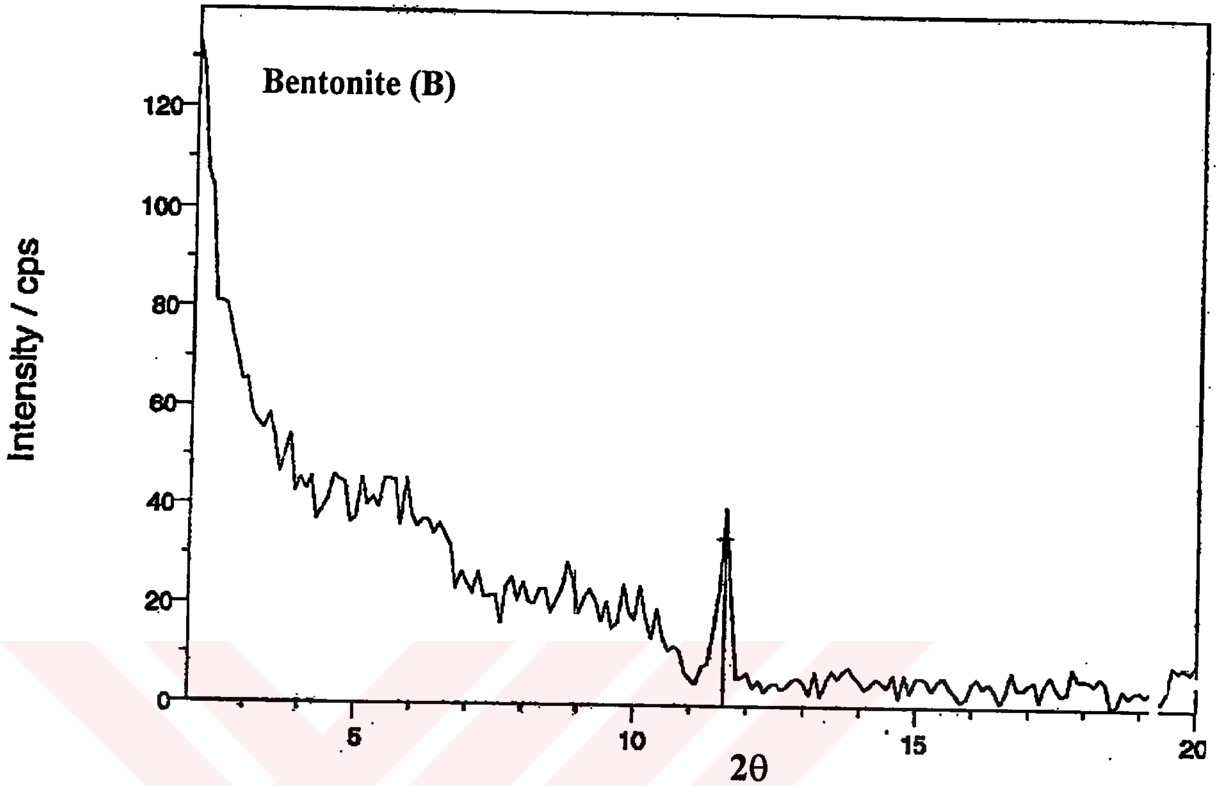


Figure 5.11 X- Ray Diffraction Patterns of Bentonite

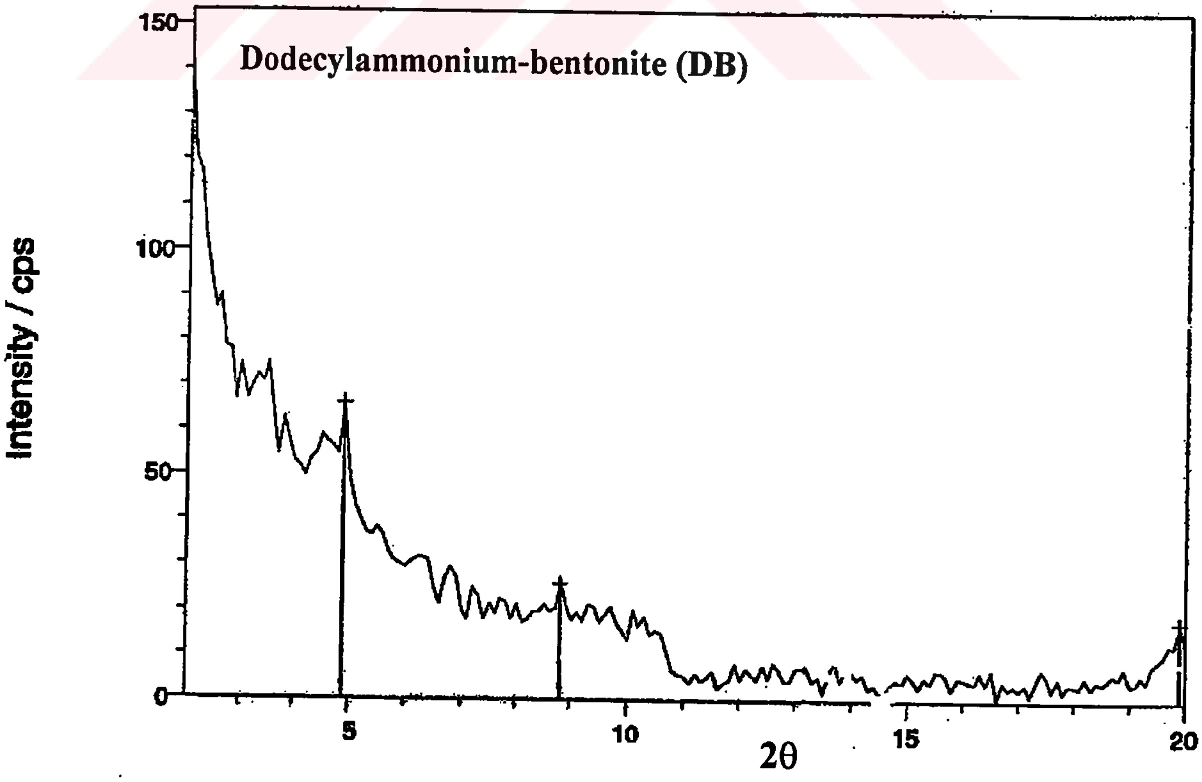


Figure 5.12 X-Ray Diffraction Patterns of the DB

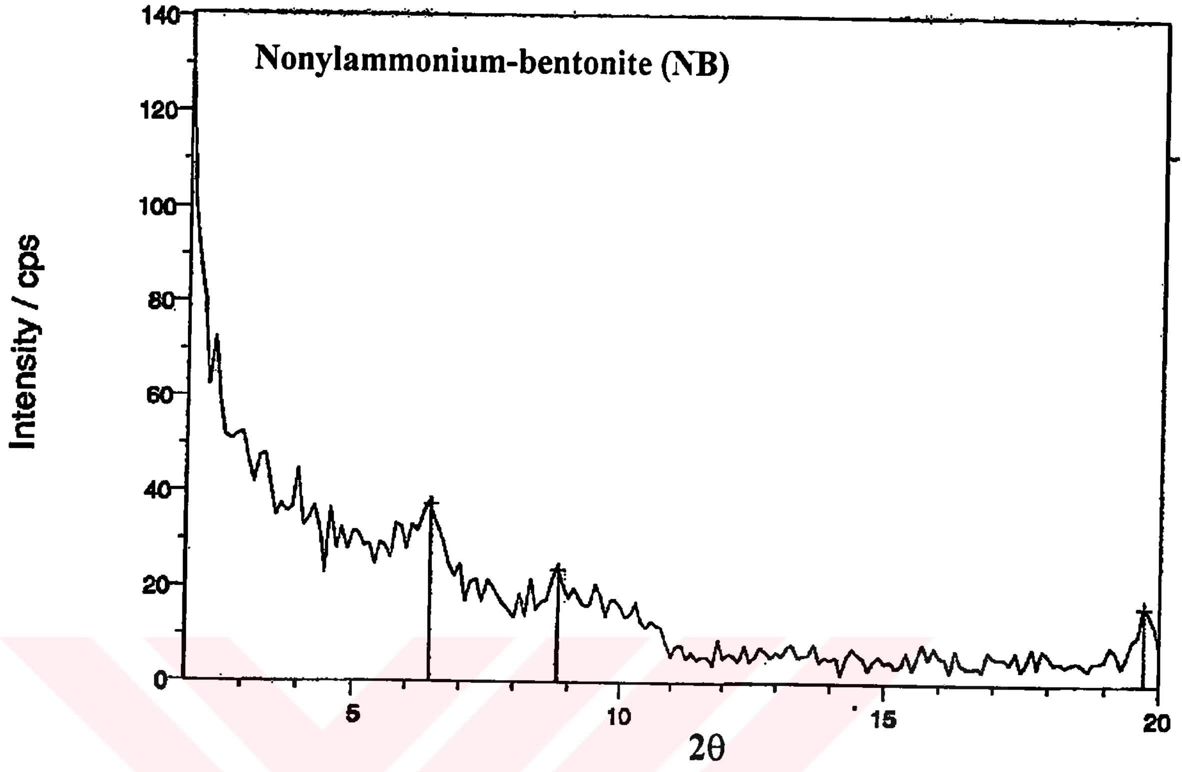


Figure 5. 13 X- Ray Diffraction Patterns of NB

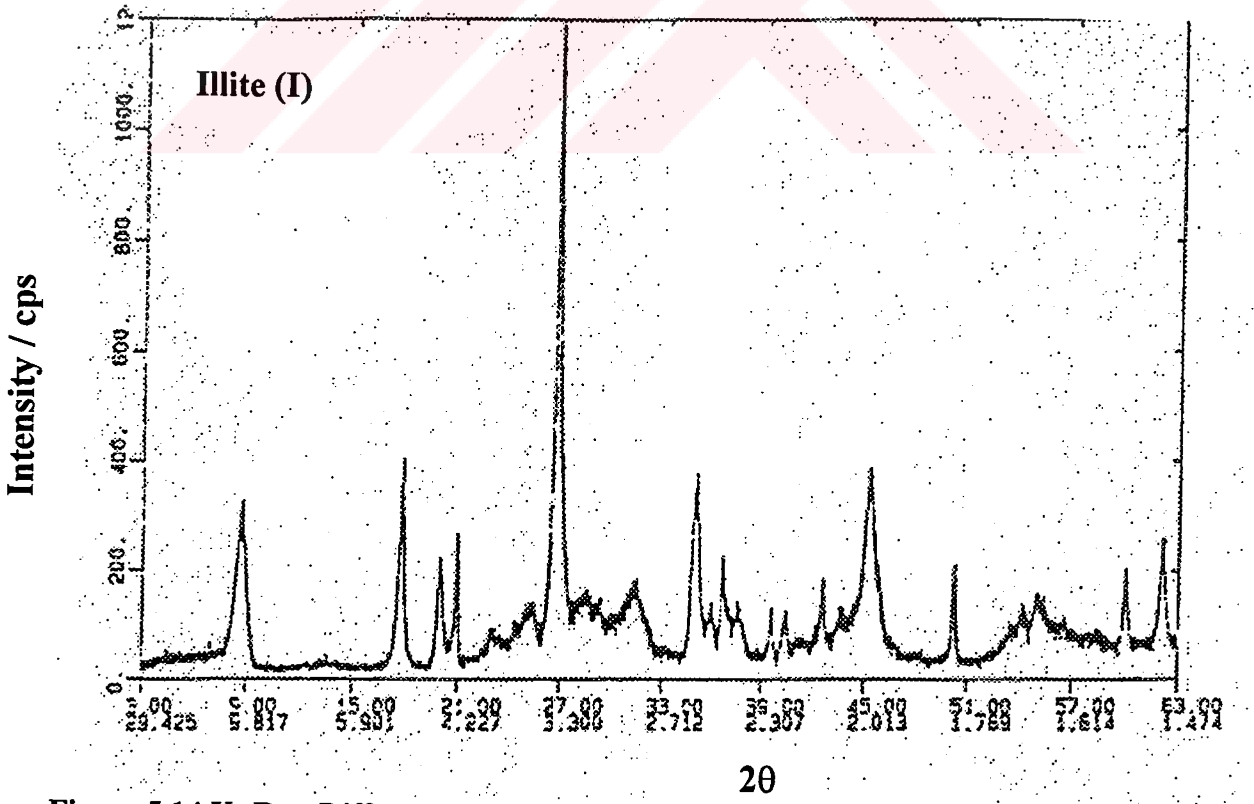


Figure 5.14 X- Ray Diffraction Patterns of Illite

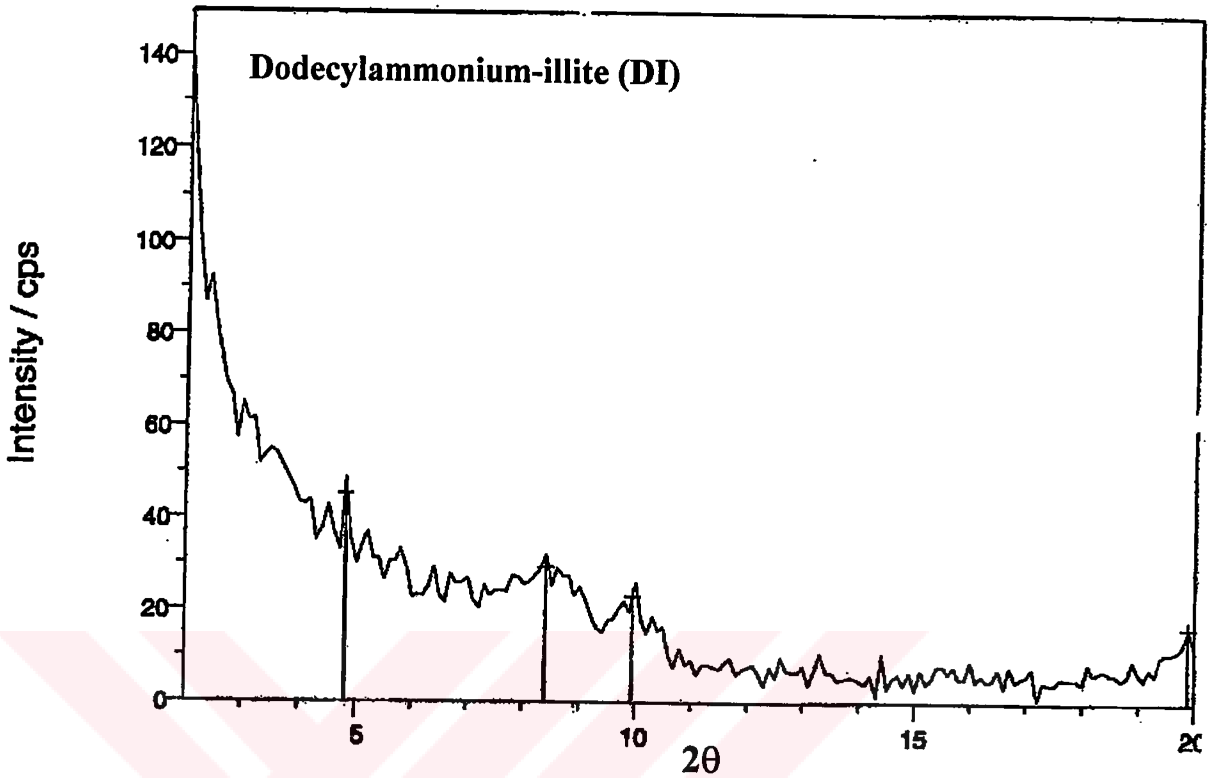


Figure 5.15. X Ray Diffraction Patterns of DI

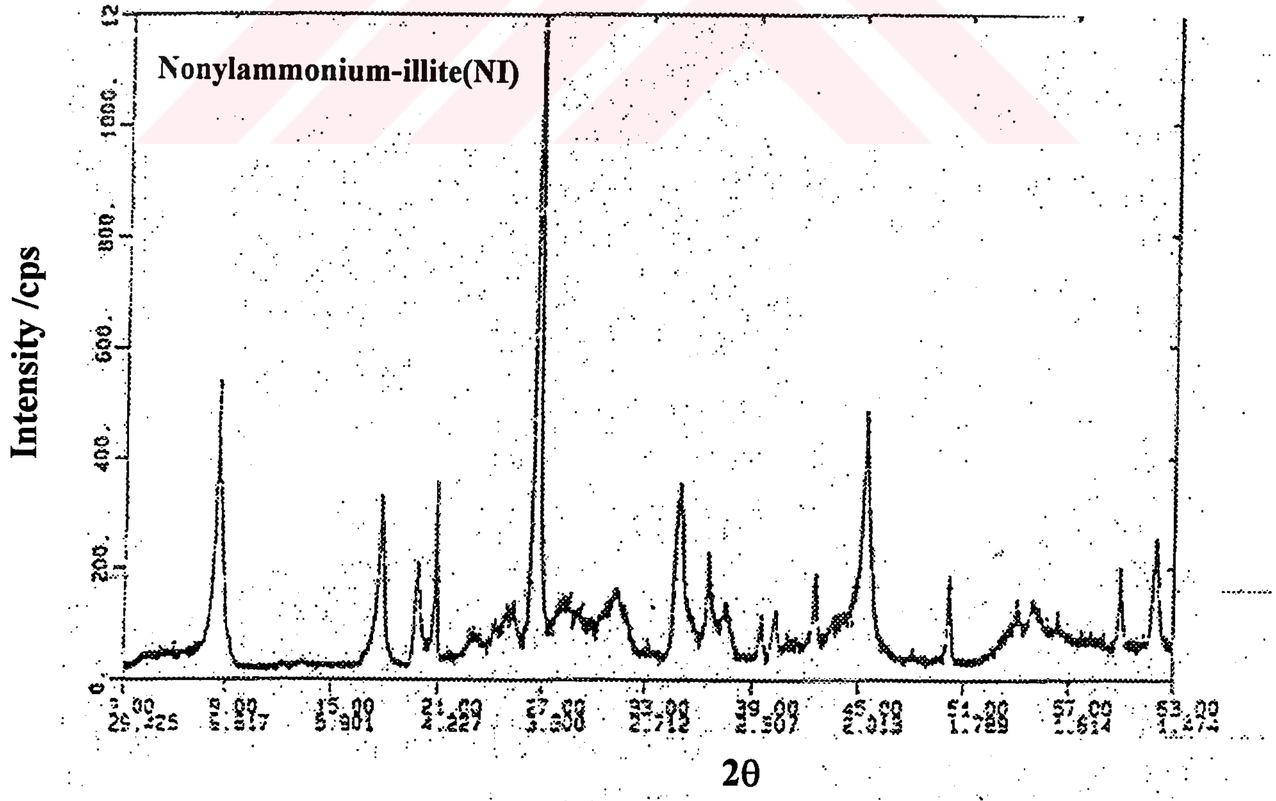


Figure 5.16. X- Ray Diffraction Patterns of NI

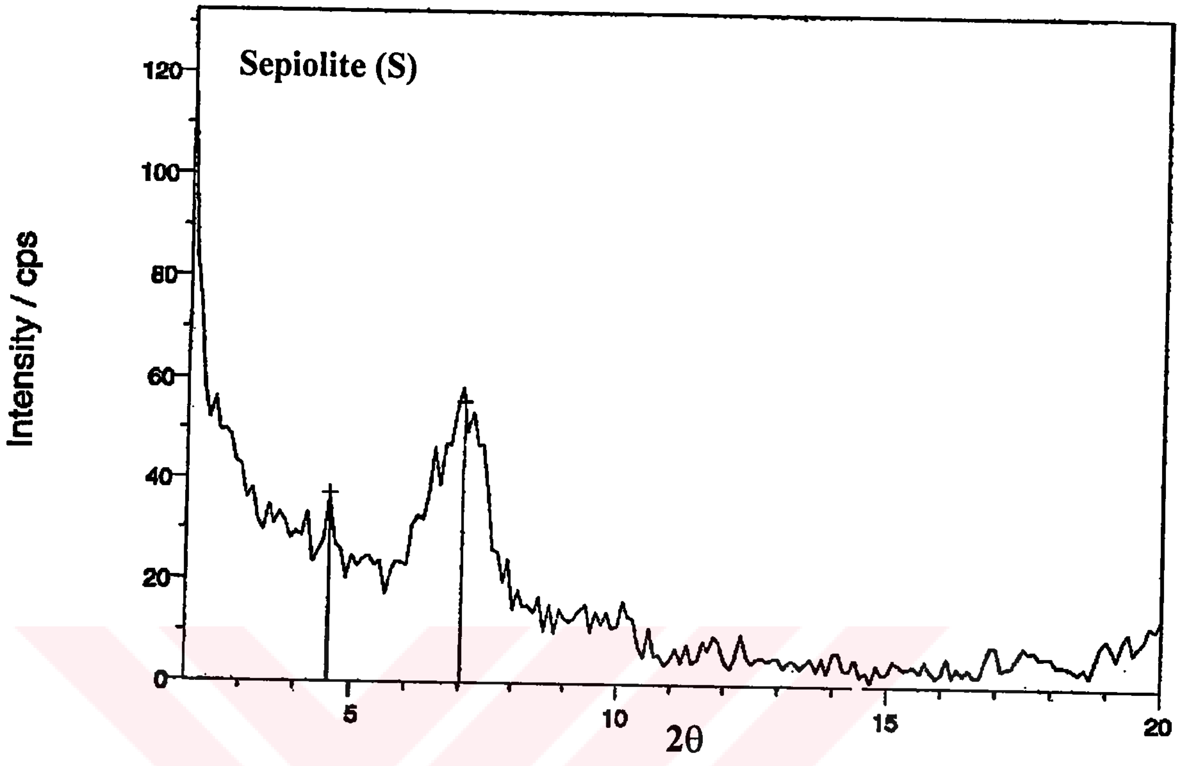


Figure 5.17. X- Ray Diffraction Patterns of Sepiolite

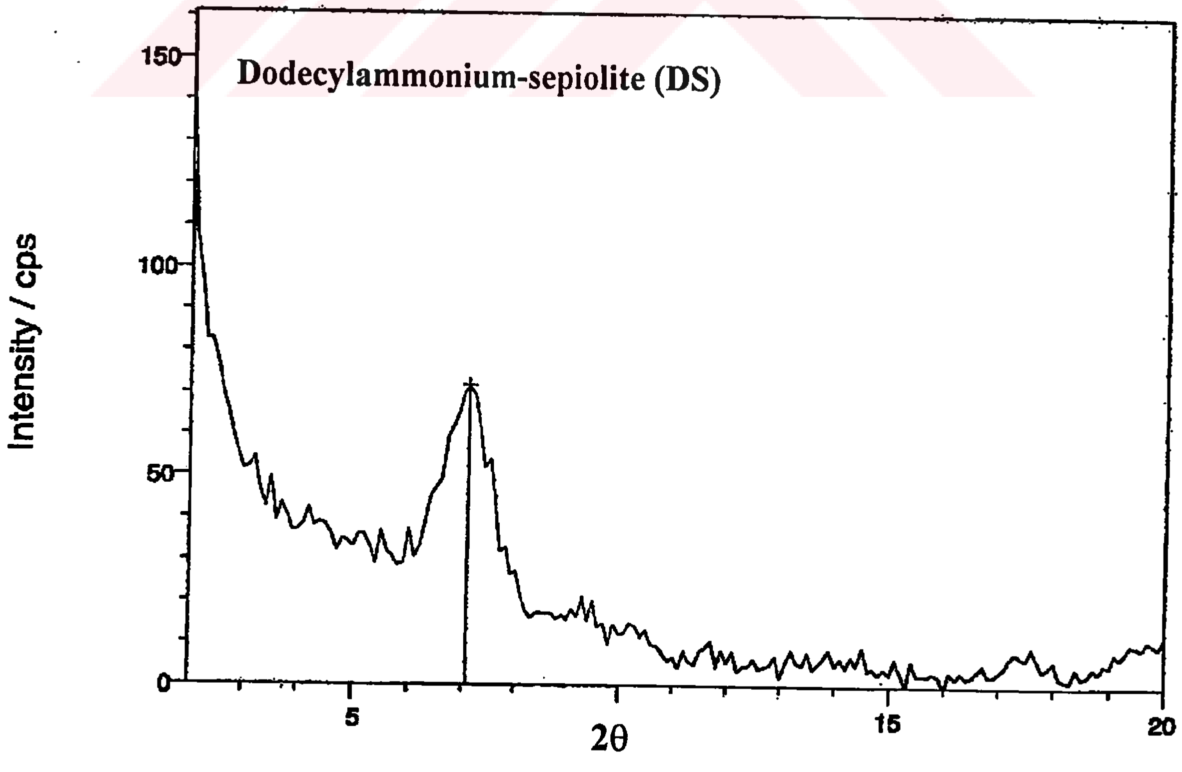


Figure 5.18 X- Ray Diffraction Patterns of DS

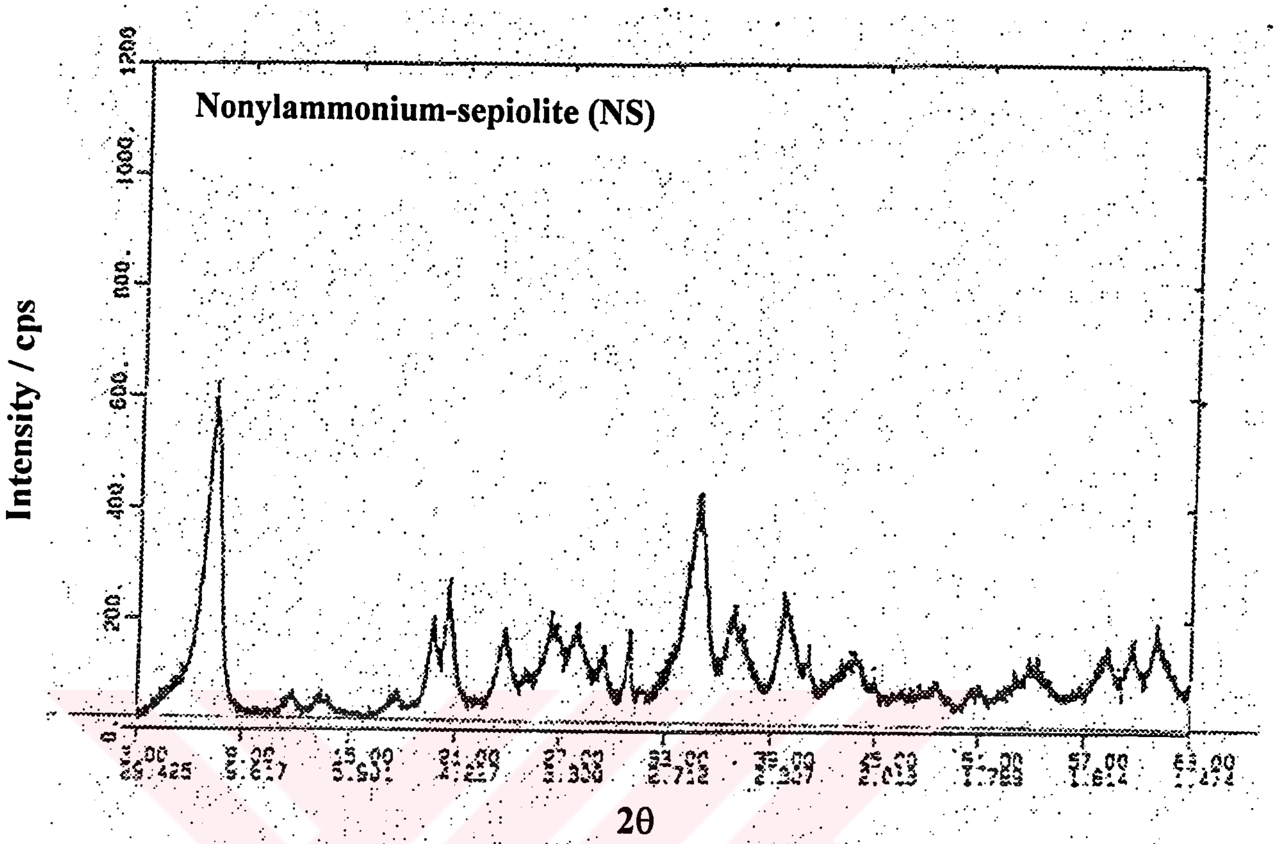
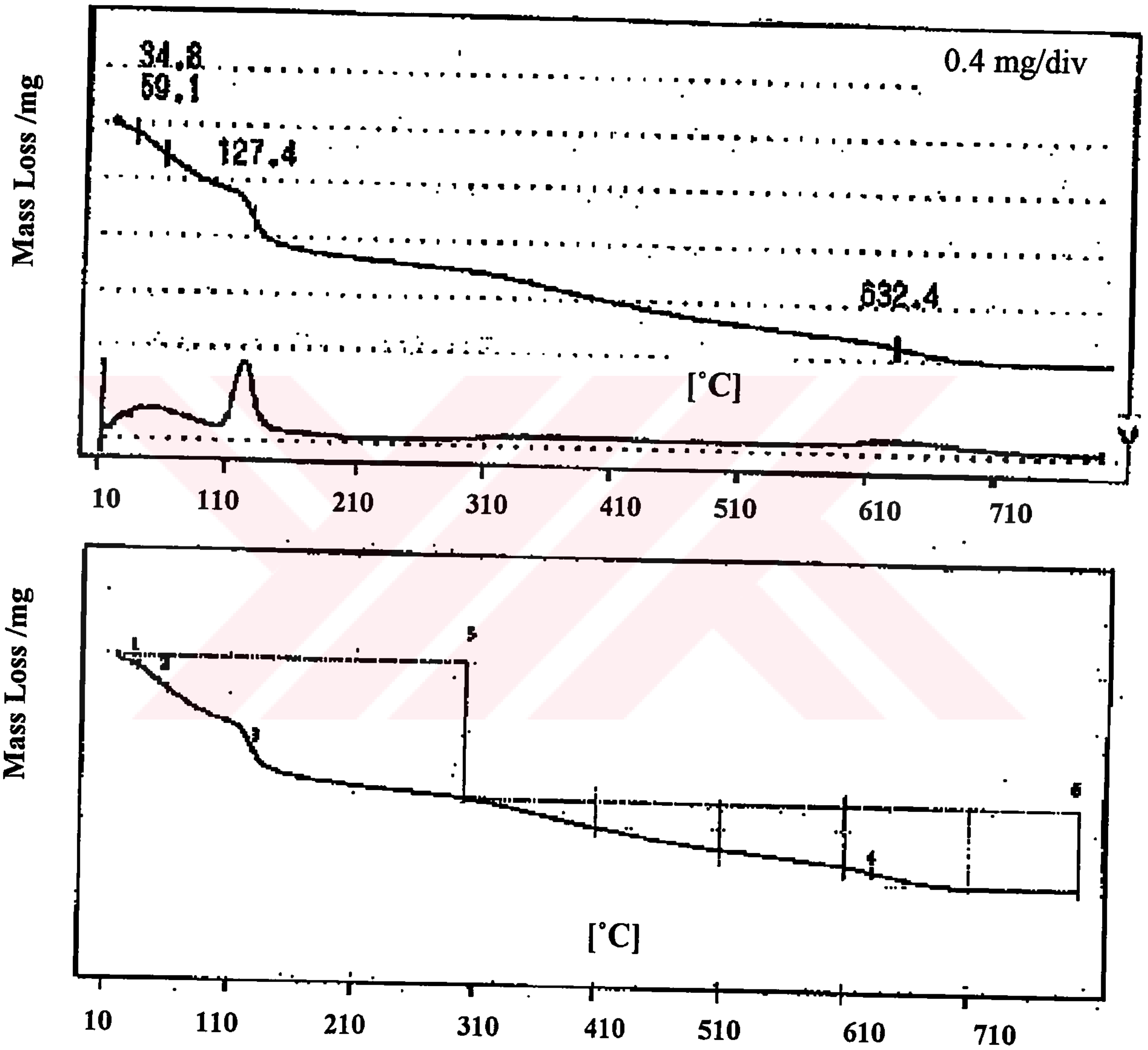


Figure 5.19. X- Ray Diffraction Patterns of NS

THERMOGRAVIMETRIC ANALYSIS DATA

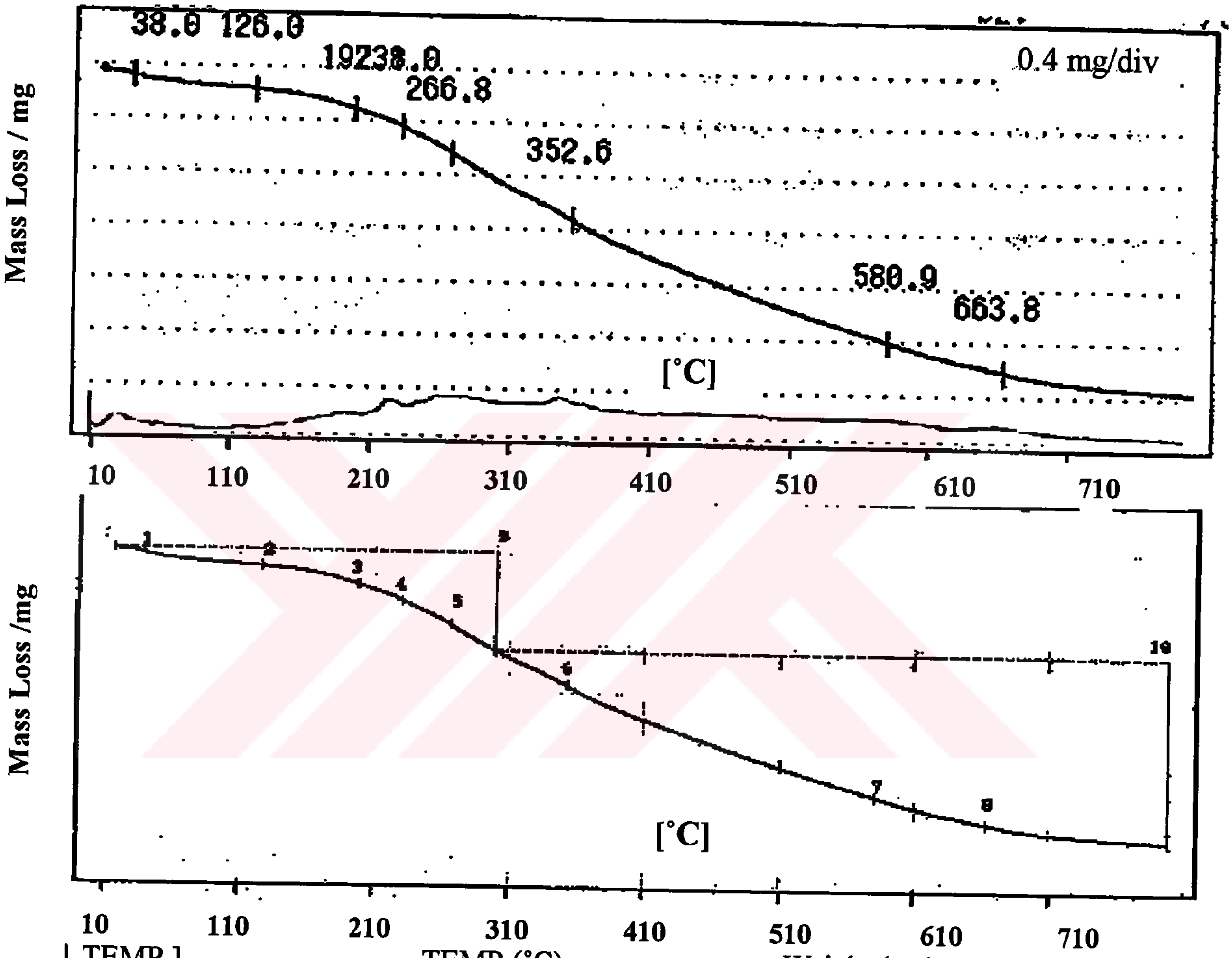
Sample : Bentonite
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 10.9 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 10°C to 800°C at a heating rate of 10 °C /min



[TEMP.]	TEMP (°C)		Weight (mg)
1	34.8		-0.0841
2	59.1		-0.2453
3	127.4		-0.6901
4	632.4		-1.5165
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
5	18	300.1	-9.404
6	300.1	799.6	-5.412

Figure 5.20 Thermogravimetric Analysis Data of Bentonite

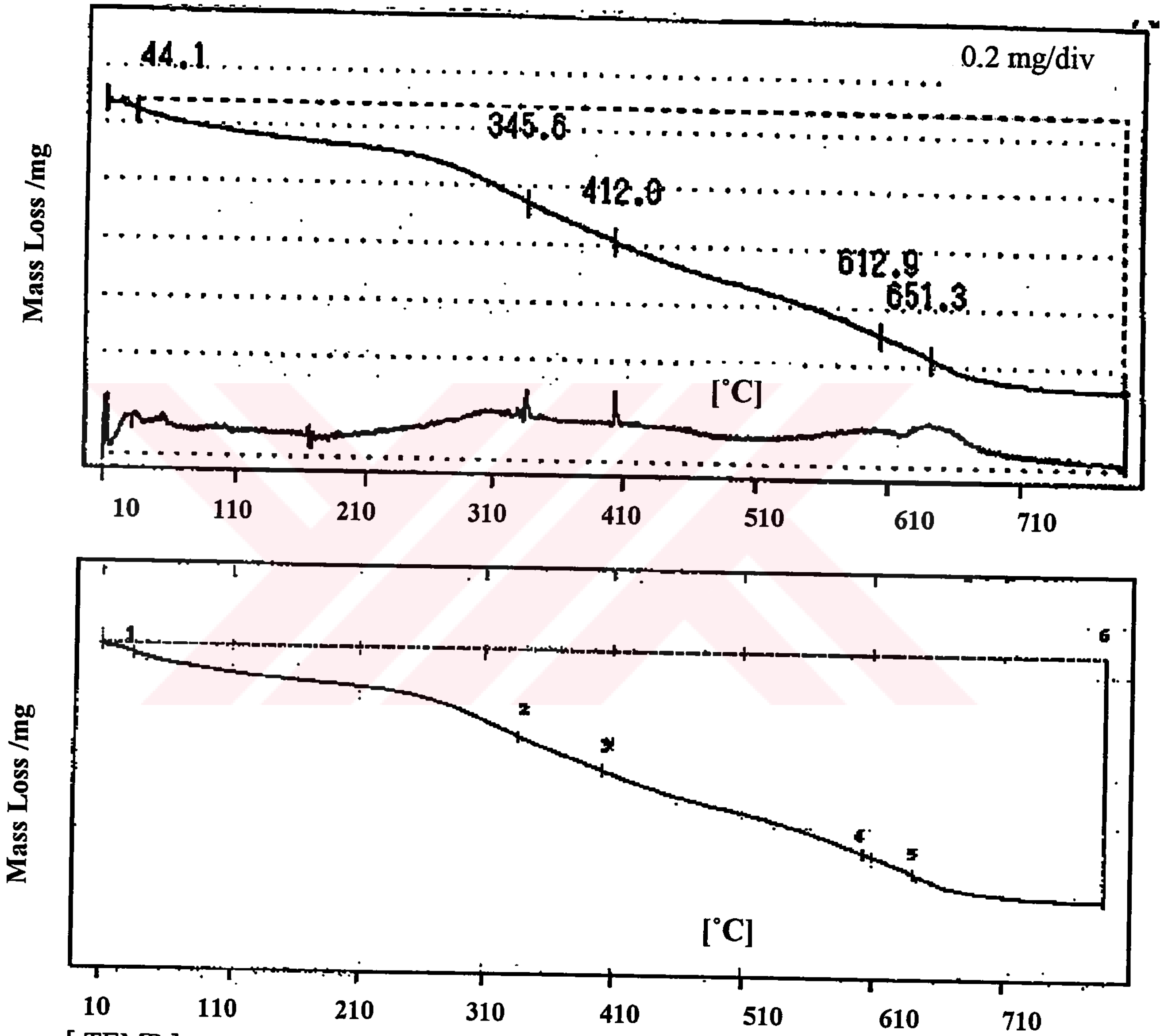
Sample : DB
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 8.077 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 10°C to 800°C at a heating rate of 10 °C /min



[TEMP.]	TEMP (°C)		Weight (mg)
1	38		-0.04
2	126		-0.1319
3	197.8		-0.2714
4	231		-0.3984
5	266.8		-0.5935
6	352.6		-1.0881
7	580.9		-1.9706
8	663.8		-2.1832
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
9	16.3	299.9	-9.923
10	299.9	799.8	-18.78

Figure 5.21 Thermogravimetric Analysis Data of DB

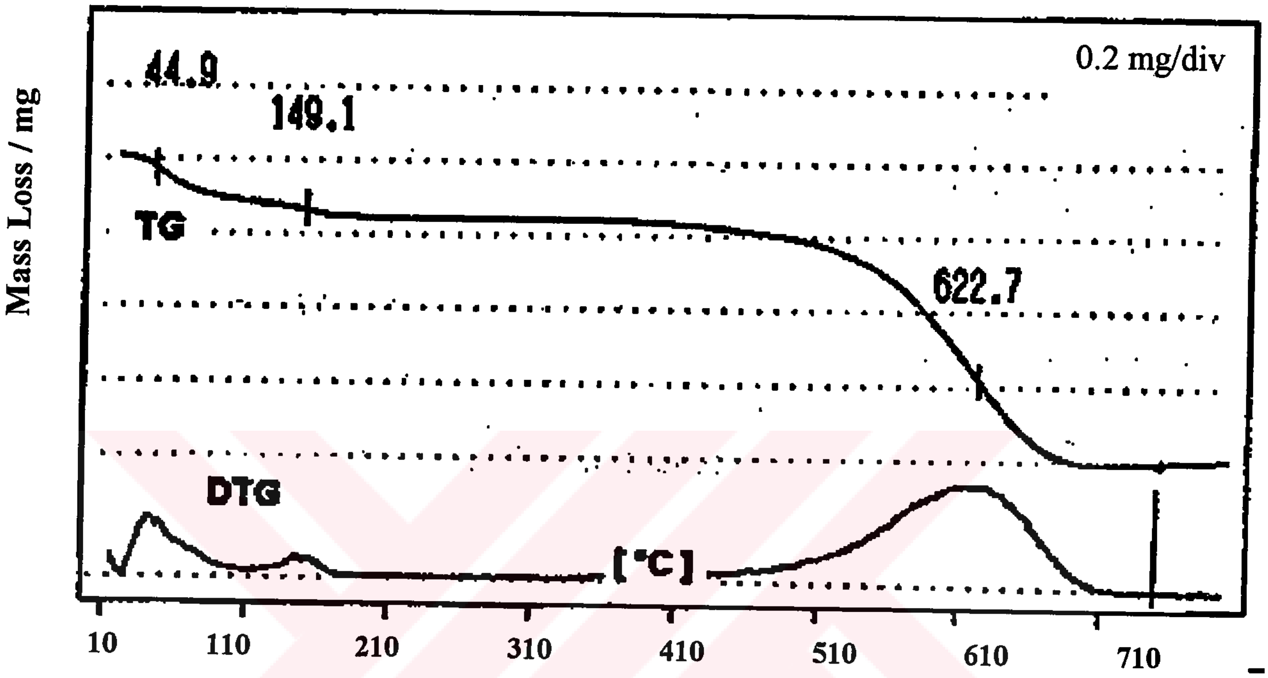
Sample : NB
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 6.987 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 10°C to 800°C at a heating rate of 10 °C /min

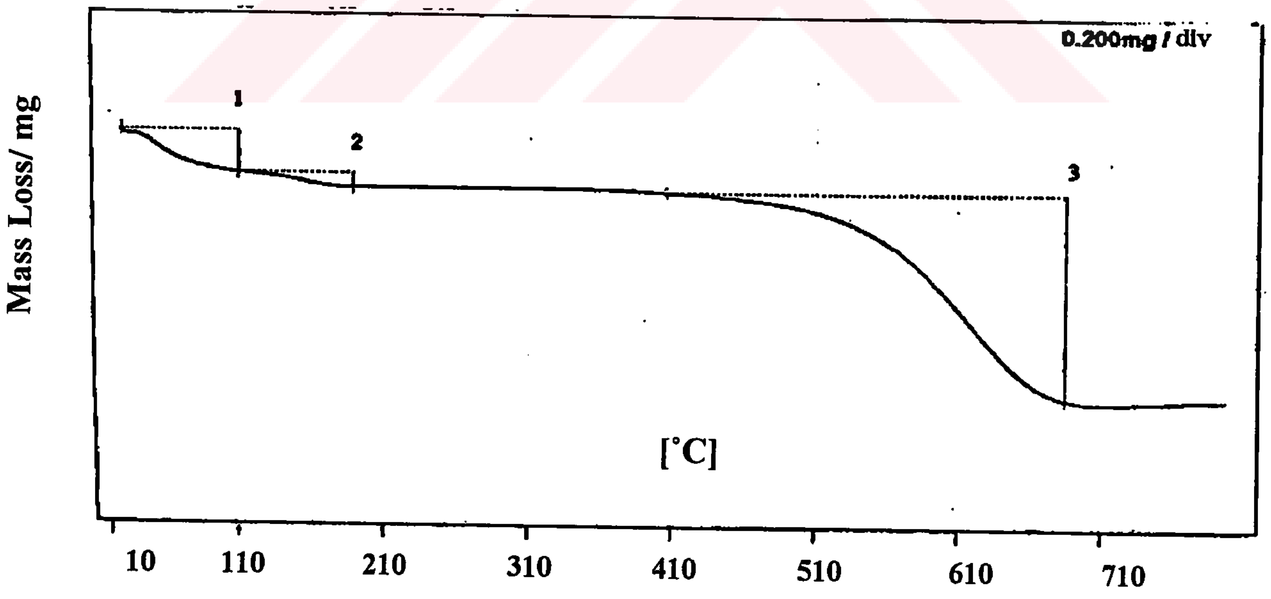


[TEMP.]	TEMP (°C)		Weight (mg)
1	44.1		-0.0354
2	345.6		-0.3423
3	412		-0.4669
4	612.9		-0.7752
5	651.3		-0.8541
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
6	20.3	799.6	-13.68

Figure 5.22 Thermogravimetric Analysis Data of NB

Sample : Illite
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 17.34 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 15°C to 800°C at a heating rate of 15 °C /min

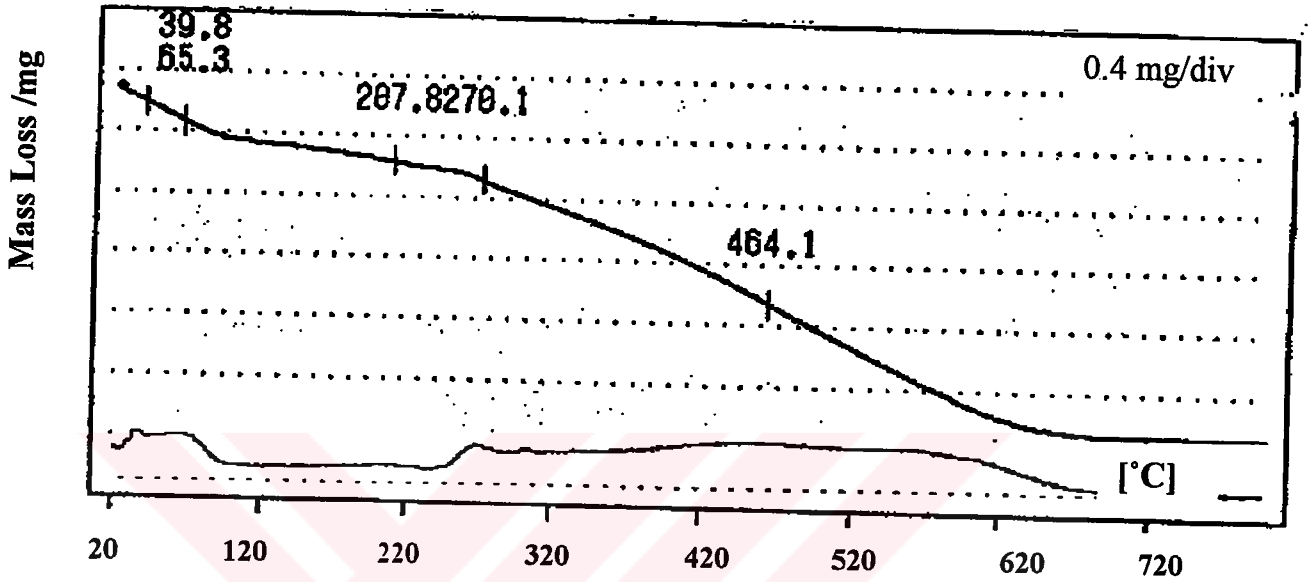


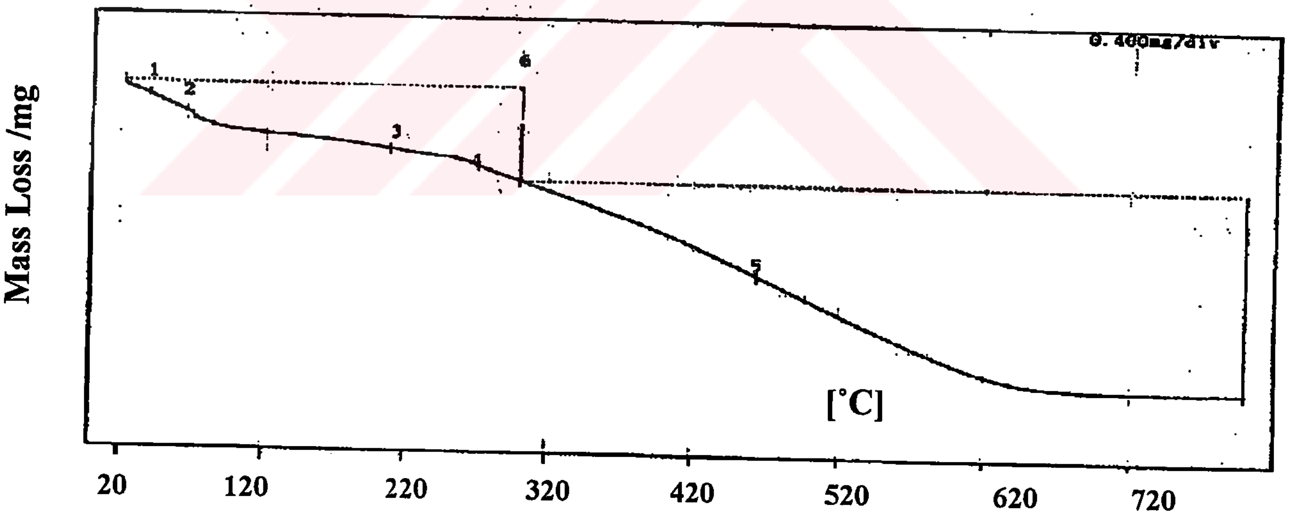


[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
1	20.0	106.3	-0.73
2	106.3	186.2	-0.24
3	405.6	685.6	-3.64

Figure 5.23 Thermogravimetric Analysis Data of Illite

Sample : DI
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 13.55 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 10°C to 800°C at a heating rate of 10 °C /min

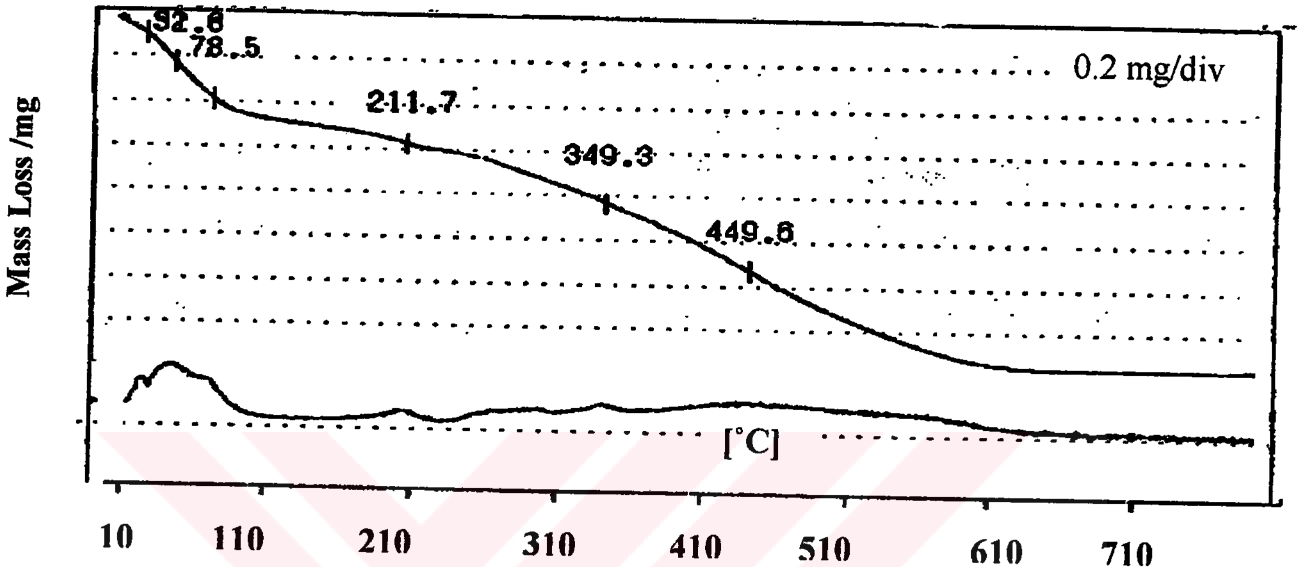


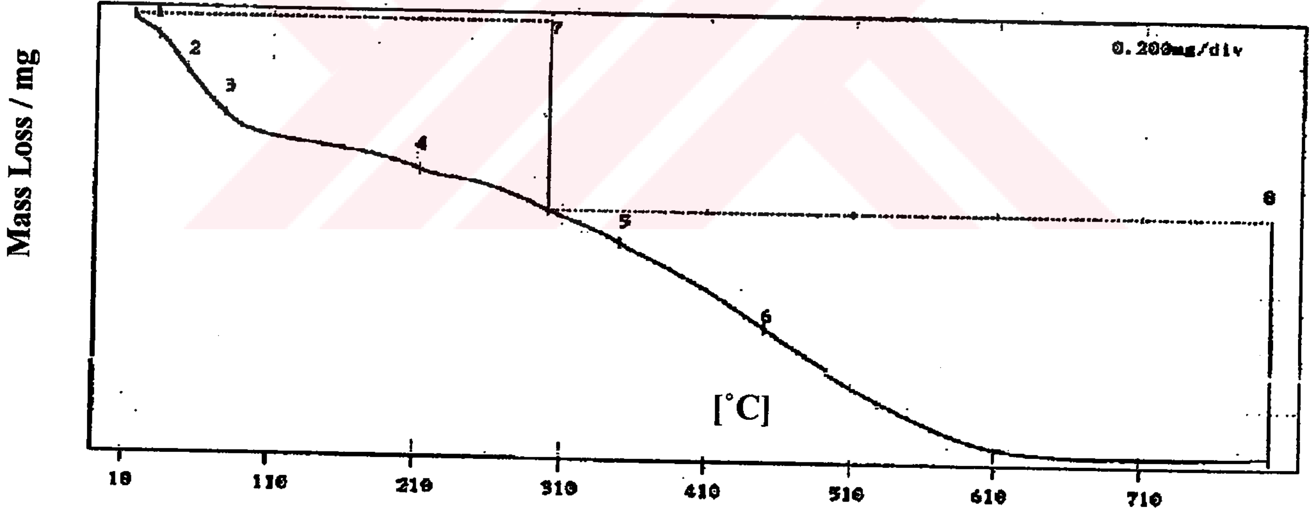


[TEMP.]	TEMP (°C)		Weight (mg)
1	39.8		-0.0969
2	65.3		-0.2212
3	207.8		-0.4561
4	270.1		-0.5682
5	464.1		-1.351
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
6	22.3	299.9	-4.98
7	299.9	799.8	-10.98

Figure 5.24 Thermogravimetric Analysis Data of DI

Sample : NI
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 11.25 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 10°C to 800°C at a heating rate of 10 °C /min

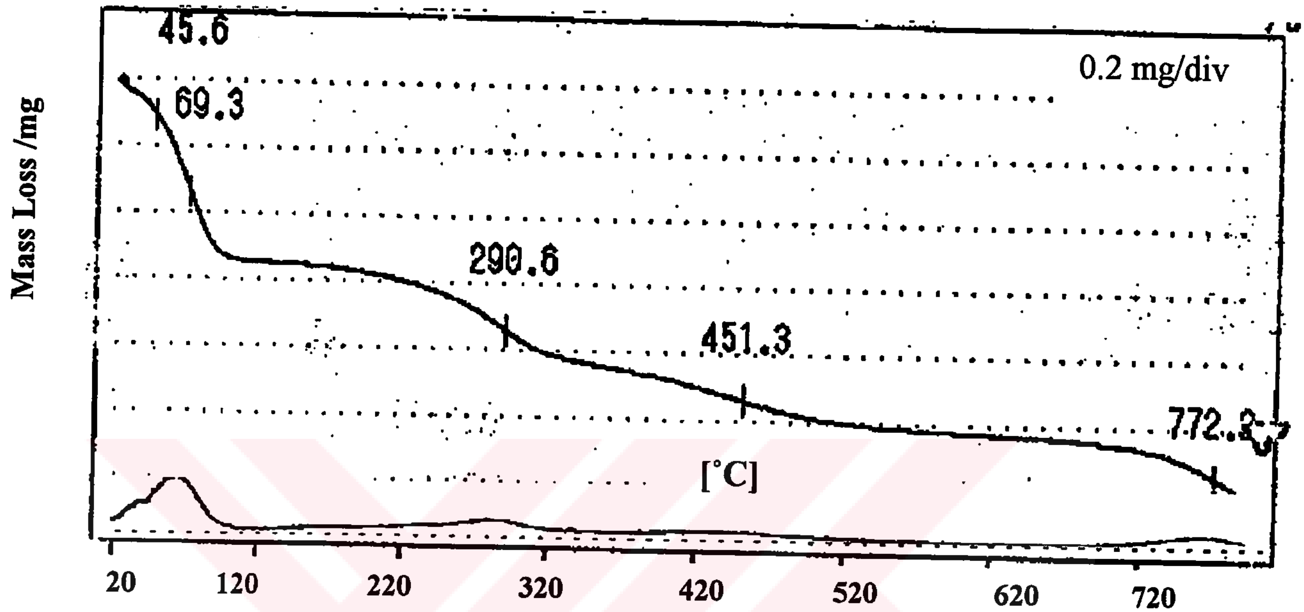


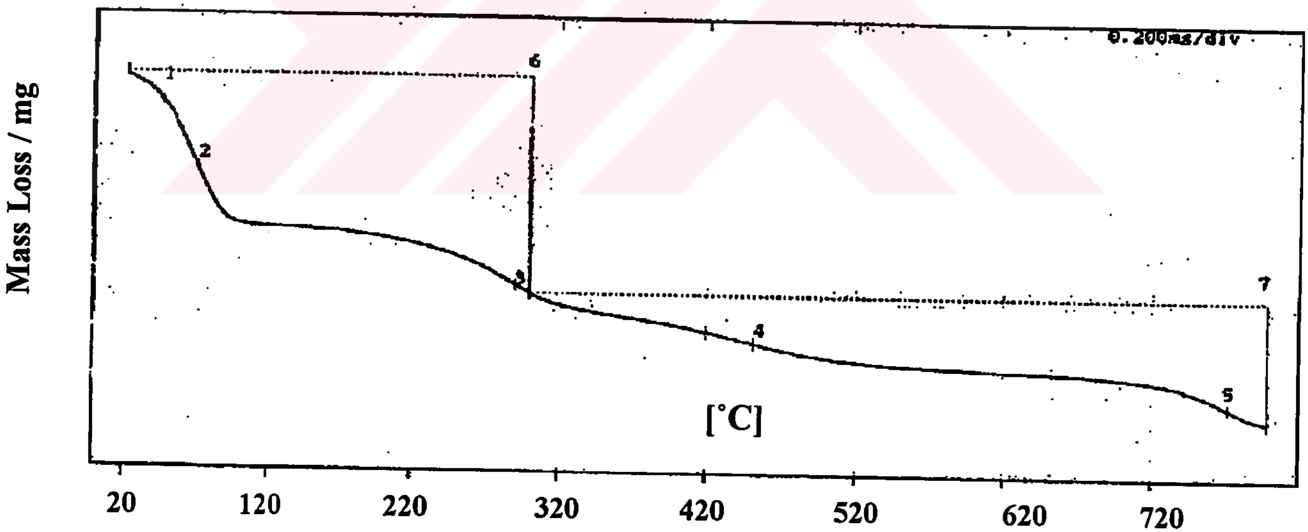


[TEMP.]	TEMP (°C)		Weight (mg)
1	32.6		-0.0745
2	51.8		-0.195
3	78.5		-0.3604
4	211.7		-0.548
5	349.3		-0.8079
6	449.6		-1.1057
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
7	15.6	299.9	-6.111
8	299.9	799.8	-7.498

Figure 5.25 Thermogravimetric Analysis Data of NI

Sample	: Sepiolite
Comment	: 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity	: 8.19 mg
Module Type	: TG
Sampling Interval	: 1sec
Temperature Program	: From 10°C to 800°C at a heating rate of 10 °C /min

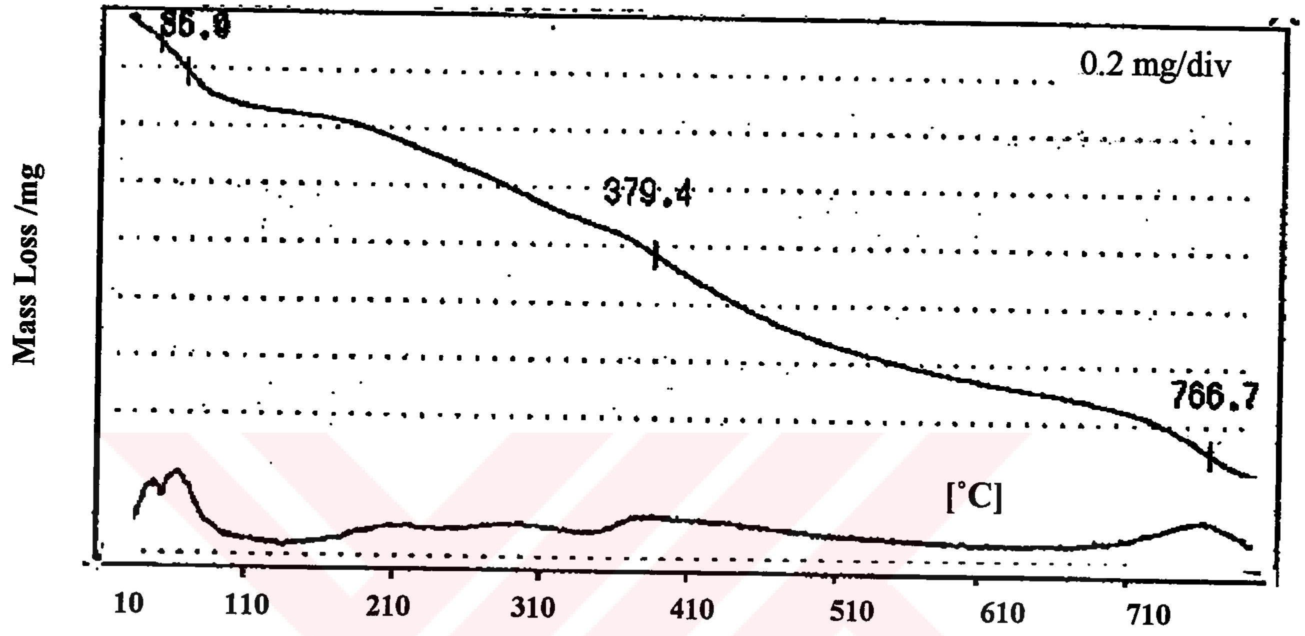


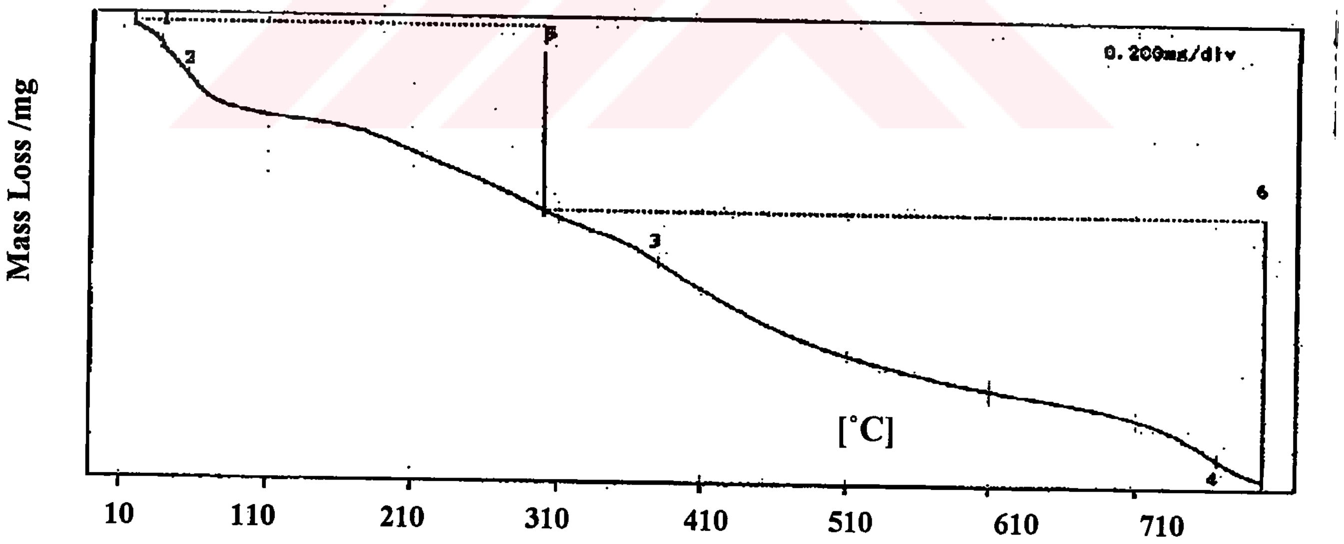


[TEMP.]	TEMP (°C)		Weight (mg)
1	45.6		-0.1006
2	69.3		-0.3262
3	298.6		-0.7355
4	451.3		-0.9311
5	772.2		-1.1414
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
6	22	300	-9.317
7	300	799.5	-5.261

Figure 5.26 Thermogravimetric Analysis Data of Sepiolite

Sample : DS
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 9.62 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 10°C to 800°C at a heating rate of 10 °C /min

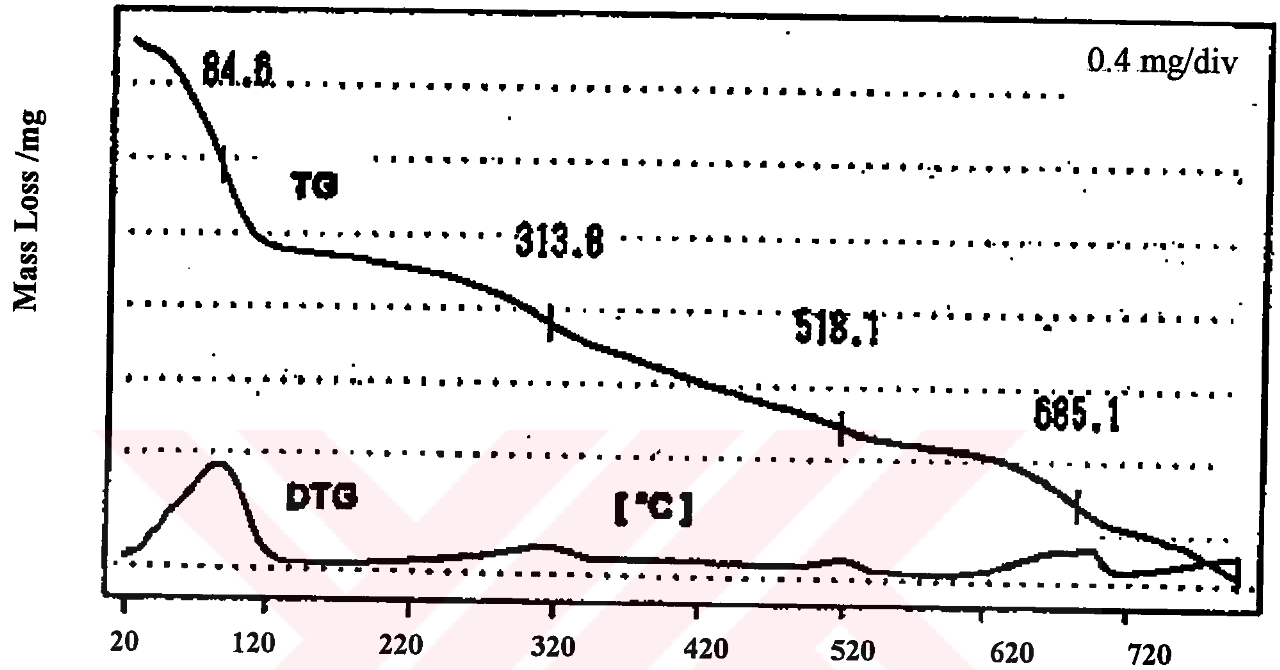


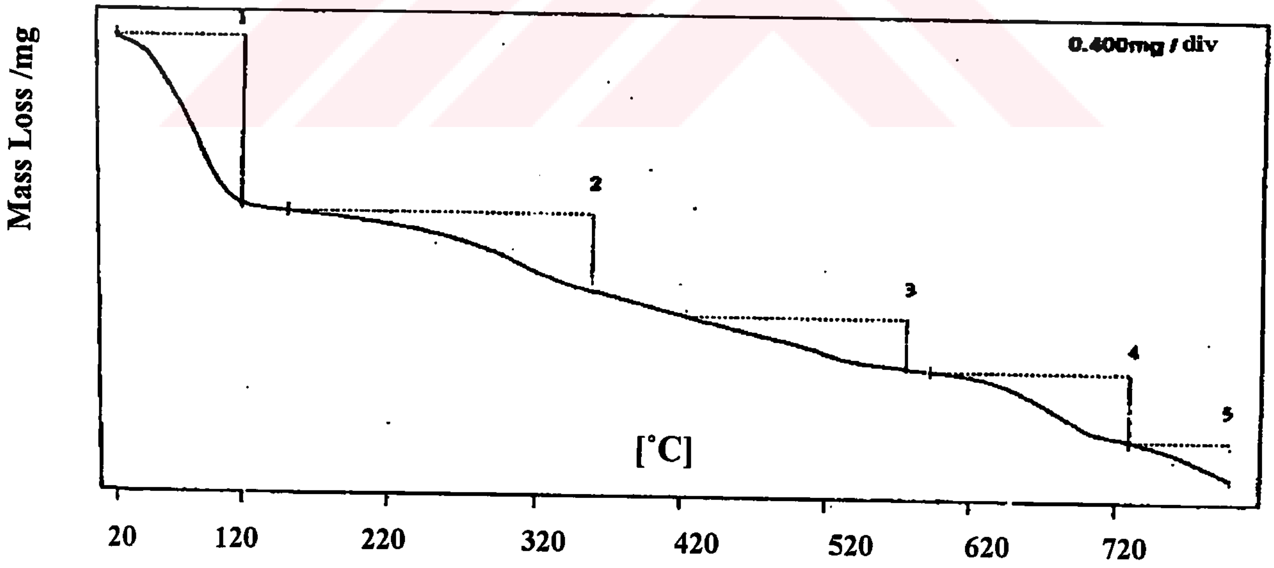


[TEMP.]	TEMP (°C)		Weight (mg)
1	36.4		-0.0758
2	55.9		-0.1858
3	379.4		-0.8043
4	766.7		-0.8043
[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
5	17.7	299.9	-6.522

Figure 5.27 Thermogravimetric Analysis Data of DS

Sample : NS
Comment : 10°C/min, N_2 15 mL/min, Pt Cell
Sample Quantity : 16.10 mg
Module Type : TG
Sampling Interval : 1sec
Temperature Program: From 15°C to 800°C at a heating rate of 15 °C /min





[WEIGHT]	Ti (°C)	Tf (°C)	Wt. Change (%)
1	21.7	116.6	-6.76
2	149.0	357.0	-3.22
3	423.0	575.0	-2.06
4	592.2	729.0	-2.79
5	729.0	800.0	-1.52

Figure 5.28 Thermogravimetric Analysis Data of NS

Chapter 6

RESULTS

6.1. Determination of Paraquat Concentration from Calibration Curve

A stock solution (2 mM) of paraquat (methylviolegen dichloride) was prepared for the experiment. 0.1286 g **paraquat** was dissolved in 500 mL distilled water and calibration solutions were prepared by diluting stock solution to appropriate concentrations. The absorbance values of calibration solutions and calibration curve were shown in Table 6.1 and in Figure 6.1 respectively. The curve was plotted absorbance values of calibration solutions versus concentration.

Table 6.1 Absorbance values of Paraquat Solutions at λ =258 nm for Calibration Curve

Number	C x10^2 (mmol/L)	Absorbance
1	10	0.199
2	15	0.274
3	20	0.376
4	24	0.471
5	30	0.567
6	40	0.738
7	45	0.862
8	50	0.925
9	55	1.045
10	60	1.128

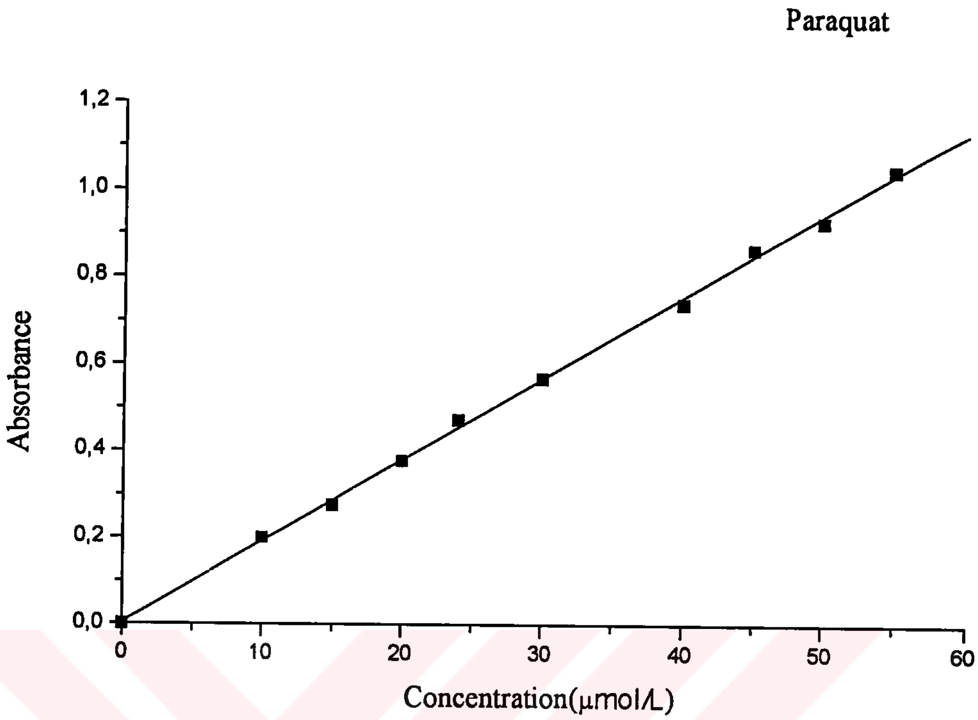


Figure 6.1 Calibration Curve of Paraquat

6.2. Adsorption of Paraquat onto Natural Clay

The adsorption isotherms of Paraquat on natural clays were determined by plotting the amount of paraquat adsorbed by clays (C_s mmol/g) versus equilibrium concentration of paraquat (C_e mmol/L). Figure 6.2 shows the paraquat sorption isotherms for unmodified clays (Bentonite, illite and sepiolite). In terms of the slope of initial portion of the curves, the shapes of these isotherms corresponding to bentonite and illite may be classified as H type according to the Giles classification (Giles et al. 1960). It means that bentonite and illite have a high affinity for paraquat that is strongly adsorbed and no competition occurs for the sorption sites between the solvent and paraquat molecules. The adsorption isotherm of paraquat on Sepiolite was of L type according to Giles classification indicating that sepiolite has a medium affinity for the paraquat molecules. The curves tend to constant value of C_s and reach a plateau showing the formation of a complete monolayer of paraquat molecules covering adsorbent surface. The plateaus define maximum adsorptions of 19 mmol/g, 15 mmol/g, and 4 mmol/g for illite, bentonite, and sepiolite respectively and each offers a surface saturation by herbicide molecules (isotherms belonging to sub group II of the Giles classification (Giles et al. 1960). The amounts of paraquat adsorbed by unmodified clays decrease from illite to sepiolite and the order is as indicated below

İllite > bentonite > sepiolite

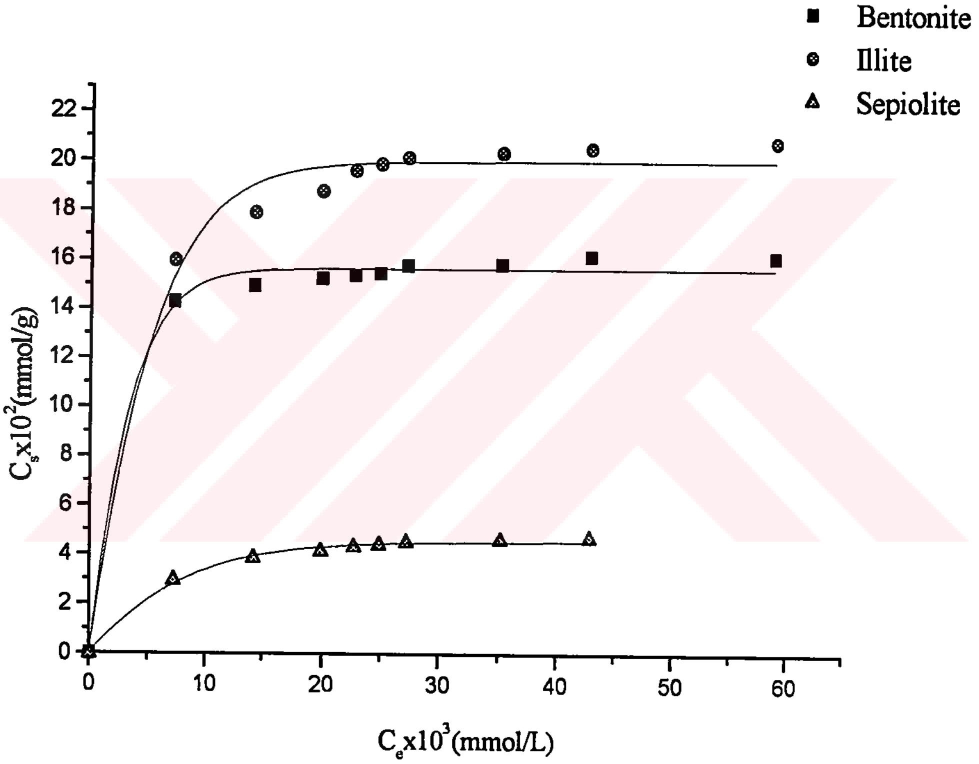


Figure 6.2. Adsorption Isotherm for Paraquat on Bentonite , Illite, Sepiolite

The fit of adsorption data to the Langmuir and Freundlich equations were investigated to find sorption capacities of the unmodified samples by using logarithmic forms as below

$C_e/C_s = 1/(C_mL) + C_e/C_m$; $\log C_s = \log K_f + n_f \log C_e$

Where

C_s = the amount adsorbed of solute (mmol/g)

C_e = equilibrium concentration of solute (mmol/L)

C_m = Adsorption capacity (maximum amount that can be adsorbed by adsorbent as a monolayer (mmol/g).

L = a constant related to the adsorption energy.

K_f and n_f are known as adsorption capacity and intensity respectively (Morela & Van Bladel, 1980). K_f can be considered as a measurement of the relative adsorption capacity since it is the value of C_s when C_e is the unity. (Hermosin & Cornejo, 1987; Akçay G., Yurdakoç M.K., 2000). n_f is a measurement of linearity. Figure 6.3 shows the results found by plotting C_e/C_s versus C_e for the adsorption process of paraquat onto bentonite, illite, sepiolite.

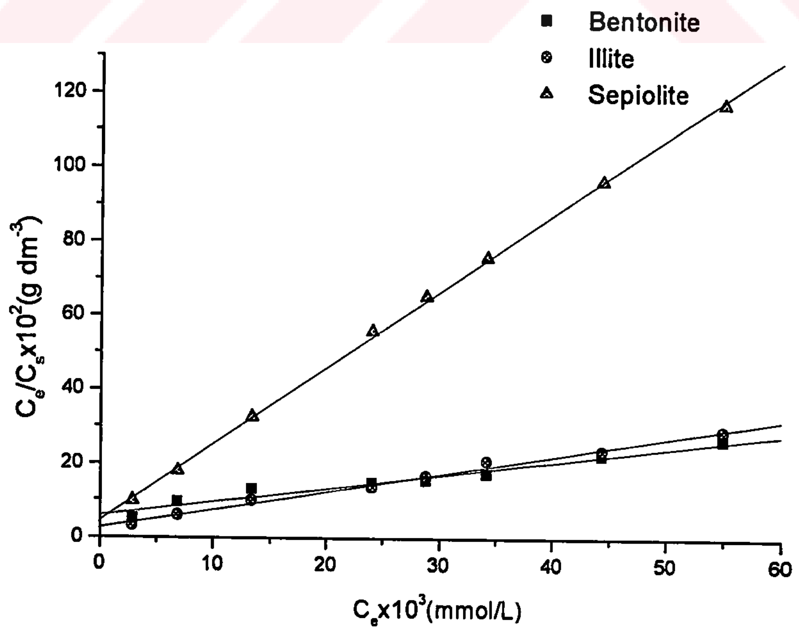


Figure 6.3 Application of Langmuir Equation to Adsorption Data of Paraquat on B, I,S

Langmuir equation gave a good fit for all adsorbents. The correlation coefficients were in all cases greater than 0.9997 being significant at the 0.0001 probability level. C_m and L parameters were determined by using the linear regression applied to the straight lines in Figure 6.3. The sorption parameters of paraquat on unmodified clays corresponding to Langmuir equation were summarised in Table 6.2. As shown in Table 6.2 C_m (maximum adsorption capacity) values are 0.484 mmol/g for sepiolite, 1.652 mmol/g for bentonite, and 2.115 mmol/g for illite respectively. L values are from 0.411 g dm^{-3} for sepiolite up to 0.732 gdm^{-3} for bentonite. Relative sorption capacities increase in order of illite > bentonite > sepiolite

Table 6.2 The Sorption Parameters of Langmuir Equation for Paraquat on Bentonite, Illite and Sepiolite Samples.

Sample	R	Cm(mmol/g)	L(g dm^{-3})
Sepiolite	0.9997	0.484	0.411
Illite	0.9999	2.115	0.690
Bentonite	0.9998	1.652	0.732

The adsorption data were further evaluated with the logarithmic form of Freundlich equation.

$$\mathrm{Log}C_s = \log K_f + n_f \log C_e$$

$\log C_e$ versus $\mathrm{Log}C_s$ was plotted for paraquat sorption on various unmodified clays in the Figure 6.4. The correlation coefficients is greater than 0.9552. In comparison with Langmuir equation, the fit of Freundlich equation is not as good as Langmuir equation. K_f (relative sorption capacity) and n_f (measure of the linearity of the sorption) were found by using the linear regression method applied to the straight lines in Figure 6.4.

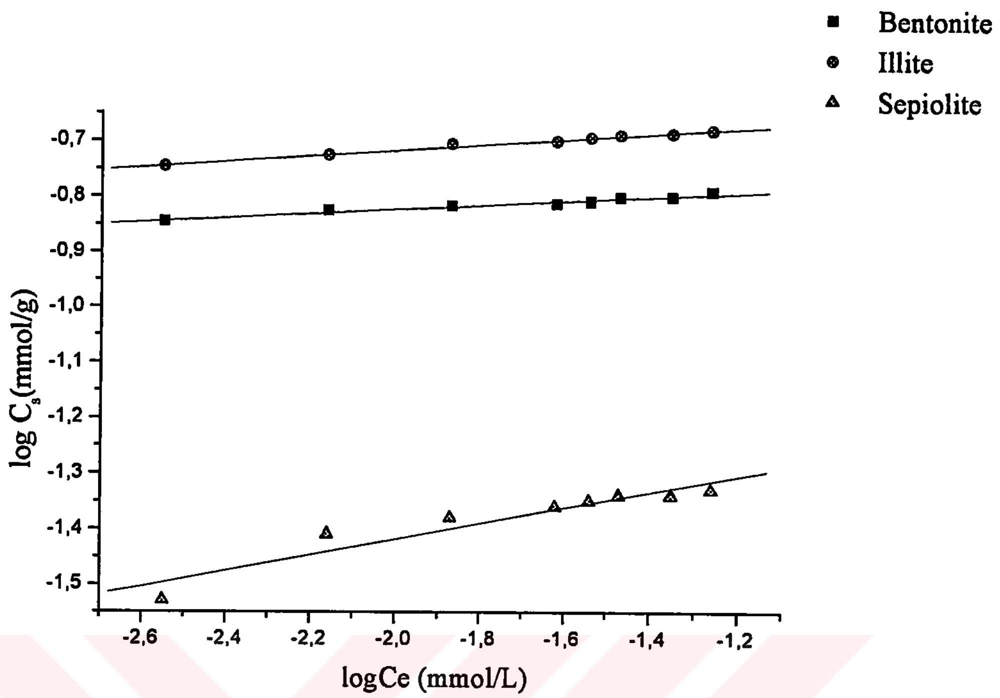


Figure 6.4. Application of Freundlich Equation to Adsorption Data of Paraquat on B, I, S

All of the parameters of Freundlich equation were shown in Table 6.3. The distribution coefficients, as a representative mean value of the concentration range studied were obtained as below;

$$Kd_{0,3} = \frac{Cs_{0,3}}{0.3}$$

$Cs_{0,3}$ values were calculated by using Freundlich equation at 300 μM (C_e) and these values were also summarised in Table 6.3

Table 6.3 The Sorption Parameters of Freundlich Equation for Paraquat on various unmodified samples Sepiolite, Bentonite and Illite

Sample	R	K_f(mmol/g)	n_f	$Cs_{0,3}$	$Kd_{0,3}$
Sepiolite	0.9552	0.0734	0.1439	0.055	0.183
Bentonite	0.9878	0.1960	0.0642	0.181	0.603
Illite	0.9961	0.2487	0.0627	0.231	0.770

As can be seen from Table 6.3, n_f values decrease from 0.0627 for illite to 0.1439 for sepiolite. In contrast with n_f values, K_f values increase from 0.0734 mmol/g for sepiolite, 0.1960 mmol/g for bentonite to 0.2487 mmol/g for illite, indicates that adsorption capacities increase in the order being sepiolite, bentonite and illite respectively. It can be deduced that illite adsorbs more paraquat than bentonite and sepiolite from water.

As summarised in Table 6.3, K_d and $Cs_{0.3}$ values decrease from 0.770 and 0.231 for illite up to 0.183 and 0.055 for sepiolite. The greatest values were found for illite compared to the others

These results can be explained by taking into account the cationic character of paraquat considering an ion- exchange reaction with inorganic cations present at the clay surface. Cation exchange is the basic mechanism uptaking of paraquat by clays but as indicated by Haque et al. that charge transfer between the organic cation and anionic slicate framework may also be involved. According to Rytwo G., et al. paraquat does not bind to the neutral silanol sites and divalent organic cations bind to the charged sites only.

6.3. Adsorption of Paraquat on Organo-Clays

The adsorption isotherms for paraquat on modified clays were shown in Figure 6.5 and Figure 6.6. NI, NS, NB can be seen in Figure 6.5 and DS, DB, DI in Figure 6.6

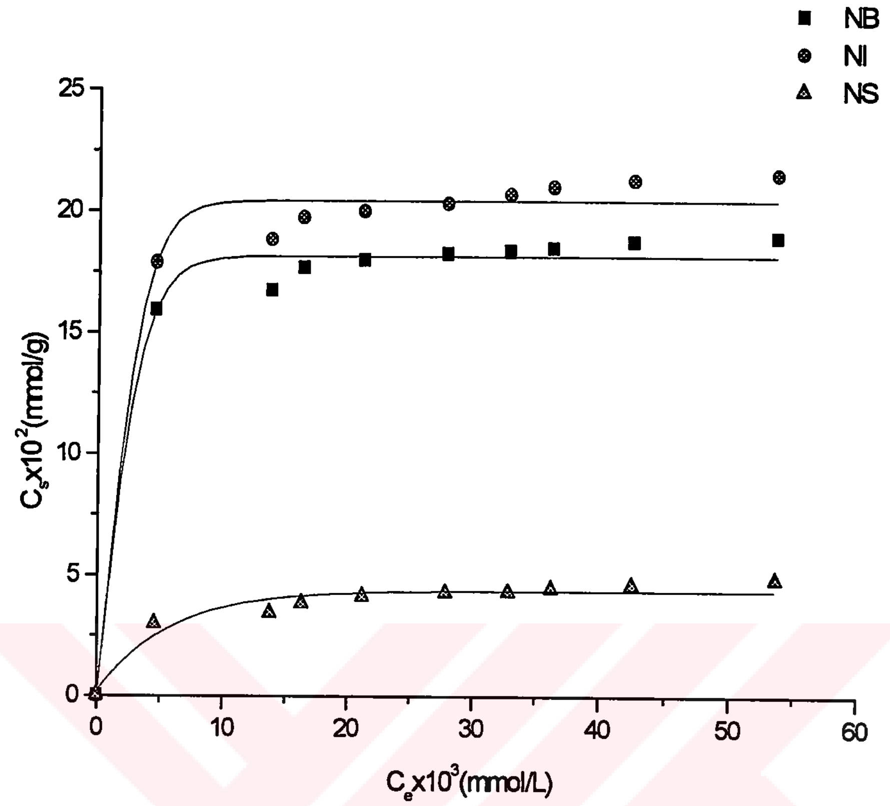


Figure 6.5 Adsorption Isotherm for Paraquat on NB, NI, NS

As can be seen from Figure 6.5, according to the slope of initial portion of the curves, the isotherms corresponding to NI and NB may be classified as H type in terms of Giles classification (Giles et al., 1960). As was mentioned above, H type isotherm suggests strong affinity of paraquat on modified samples and indicates no competition between paraquat molecules and solvent for sorption sites. On condition that the curves reach plateau, a complete monolayer of paraquat molecules covering the modified clays will form. This fact is also valid for NI, NB, and NS sample indicating a complete saturation of the surface by paraquat molecules. Surface saturation occurs within 0.200 mmol/g for NI, 0.175 mmol/g for NB. From NS curve, we deduced that it displayed L type isotherm according to Giles classification. NS has a medium affinity for paraquat showing a saturation plateau from 0.04 mmol/g implying a competition between paraquat molecules and solvent molecules for sorption places.

Adsorption isotherms of clays modified with dodecylammonium ion can be seen in Figure 6.6.

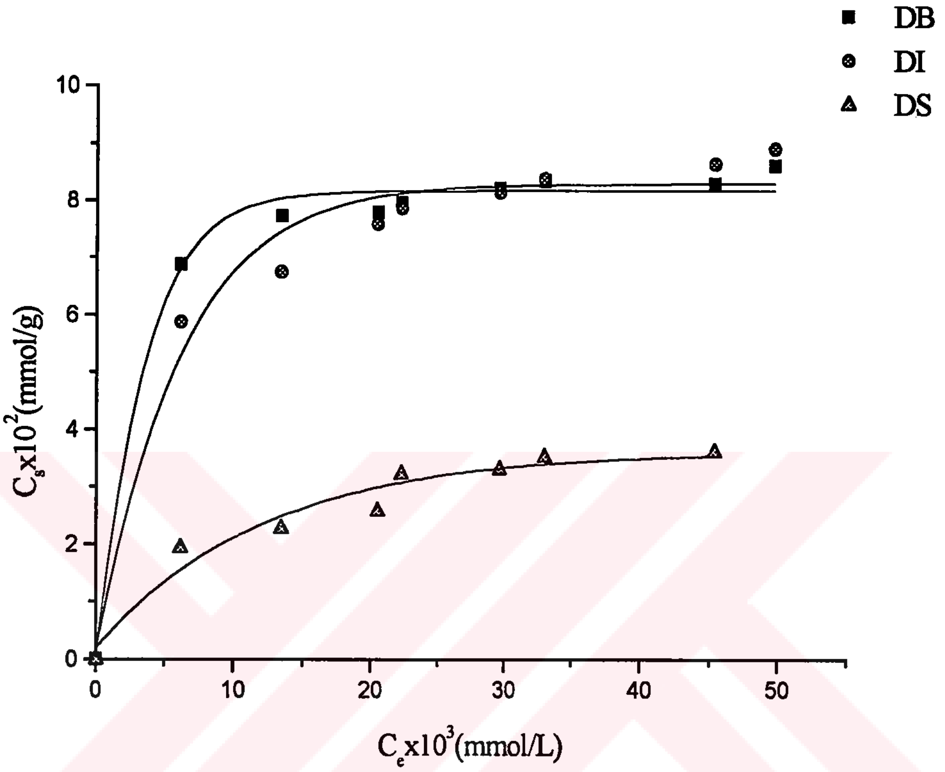


Figure 6.6 Adsorption Isotherm for Paraquat on DB, DI, DS

From this point of view, DB and DI have H type isotherm and DS has L type isotherm reaching plateau and showing surface saturation in 0.08 mmol/g for DB and DI, 0.03 mmol/g for DS by paraquat molecules, as can be seen in Figure 6.6

As a result of fact that modifying natural clays with nonylammonium chloride is more effective way to remove paraquat from water than modifying them with dodecylammonium ion. In order to determine the adsorption capacities of modified clays the logarithmic forms of Langmuir and Freundlich equations were used. Both equations described paraquat adsorption quite well on all adsorbents

Figure 6.7 and 6.8 represent the application of Langmuir equation to adsorption data of paraquat on NI, NB, NS and DI, DB, DS respectively.

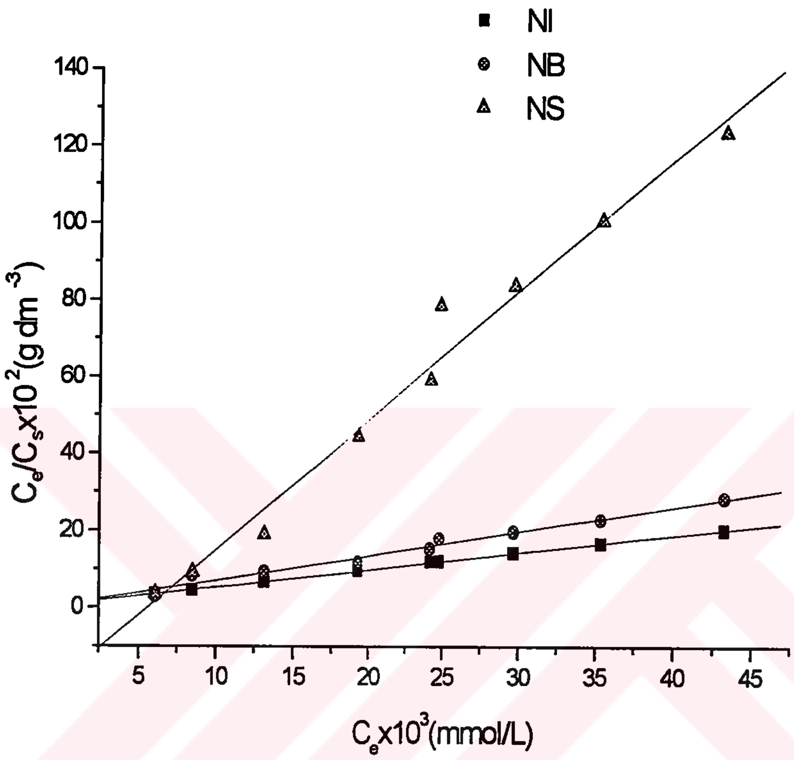


Figure 6.7 Application of Langmuir Equation to Adsorption Data of Paraquat on NB, NI, NS

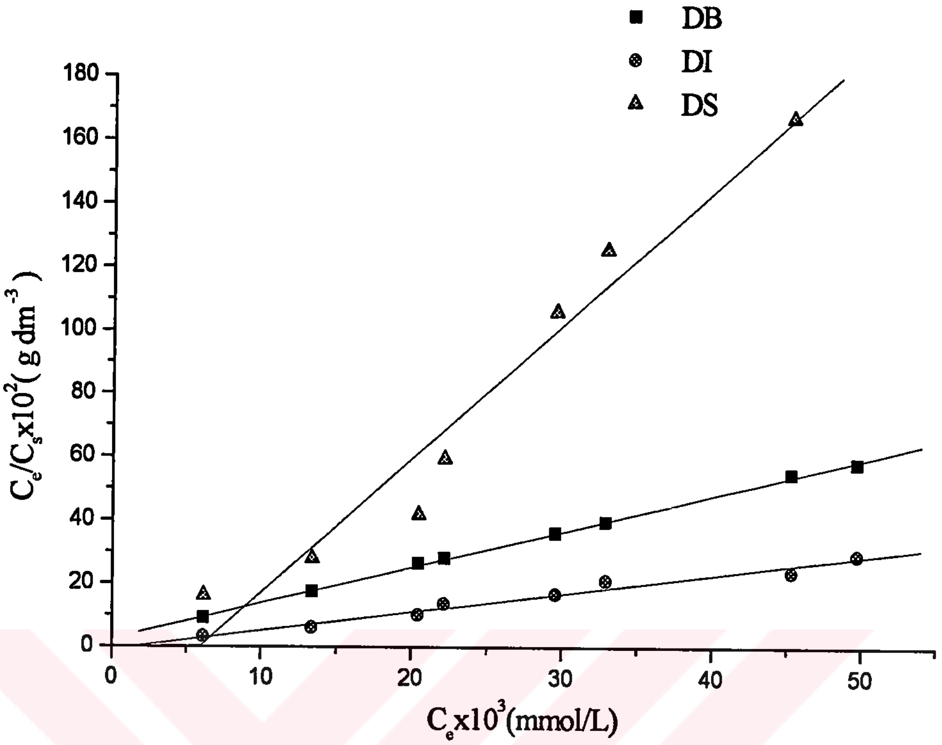


Figure 6.8 Application of Langmuir Equation to Adsorption Data of Paraquat on DB, DI,

For all of them, the correlation coefficients were greater than 0.9980 being significant 0.0001 probability level. Parameters of Langmuir equation for adsorption of paraquat on modified clays (NI, NB, NS, DI, DB, DS) were calculated from linear regression method applied to straight lines in Figure 6.7 and Figure 6.8 and these results were summarised in Table 6.4.

Table 6.4 Langmuir Parameters of DS, DB, DI, NS, NB and NI

Sample	R	C_m (mmol/g)	L
DS	0.9991	0.382	0.240
DB	0.9999	0.905	0.367
DI	0.9989	0.949	0.208
NS	0.9980	0.479	0.499
NB	0.9997	1.940	0.606
NI	0.9998	2.229	0.557

Adsorption capacities increase in the order of 0.382 mmol/g for DS, 0.479 mmol/ g for NS, 0.905 mmol/g for DB, 0.949 mmol/g for DI, 1.940 mmol/g for NB and 2.229 mmol/g for NI. The order is as indicated below;

NI > NB > DI > DB > NS > DS

Dodecylammonium modified clay samples showed low sorption of paraquat herbicide. On the contrary of this result, the highest sorption values for paraquat were obtained with clays modified nonylammonium ions. Among the modified samples, NI is the best adsorbent for paraquat molecules and also DS is the worst adsorbent for adsorbate. As given in Table 6.4, L values increase from 0.240 for DS up to 0.606 for NB. The other values are 0.367 for DB, 0.208 for DI, 0.499 for NS, and 0.557 for NI. The order of the adsorbents against paraquat is as follows:

DI < DS < DB < NS < NI < NB

In order to evaluate the adsorption data efficiently, Freundlich equation was applied to results of modified samples. Figure 6.9 and Figure 6.10 depict the application to adsorption data of paraquat on NI, NB, NS and DI, DB, DS respectively. The correlation coefficients were bigger than 0.9742 being significant at the 0.0001 probability level.

Parameters of Freundlich equation were obtained by using linear regression applied to the straight lines in Figure 6.9 and Figure 6.10. Freundlich constants and distribution coefficients were displayed in Table 6.5 and Table 6.6 respectively. The higher paraquat sorption measured in nonylammonium modified clays as compared with dodecylammonium modified samples and unmodified samples. An important contribution of modifying agents in the paraquat – organoclay interaction can be concluded. As a measure of the organic moiety efficiency to sorp paraquat was given in Table 6.6 and calculated as below

$$K_{oc} = Kd_{0.3}\ /\ (\%\ OC)\ \times 100$$

$Kd_{0.3}$: Distribution coefficient ($C_e = 0.3$ mM)

OC : Organic carbon

K_{oc} : Distribution coefficient on organic carbon basis

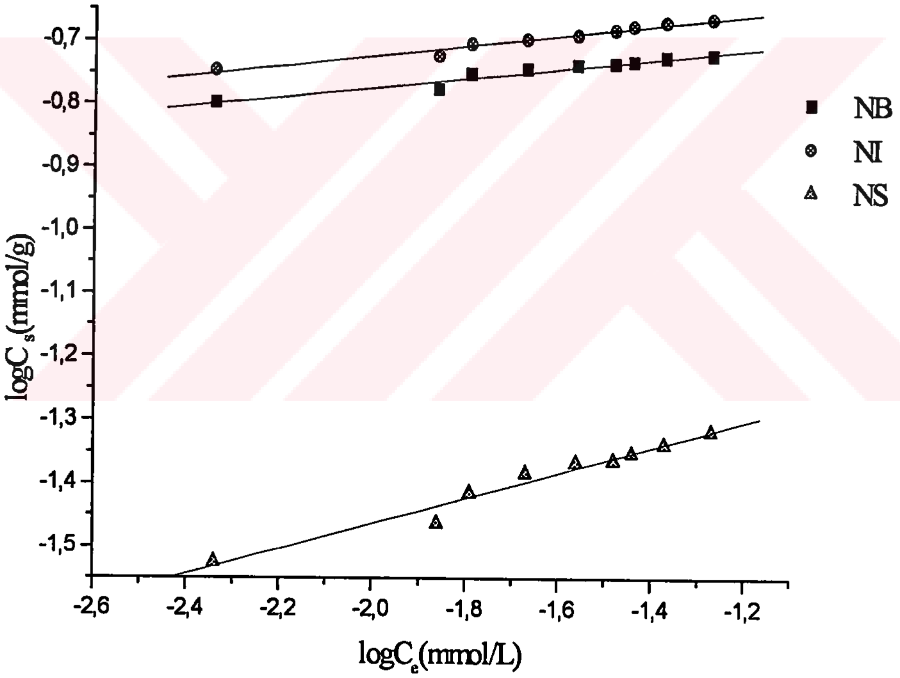


Figure 6.9 Application of Freundlich Equation to Adsorption Data of Paraquat on NB, NI, NS

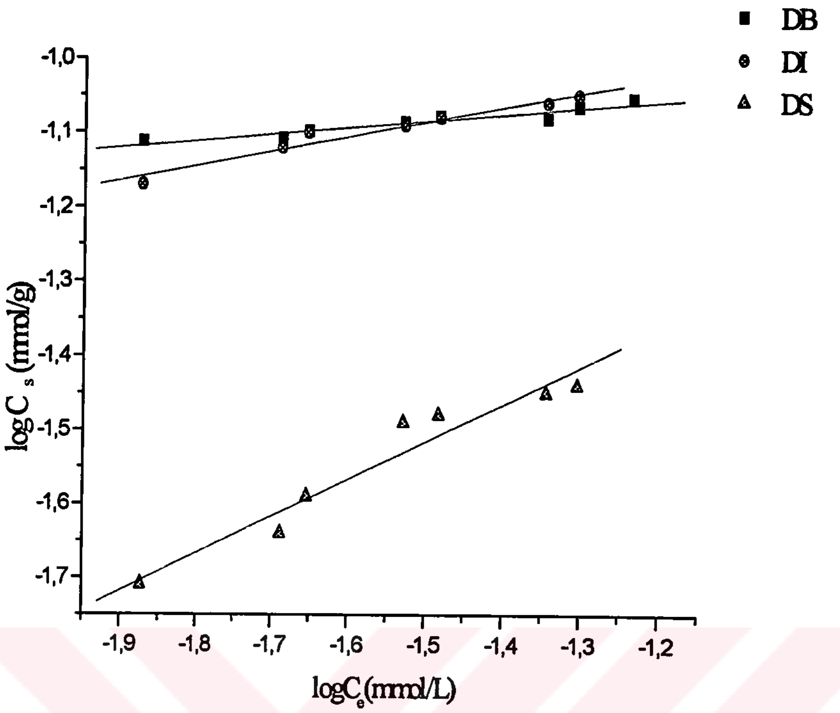


Figure 6.10 Application of Freundlich Equation to Adsorption Data of Paraquat on DB, DI, DS

Table 6.5 Freundlich Parameters of Paraquat on Organo-clays

Sample	R	K_f (mmol/g)	n_f
DI	0.9970	0.151	0.182
DB	0.9789	0.116	0.101
DS	0.9837	0.070	0.217
NI	0.9821	0.280	0.084
NB	0.9742	0.236	0.074
NS	0.9942	0.065	0.111

As pointed out in Table 6.5, Kf values are in order of 0.065 mmol/ g for NS, 0.070 mmol/g for DS, 0.116 mmol/g for DB, 0.151 mmol/g for DI, 0.236 mmol/g for NB and 0.280 mmol/g for NI. This led to conclusion that maximum K_f value was found for NI, removing more paraquat than the other adsorbents from water. The order is NI > NB > DI > DB > DS > NS.

As can be seen above, modifying sepiolite with nonyl or dodecylammonium is not effective way to remove paraquat from water like sepiolite

In contrast with K_f values, n_f values decrease from 0.217 for DS up to 0.084 for NI the order being

DS > DI > NS > DB > NI > NB

Table 6.6 Distribution Coefficients for Organo-clays

Sample	$Cs_{0.3}$ (mmol/g)	$Kd_{0.3}$	K_{oc} x10^4
DI	0.122	0.407	6.35
DB	0.103	0.343	2.04
DS	0.053	0.177	1.35
NI	0.253	0.843	23.7
NB	0.216	0.72	10.3
NS	0.056	0.187	9.84

According to the Table 6.6, $Cs_{0.3}$ and $Kd_{0.3}$ values increase in order of DS, NS, DB, DI, NB, NI and the highest $Cs_{0.3}$ and $Kd_{0.3}$ values were observed for NI as 0.253 mmol/g and 0.843 respectively. K_{oc} values reduce from 23.7 x 10^{-4} for NI to 1.35 x10^{-4} for DS. In combination with the previous results, it is probable that modification of clays with nonylammonium is more effective than unmodified clays and clays modified with dodecylammonium chloride ion. NI is the most effective adsorbent to remove paraquat from aqueous solution. The distribution coefficient on organic carbon basis K_{oc} values is in accord with the justification mentioned above.

CONCLUSIONS

The specific surface areas of modified and unmodified samples were determined by using BET method after N_2 adsorption at 77 K and the results were given in Table 5.1 and Table 5.13. As shown in Table 5.1 and 5.13 the surface areas of bentonite, DB and NB are 73 m^2/g, 10 m^2/g, 50 m^2/g respectively. As can be seen from tables, after modification the surface area values are decreasing due to the blocking of the pores. The surface area of NB is greater than DB because nonylammonium ion is smaller than dodecylammonium ion. DB has the lowest surface area because of the being long alkyl chain that covers the pores. This trend is valid for monolayer volume of samples whose order of DB < NB < B as indicated in Table 5.13. The surface area values are 200 m^2/g, 136 m^2/g, and 100 m^2/g for illite , NI, DI samples and also monolayer volume results are proportion to surface area values decreasing in order of illite, NI and DI respectively. In case of sepiolite, NS and DS samples, surface areas are 292 m^2/g, 171 m^2/g, and 178 m^2/g respectively. The monolayer volumes are increasing from 67.07 cm^3/g for sepiolite to 40.97 cm^3/g for DS. In addition to this, there is not a great difference between the surface area values of DS and NS. The monolayer volumes of DS and NS are also similar. It is probable that the saturation of nonylammonium ion occurs greater than dodecylammonium ion. The adsorption- desorption isotherms of the samples were given in Figures 5.2, 5.3, 5.4, 5.5, 5.6 5.7, 5.8, 5.9, 5.10. The shapes of isotherms can be classified as Type II according to the BDDT classification (Brunauer et al., 1940). The isotherms of Type II show the physical adsorption of gases by solids which reflect mainly mesoporosity.

The specific surface areas of dodecylammonium modified samples are lower than nonylammonium modified samples and natural clays and nonylammonium modified samples adsorbs more paraquat in our work. It can be anticipated that the adsorption mode of paraquat onto samples is not only as a physical adsorption but also appears as chemical adsorption. As can be seen from results surface areas reduce after modification in the natural clays and especially in dodecylammonium ion treated samples. Since these organic ions degrade the porous structure as a consequence of ion exchange reaction with inorganic cations. The pore size distribution of natural samples and modified samples were shown in Tables 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 5.10, 5.11 and 5.12. As given in Tables 5.4, 5.5, 5.6, there is no any micropore in bentonite and modified bentonite samples. As can be seen in Tables 5.7, 5.8, 5.9 the amounts of micropores increase in order of illite, DI and NI, however the amounts of mesopores reduce. As displayed in Tables 5.10, 5.11, 5.12, micropores of DS are greater than sepiolite and NS. The macropores volume of NS was also greater than the others. The samples have mainly mesopores with a pore size of 20-100 nm. This case reduces the surface areas and adsorption capacities of the samples.

The basal spacing and XRD data were determined from XRD analysis of bentonite and modified bentonite samples which were given in Tables 5.1, 5.3, Figures 5.11, 5.12 and 5.13. The basal spacing values of bentonite, NB and DB are increasing in order of 7.629 Å for bentonite, 13.689 Å for NB and 18.059 for DB implying that an external organic thickness of 6.060 Å for NB and 10.430 Å for DB respectively. In agreement with the length of alkyl chains of dodecylammonium ion, DB posseses the longest basal spacing values. The organic layer thickness of NB (6.060 Å) is approximately two times bigger than the thickness of the paraquat molecules (3.6 Å). In the case of NB, the thickness of organic layer (10.430 Å) is the smaller than the length of paraquat molecules (13.4 Å) which could be adsorbed by weak liophylic (ring–tail) attraction. An ion-exchange can occur between organic cations and paraquat molecules because of the being a cationic organic substances.

The basal spacing values and XRD data obtained from XRD analysis of illite and modified illite samples were shown in Tables 5.1 and 5.3. and Figures 5.14, 5.15, and 5.16. The results are 10.106 Å, 18.392 Å, 14.482 Å for illite, DI, and NI respectively. The longest basal spacing value was observed for DI and it may be ascribed to the fact that of all the modifying agents, dodecylammonium ion is the longest one. In accordance with the basal spacing values, the organic layer wideness is increasing in the order of NI (4.37 Å) and DB (8.5 Å). This means that paraquat molecules may penetrate parallel to the silicate layer as in the case of NI. On the other hand, it may arrange with a tilting into the interlayer in DI sample

The d_{001} values of Sepiolite were shown in Figures 5.17, 5.18, and 5.19 and in Tables 5.1, 5.2. The d_{001} results are 12.561 Å, 12.096 Å and 12.470 Å for sepiolite, NS and DS respectively. As can be seen from Figures, there is no further difference with the d_{001} values of sepiolite and modified sepiolite samples. Sepiolite has an open structure exhibiting microfobrous morphology with a specific surface area (292 m^2/g) and monolayer volume (67.07 cm^3/g) due to intracrystalline cavities (tunnels). Silanol groups (Si-OH) are present at the border of each block (at external surface). Silanol groups are usually accessible to organic species (N sites). Due to isomorphic substitution (in the tetrahedral sheet such as Al^{+3} for Si^{+4} and in the octahedral sheet such as Mg^{+2} for Al^{+3}) exchangeable cations such as Na^+, Ca^{+2} exist to compensate for the electrical charge. It constitutes charged adsorption sites (P sites). There is no further difference because modifying agents such as dodecylammonium and nonylamonium couldn't enter the interior channels of sepiolite. These cations can subject to an ion exchange reaction with inorganic cations located external surface. In addition to this adsorption of organic cations can occur to external neutral sites or sites where large structural defects exist.

TGA and DTG curves of Bentonite were shown in Figure 5.20. In the range of 10-160 °C, 9.404 percent of total mass loss occurs owing to the releasing of adsorbed water. There is a peak at 610-710 °C because of the releasing of lattice OH water. TGA and DTG curves of NB were given in Figure 5.22. Mass loss with five steps can be seen in TGA curves. The maximum values of the peaks are 44.1, 345.6, 412, 612.9 and 651.3 °C. In the range of 310-410 °C, decomposition of nonylammonium ion occurs. Lattice OH water was released in two steps between 610-710 °C. TGA and DTG curves of DB were shown in Figure 5.21 consisting of eight steps. The loss in weight at 210-410°C can be attributed to the decomposition of dodecylammonium ion. Lattice OH water was released in two steps as NB. In terms of TGA results, total weight losses are 14.86 percent, for natural bentonite 13.68 percent for NB, 28.703 percent for DB respectively. The difference between B and NB is near but between B and DB is very high. Modification process couldn't occur as successful as for NB. This means that dodecylammonium ion subjects to ion exchange reaction more than nonylammonium ion. An ion exchange reaction occurs between paraquat molecules and inorganic cations within adsorption process. As a result the adsorption capacities of NB for paraquat increased

TG and DTG curves of illite were shown in Figure 5.23. Dehydration of illite proceeded in three steps.The mass loss between 20-180°C is less than 1 percent and this can be attributed to the loss of adsorbed water. When the sample was heated to higher than 500 °C the loss of lattice OH water occurs. This case can be seen in DTG curve with a big peak. TG and DTG curves of NI were shown in Figure 5.25. In TGA curve, the loss weight of NI upon heating consist of six steps. Maximum values of these peaks are 32.6, 51.8, 78.5, 211.7, 349.3 and 449.6 °C. The peaks between 10-110 °C are due to the loss of adsorbed water. In the range of 210-360 °C, decomposition of nonylammonium ion occurs. The loss in weight from 410 to 510 °C can be attributed to the loss of lattice OH water. This can be seen with a broad peak in DTG curve. TGA and DTG curves of DI were given in Figure 5.24 consisting of five steps. In 10-110 °C, total mass loss is 11.8 percent which is because of the adsorbed water. In the range of 180 °C and 320 °C decomposition of dodecylammonium ion occurs. Dehydroxylation can be seen between 420 - 520 °C.

According to TGA results total weight changes are 4,68 percent for natural illite, 13.69 percent for nonylammonium illite, 15.96 percent for dodecylammonium illite at 20-800°C respectively. Differences between illite and NI are 9.01 percent, for illite and for DI, 11.28 percent. This led to conclusion that dodecylammonium ions subject to ion exchange reaction more than nonylammonium ions. The modification process with dodecylammonium ion and nonylammonium ion occur successfully. After an ion exchange reaction between nonylammonium ion and inorganic cations existing on clay surface and at interlayer, remaining inorganic cations subject to ion exchange reaction with paraquat molecules in such a way that raised up adsorption of paraquat molecules for NI than DI

TGA and DTG curves of Sepiolite samples are presented in Figure 5.26. Sepiolite contains hygroscopic water, channel water (zeolitic water), bound water and lattice OH water in its structure. In TGA curve five steps were observed. Sepiolite showed the 13.2 percent weight loss below 250 °C. The loss was owing to the elemination of channel water as well as hygroscopic water. The loss of bound water began above 250 °C and it is probable that the structure of sepiolite gradually changed into sepiolite anhydride. The transformation of sepiolite to sepiolite anhydride was accomplished at about 451 °C. These peaks were hardly discernible in DTG curve. The peak near 772 °C was due to loss of hydroxyl group and this case can be seen in DTG curve at 772 °C. TGA and DTG curves of NS were presented in Figure 5.28. In TGA curve of NS five mass loss steps were observed. In the range of 20-120 °C, mass loss is about 6.8 percent, because of the loss of channel water. 3.22 percent of weight change occurs owing to decomposition of nonylammonium ion and loss of channel water at 149-357 °C. In the range of 420-620 °C, loss in mass can be attributed to the bound water. This peak can be seen at 520 °C in DTG curve. Lattice OH water was released between 620-800 °C. TGA and DTG curves of DS can be seen in Figure 5.27. Maximum values of peaks are 36.4, 55.9, 379.4 and 766.7 °C. In TGA curve, 10.3 percent of the total weight change occurs in the range of 10-110 °C. But in natural sepiolite, this value was 13.2 percent. This loss can be seen as a big peak in DTG curve. Decomposition of dodecylammonium ion occurs between 310-410, and a broad peak was observed in DTG curve for this case. The mass loss at 720-800°C which can be attributed to the releasing of lattice OH water was 43.0 percent. According to the TGA results for sepiolite total weight losses values are 14.58 percent for natural sepiolite, 16.02 percent for DS, 16.35 percent for NS being the difference between S and NS 1.77 percent, for S and DS 1.44 percent respectively. As can be seen that the difference between DS and NS is very close. Dodecylammonium ion and nonylammonium ion subject to a poor ion exchange reaction. As mentioned above, after ion exchange reaction, there will be another ion exchange reaction among divalent paraquat molecules and remaining inorganic cations.

In terms of B, NB, DB adsorption data which were given in Tables 6.2, 6.3, 6.4, and 6.5 that the amount of paraquat adsorbed is increasing in order of DB, B, NB respectively. With respect to dodecylammonium ion, modification bentonite with nonylammonium ion enhanced the adsorption capacity of Bentonite. NB and B were of H type isotherm but DB of L type in terms of Giles classification. As can be seen from Figures 6.2, 6.5, 6.6. This can be conclusion of that dodecylammonium ion exposed to ion exchange reaction with inorganic cations more than nonylammonium ion. As for illite, DI and NI, adsorption data were shown in Tables 6.2, 6.3, 6.4, and 6.5. The amount of adsorbed is decreasing in order of NI, I and DI respectively. The isotherms of NI and I can be classified as H type but DI, L type isotherm. NI is the most efficient adsorbent between illite and modified illite samples. It can be pursued about the conclusion that nonylammonium ion subjects much more ion-exchange reaction with inorganic cations than dodecylammonium ion. The adsorption results of sepiolite and modified sepiolite samples were presented in Tables 6.2, 6.3, 6.4, and 6.5. The amount of adsorbed paraquat is in agreement with previous findings for bentonite and illite samples and being order NS > S > DS respectively.

The experimental data indicated that the rate of adsorption have increased in order of dodecylammonium modified samples, natural clays, nonylammonium modified samples for paraquat respectively. The slopes of the curves are smaller than 1 ($n < 1$) and it expressed that as the initial concentration of paraquat increased, the percentage adsorbed by treated samples and natural clays decreased

It can be concluded that in emergency treatment, NI can be used as an excellent oral adsorbent for the acute paraquat poisoning. The second conclusion is that NI can be used to remove paraquat herbicide from water

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