ORGANOCLAY PREPARATION FOR ANIONIC CONTAMINANT REMOVAL FROM WATER

DENİZ İNAM

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ORGANOCLAY PREPARATION FOR ANIONIC CONTAMINANT REMOVAL FROM WATER

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Approval of the Graduate School of Natural and Applied Sciences.

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ABSTRACT

ORGANOCLAY PREPARATION FOR ANIONIC CONTAMINANT REMOVAL FROM WATER

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Increasing concern about the pollution of environment by inorganic and organic chemicals arising from naturally occurring ecological events and industrial processes has created a need for the search of new techniques in the removal of these contaminants.

One of the natural material that can be used in such processes is clay. Clay minerals have large surface areas and high cation exchange capacities which enables them to be modified by cationic surfactants. The material prepared, often called as ‘organoclay’, can be used to remove hydrophobic organic and anionic contaminants from polluted water.

Among the anionic contaminants, oxyanions such as nitrate, chromate are detrimental to human life and environment even at µg/L- mg/L levels. Application of organoclays for their removal from polluted water appears as one of the practical and rather cheap solution.

In this study, a local clay from Ankara-Kalecik (Hançılı Bentonite) was modified by hexadecyltrimethylammonium bromide (HDTMA-Br) to a level of twice of its cation exchange capacity. This process alters the negatively charged surface of the clay into a positively charged one, providing sites for the removal of anionic contaminants. In this study, the degree of $HDTMA^+$ uptake by the clay within a period of eight hours is found to be 97% of the initial amount added.

In desorption studies it was revealed that only about 1% of the sorbed $HTDMA^+$ was leached in a seven days of water-organoclay interaction revealing a rather stable organoclay structure in aqeous media.

Sorption experiments with nitrate, borate, and chromate solutions were performed in order to determine the anion sorption capacity of the organoclays prepared. It turns out that while untreated clay has insignificant capacity, the modified clay can remove considerable amount of nitrate and chromate ions from aqeous solutions. While the nitrate sorption was increased about eleven fold, change in chromate sorption was reached to a level of twenty fold compared to that of the untreated clay. Sorption data for nitrate and chromate are both well described by the Langmuir isotherms. No

significant change was observed in case of borate-organoclay interaction. Desorption of nitrate and chromate ions from organoclay surface were also investigated. Sorption of these oxyanions were found to be almost irreversible in aqeous media.

The results imply that a properly prepared organoclay can be used for the removal of oxyanions, such as nitrate and chromate from polluted water systems.

Keywords: Organoclay, Hexadecytrimethylammonium Bromide, Nitrate, Chromate, Borate, Sorption, Desorption.

ÖZ

SUDAKİ ANYONİK KİRLETİCİLERİN UZAKLAŞTIRILMASINDA KULLANILMAK ÜZERE ORGANO-KİL HAZIRLANMASI

İnam, Deniz

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Tez Yöneticisi: Prof. Dr. E.Hale Göktürk

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Endüstriyel gelişmeler ve kendiliğinden gerçekleşen ekolojik olaylardan kaynaklanan anorganik ve organik kimyasallar ile çevrenin kirlenmesi konusunda giderek artan endişe, bu kirliliklerin uzaklaştırılmasında yeni tekniklerin araştırılması ihtiyacını doğurmuştur.

Kil, bu işlemlerde kullanılabilecek tabii malzemelerden biridir. Kil mineralleri, katyonik yüzey tutucular ile değiştirilebilmeye olanak sağlayan geniş yüzey alanlarına ve yüksek katyon tutma kapasitelerine sahiptir. Bu şekilde hazırlanan ve genellikle ‘organik kil’ olarak adlandırılan bu

materyal kirlenmiş sudan hidrofobik ve organik kirliliklerin uzaklaştırılmasında kullanılabilir. Sudaki anyonik kirliliklerden nitrat ve kromat gibi oksianyonlar insan yaşamı ve çevre için µg/L-mg/L seviyelerde bile zararlıdır. Bunların kirli sudan uzaklaştırılmasında organik killerin kullanılması pratik ve oldukça ucuz bir çözüm olarak ortaya çıkmaktadır.

Bu çalışmada, Ankara-Kalecik bölgesinden alınan yerel kil heksadesiltrimetilamonyum bromür (HDTMA-Br) ile katyon tutma kapasitesinin iki katı oranında muamele edilmiştir. Bu işlem ile negatif yüklü kil yüzeyi pozitif yüklü hale getirilerek anyonik kirliliklerin uzaklaştırılması için kil yüzeyinde gerekli yapı sağlanmıştır. Bu çalışmada, sekiz saatlik bir zaman aralığında, kil yapısına, başlangıçta ilave edilen $HDTMA^+$'nın 97%'inin tutulduğu gözlenmiştir.

Geri bırakma deneyleri sonucunda ise yedi gün süresince su ile etkileşimde bulunan organik kil yapısından sadece 1% mertebesinde $HDTMA^+$ iyonunun ayrıldığı gözlenirken organik kil yapısının sulu ortamda oldukça kararlı olduğu açığa çıkmıştır.

Hazırlanan organik killerin oksianyon tutma kapasitelerinin tayini için nitrat, borat ve kromat çözeltileri ile tutunma deneyleri gerçekleştirilmiştir. Modifiye edilmemiş kilin bu anyonları tutma kapasitesi çok düşük olarak gözlenirken, organo kilin sulu ortamdan önemli miktarda nitrat ve kromat iyonlarını uzaklaştırdığı anlaşılmıştır.

Nitrat tutunması orjinal kile göre onbir kat artarken, kromat tutunmasındaki değişiklik modifiye edilmemiş kile oranla yirmi kat seviyesine ulaşmıştır. Nitrat ve kromat iyonlarının organik kile tutunma şekli Langmuir izotermlerine uygunluk göstermektedir. Borat-organik kil etkileşimi sonucunda önemli bir değişiklik gözlenmemiştir.

Nitrat ve kromat iyonlarının organik kil yüzeyinden geri bırakılmaları da incelenmiştir. Bu oksianyonların organik kile tutunmalarının sulu ortamda hemen hemen tersinir olmadığı gözlenmiştir.

Sonuçlar, uygun şekilde hazırlanmış organik killerin nitrat ve kromat gibi oksianyonların kirlenmiş sudan uzaklaştırılmasında kullanılabileceğini göstermektedir.

Anahtar Kelimeler : Organik kil, Heksadesiltrimetilamonyum bromür, nitrat, kromat, borat, tutunma, geri bırakılma.

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INTRODUCTION

1.1 Clays and Clay Minerals

In general, the term **clay** implies a natural, earthy, fine grained material which develops plasticity when mixed with a limited amount of water. Clay material is also highly impermeable, easy to engineer and highly abundant.

A natural clay consists of one or different type of clay minerals together with some impurities. The most common impurities in a natural clay are quartz, calcite, feldspar, mica and organic matter while hydrated iron oxide, ferrous carbonate and pyrite are being the minor impurities. Clay mineral is a well defined substance that gives the characteristic properties to a natural clay. Clay minerals are concentrated in a size less than 2 μm and are phyllosilicates with continuous sheet structures like micas. Clay minerals are formed by the hydrolysis of aluminum or magnesium silicates of alkali and alkaline earth metals. Most of them are entirely or almost entirely crystalline (Grim, 1953).

The properties that affect most of the physical properties of a clay are particle size, shape, cation exchange capacity and the type of impurities present.

The main three reasons for the importance of clay minerals as solid phase components in natural systems are as follows: First, they have very large specific surface areas (between 10 and 700 m^2/g) in comparison to other components. Second, this surface often has an electrical charge due to their structure and the presence of broken bonds at the crystal edges. This causes the accumulation of inorganic and/or organic cations and it is responsible for the high water retention capacity for many clays. Finally, naturally occurring clay particles are often coated by amorphous oxides and humic materials and they serve as efficient templates for secondary solid phases. As a result, the presence of even small amounts of these fine-grained materials on a mass basis exerts a large influence on the behaviour of organic and inorganic solutes in soil and subsurface environments. Although other solid phases present in the soil are known to interact strongly with organic solutes such as humic substances, the role of clay minerals has been consistently implicated as a major component in influencing the behaviour of certain classes of organic chemicals in natural systems (Johnston, 1996).

Clays are widely used in various industrial processes and products such as paper, paints, coatings, dyes, cement, ceramics, and filling fluids, etc.

In addition, clay minerals have been commonly used as catalysts for oxidation and/or polymerisation reactions and as molecular sieves in the adsorption of some polar and nonpolar molecules (Esmer and Tarcan, 2001).

1.1.1 Structure of Clay Minerals

Clay minerals are layer-lattice silicates (phyllosilicates). The layer-lattice silicates are made up of combinations of two structural units, a silicon-oxygen tetrahedron, and an aluminum-oxygen-hydroxyl octahedron.

In the tetrahedral sheet, each of the three basal oxygens of a tetrahedron is linked to a neighboring tetrahedron, while the fourth and apical oxygen of all tetrahedra points in the same direction above or below the plane of basal oxygens. The apical oxygens form a hexagonal to pseudohexagonal ring (Figure 1.1a-b). The tetrahedral cations are commonly Si^{4+} and Al^{3+}, but may occasionally be Fe^{3+} and Cr^{3+}.

In the octahedral sheet, each octahedron is linked to its neighbours by shared edges. The cation of each octahedron is co-ordinated by a combination of OH and O ions in the sheets. Ideally, with OH anions co-ordinating the octahedral cation, the octahedral layer sheet forms either a trioctahedral structure in which all cation positions are filled, or dioctahedral structure in which two-thirds of the cation positions are filled.

Because of the size limit, the cation positions are filled by such common medium-sized ions as Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, Mn^{2+} and Li^{+}, and less commonly by Zn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, and the others with similar ion size (Figure 1.1c-d).

The clay mineral structures, based on the combination of tetrahedral and octahedral sheets, are of 1:1, 2:1, and 2:1:1 types. In the 1:1 types consisting of one octahedral sheet and one tetrahedral sheet, the plane of apical oxygens of the tetrahedral sheet is superimposed on the OH plane of the octahedral sheet. The common plane of junction consists of both oxygen and unshared OH. The unshared OH occurs at the center of each six-fold ring defined by the apical tetrahedral oxygens. The 2:1 type is the stacking of an octahedral sheet sandwiched between two tetrahedral sheets, so that their planes of apical oxygens face towards each other. The common planes between the two tetrahedral sheets and the octahedral sheet consist of sharing oxygens and unshared OH's, each unshared OH being at the center of tetrahedral apical oxygen hexagonal rings (Figure 1.2). The 2:1:1 structure consists of a 2:1 layer arrangement with an additional octahedral sheet between 2:1 layers (Clauer and Chaudhuri, 1995).

The thickness of each structural unit depends not only on the number of sheets involved, but also on the composition of tetrahedral and octahedral sheets and the charge compensations as a result of unbalanced

substitutions of cations in the sheets. The net compensating charge may be located either in the interlayer site as in 2:1 layer arrangements or in the additional octahedral sheet as in 2:1:1 layer arrangements. The most common interlayer cations are Ca^{2+}, Mg^{2+}, H^{+}, Na^{+}, K^{+}, NH_4^{+}. Interlayer sites might also be occupied by Fe^{3+} and Al^{3+} in a hydroxy form.

Clay minerals are characterized by the type of layer structure, the composition of the sheets that make up the layer structure, the layer charge, and the composition of the interlayer material. Kaolinite and montmorillonite types of clay minerals are described in the following sections.

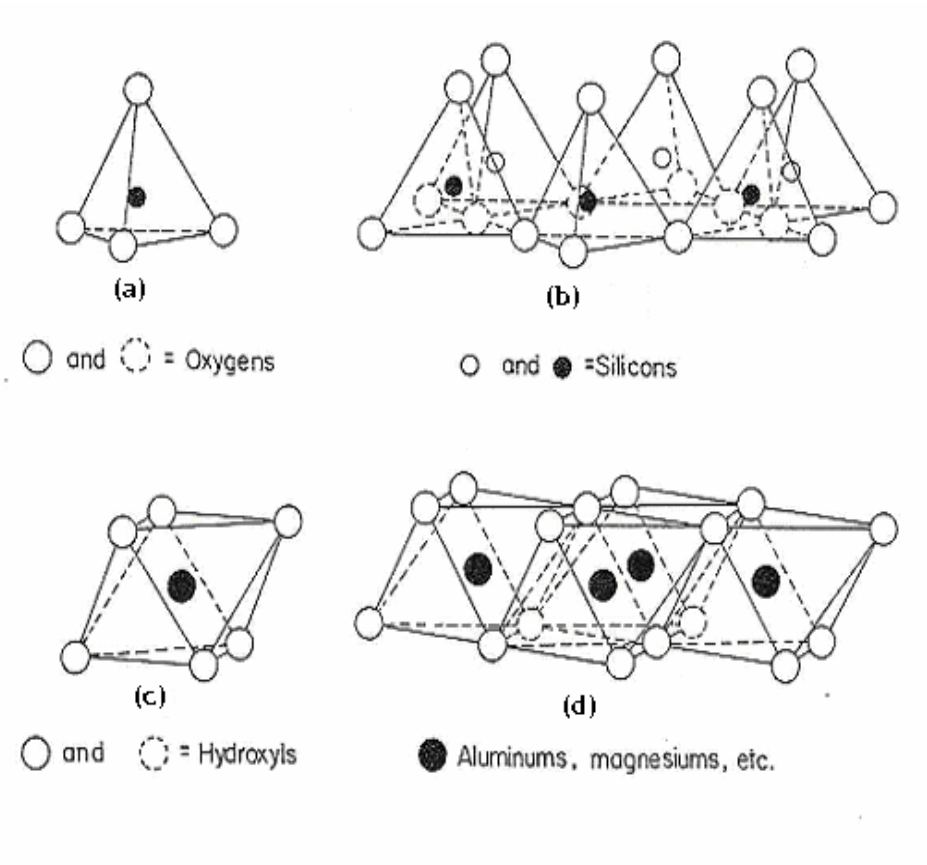


Figure 1.1 Tetrahedral and octahedral layer structures in clay minerals (Grim,1953)

(a) Single tetrahedral unit

(b) Sheet structure of the tetrahedral units

(c) Single octahedral unit

(d) Sheet structure of octahedral units

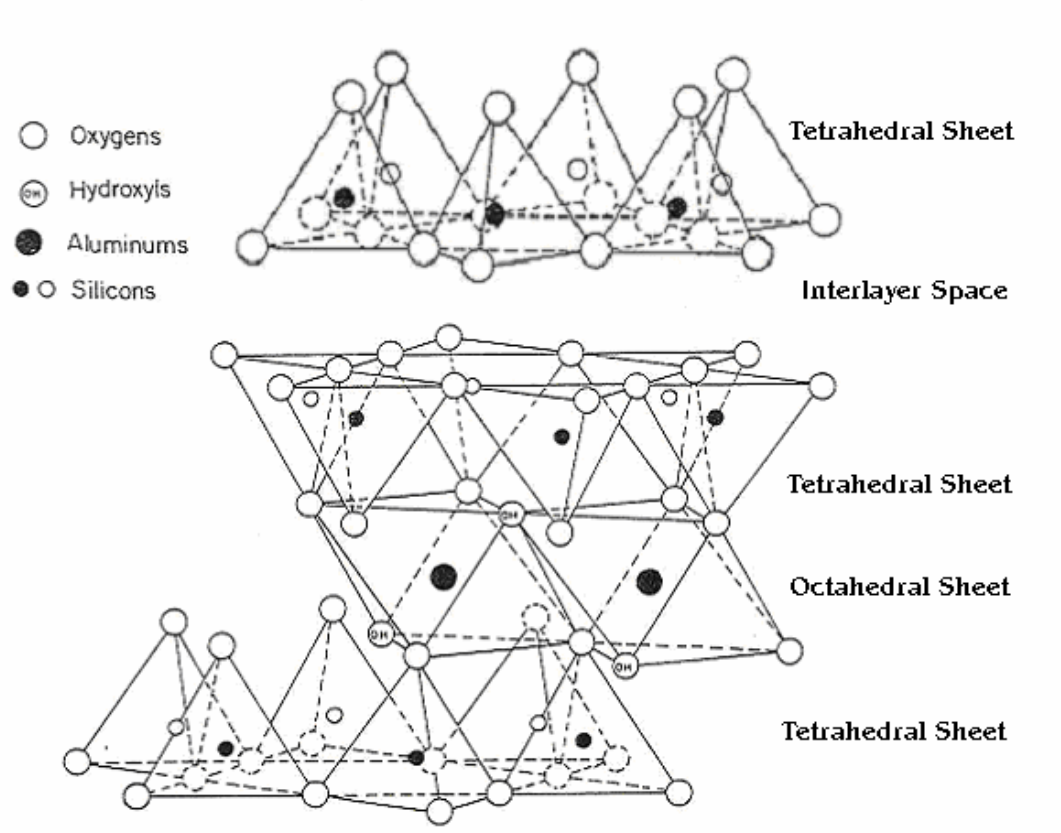


Figure 1.2 Schematic representation of the crystal structure of a 2:1 type clay mineral showing the relations between tetrahedral and octahedral layers,and interlayer spaces. (Clauer and Chaudhuri, 1995)

1.1.1.1 The Kaolin Group; Kaolinite Type of Clay Mineral

Kaolin group is chracterized by a 1:1 layer type without layer charge, and it has a [001] layer spacing of about 7 Aº.

Kaolin minerals consist of Si-O tetrahedral sheet and an Al dioctahedral sheet (Figure 1.3 a). As former one is larger than the latter one, a distortion of the tetrahedral sheet occurs so that its basal dimensions nearly equal that of the octahedral sheet to accommodate the fit between the hexagonal networks of the tetrahedral and the octahedral sheets. Each 1:1 layer is bonded to the adjacent layers by hydrogen bonds between the OH ions in one of the planes of an octahedral sheet in one layer and the basal O ions of the tetrahedral sheet in the next layer. The [001] spacings of the 1:1 kaolin layers range from 7.1 to 7.3 Aº, depending on stacking imperfections. Stacking sequences of layers with different interlayer shifts and different locations of the vacant octahedral cation site result in different polytypes of kaolin minerals. The kaolin subgroup consists of kaolinite, dickite, nacrite, and halloysite minerals.

In kaolinite, the vacant octahedral cation site is same in successive layers. An ideal chemical formula for kaolinite is $Si_4Al_4O_{10}(OH)_8$. However, chemical analyses of kaolinite samples have frequently indicated presence of small amounts of Fe, Ti, Ca, Mg, K, and other elements in trace amounts.

Kaolinite, a common product of weathering in soils, is often present as a detrital component of coastal and off-shore sediments and also sedimentary rocks, especially sandstones (Clauer and Chaudhuri, 1995).

1.1.1.2 The Smectite Group; Montmorillonite Type of Clay Mineral

The minerals belonging to smectite group have 2:1 layer with a range of negative charges between 0.2 to 0.6 per unit cell, averaging at about 0.35 per unit cell. The charge deficiency results from combined isomorphous substitutions in octahedral and tetrahedral sheets. The net charge deficiency is balanced by interlayer cations with one or two water layers at about 50-70 % relative humidities. The interlayer water constitutes an ice-like hexagonal structure.

Dominant exchangeable cations for smectites are Ca^{2+}, Mg^{2+}, Na^{+}, and H^{+} ions differing in the hydration energy, which in part accounts for the variations in the [001] spacings.

Smectites are known as both dioctahedral and trioctahedral types. Common dioctahedral types are montmorillonite, beidellite, and nontronite, whereas common trioctahedral smectites are saponite, hectorite, and stevensite. Dioctahedral types can be differentiated from trioctahedral types by the location of the [060] peak on an X-Ray powder diagram, the former having the reflection at 1.49 to 1.52 Aº, the latter at 1.53 to 1.57 Aº.

In montmorillonite, the layer charge commonly vaires between 0.4 to 1.0, averaging at about 0.7 per unit cell. The origin of layer charge is primarily in the octahedral sheet due to the substitution of Mg^{2+} and also some Fe^{2+} for Al^{3+} and Fe^{3+}. A small amount, less than 5% on the average, of tetrahedral substitution of Al^{3+} for Si^{4+} may also occur in montmorillonite. Representative chemical formula for montmorillonite is $Si_8(Al_{3.34}Mg_{0.66})Na_{0.66}\ (OH)_4O_{20}$ (Clauer and Chaudhuri, 1995).

The structure of montmorillonite; an octahedral sheet sandwiched between two tetrahedral sheets, is shown in Figure 1.3.

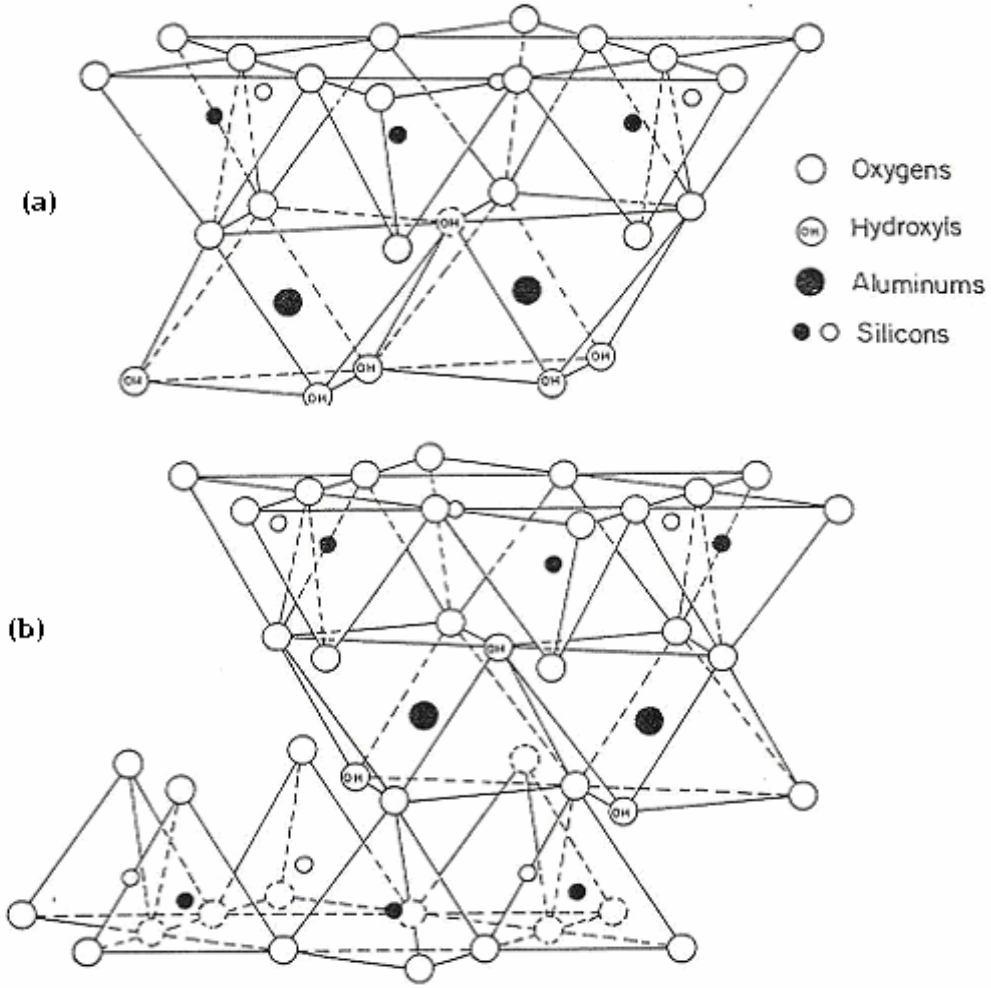


Figure 1.3 Structure of **(a)** Kaolinite, **(b)** Montmorillonite

1.1.2 Cation Exchange Capacity (CEC)

Clay minerals have the ability of adsorbing certain cations and retaining them in exchangeable state. For a given clay, the maximum amount of any one cation that can be taken up is constant and is defined as **cation exchange capacity (CEC) (**Cremers, Pleysier, Chhabra, 1975**)**. It is usually expressed in milliequivalents of cation adsorbed per hundred grams of clay.

The cation exchange capacity (CEC) of kaolinite minerals range from about 3 to 15 meq/100 g. The low values are probably representative of pure kaolinite, and the increase could be due to impurities. Much of the CEC of pure kaolinite is owed to broken bonds at the edges of the crystals, occurring as hexagonal to pseudohexagonal plates and flakes. In the lattice of kaolinite and halloysite type of clays, the oxygen and hydroxyl valancies at the planar surfaces are completely satisfied. At the edges however, there are Al, Si, oxide and hydroxide ions which are not so satisfied. These unsatisfied valancies or broken bonds, as they are often called, are satisfied in practise by external ions that do not form part of the structure but mainly act as ‘balancing’ ions, preserving electrical neutrality. These balancing ions are capable of being exchanged for others and are possible cause of cation exchange in clay minerals.

If a clay is placed in a solution of a given electrolyte following exchange occurs:

$$\mathbf{X\text{-}Clay + Y^{+} = Y\text{-}Clay + X^{+}}$$

Smectites have varied CEC between 80 and 150 meq/100 g. The CEC of smectites is about ten times higher than that of other clay minerals. About four-fifths of the CEC relates to the exchangeable interlayer cation and the rest to bonds at the edges of the crystallites. Additional balancing cations which are present because of the isomorphous substitution of cations, like Al^{3+} substitution for Si^{4+}, are the principal cause of cation exchange in many phyllosilicate clay minerals like montmorillonite and illites.

1.1.3 Bentonite Clay in General

The term **'bentonite'** stands for a soil or rock containing mostly montmorillonite type of clay mineral. First occurrence of bentonite clay was observed near Fort Benton in the state of Wyoming, USA **(**Data Handbook, Clay Minerals Society**)**

Bentonite clay is an alteration product of glassy igneous material, usually a tuff or volcanic ash. The composition of tuff or ash is an important factor affecting the characteristic properties of the resulting bentonite structure.

Sodium, calcium, and magnesium cations are exchangeable giving the montmorillonite a high cation exchange capacity. The industrial bentonites are generally either in sodium or calcium variety. Sodium bentonite has a high swelling capacity, and forms gel-like masses when added to water (Murray, 2002).

The general properties that make the bentonite clay commercially important are:

- the ability of swelling to several times of its orginal volume in water, caused by adsorption of water molecules at the interlayer cations and at the clay mineral surface
- the high cation exchange capacity
- the very small particle size, compared with other clay minerals such as illite and kaolinite

There are bentonite deposits all over the world. Their mineralogical composition varies significantly. In Europe, there are bentonite clays with large quantities and high qualities in Greece, Italy, Spain, Great Britain, Cyprus, Bulgaria, Hungary, the Czech and Slovakian Republics . The largest sodium bentonite deposits are located in the Western United States in Wyoming, Montana, and South Dakota. These sodium bentonites are also called Western or Wyoming bentonite which means a high swelling sodium bentonite.

Other smaller sodium bentonite deposits occur in Argentina, Canada, China, India, and South Africa (Murray, 2002). The bentonite reserves of world is given in Table 1.1.

Table 1.1 Bentonite reserves of world in billion tones (VIII. Beş Yıllık Kalkınma Planı, Madencilik Özel İhtisas Kurulu Raporu, 2001)

AMERICA	950
EUROPE	720
USSR TURKEY OTHERS	250 370 50
AUSTRALIA	50
OTHERS	150
TOTAL	1870

White bentonite occurences are in Texas, Nevada, US, Greece, Turkey, Italy, and Argentina. About 150,000 tons of white bentonite is consumed annually for markets including detergents, ceramics, paper industry, cosmetics, paint, and wine clarification.

Bentonite clay is very abundant in Turkey, the bentonite reserves are given in Table 1.2. Bentonite is mostly used as drilling fluid, foundry and in casting industries. The use of bentonites in the production of detergents, and paper industry have been also reported (VIII. Beş Yıllık Kalkınma Planı, ÖİK, 2001).

Table 1.2 Bentonite reserves in Turkey (Türkiye Bentonit Envanteri, 182, 1982, MTA)

AREA	RESERVE, ton
Ankara-Kalecik-Hançılı	19.000.000
Ankara-Keskin-Besler	240.000
Artvin-Derinköy	800.000
Çankırı-Çerkes-Bayındır	43.000
Çankırı-Eldivan-KüçükHacıbey	300.000
Çankırı-Eldivan-BüyükHacıbey	100.000
Çankırı-Ilgaz-Kızılibrik	200.000
Çankırı-Eskipazar-Başpınar	800.000
Çorum-Sungurlu-Mecitözü	400.000
Edirne-Enez	50.000.000
Giresun-Tirebolu	4.000.000
İstanbul-Sile-Kızılcaköy-	180.000
Konya-Sağlık	2.400.000
Konya-Sille	24.000
Ordu-Fatsa-Ünye	2.564.000
Tokat-Reşadiye-Akdoğmuş-Kaşpınar	200.000.000
Trabzon-Araklı-Arsin-Yolüstü	60.000

1.2 Hançılı Bentonites

1.2.1 Location of Hançılı Bentonite Clay Used in Experiments

Bentonite beds are observed in widespread areas in Turkey. In this study, commercial Na bentonites from Hançılı, Kalecik in Turkey was used. They are so called 'Hançılı Bentonites'. Bentonites beds exist in Killik site located on 48 km northern part of Kalecik and on 1.5 km southwestern part of Hançılı village. The extend of these beds is 15 km in this region (Güngör, 1992). The location map of Hançılı bentonites is given in Figure 1.4.

1.2.2 Geological Properties of Hançılı Bentonite Clay

The source of Hançılı bentonites was suggested to be andesites and andesitic tuffs which were located on the western part of the Çankırı Basin. After the sedimentation of detritus on a lake floor, by means of the basic influence of the lake water, bentonites were originated (Kurhan, 1966; Özoğul, 1976). In Figure 1.5, the general view of Hançılı bentonite sequence including white(wb), yellow(yb), and green (gb) bentonite is given. Hançılı white bentonite has the highest quality among all the other bentonites in this sequence. The white bentonite becomes greenish when it is in moist state. The colour change also occurs when Hançılı bentonite associates with organic material.

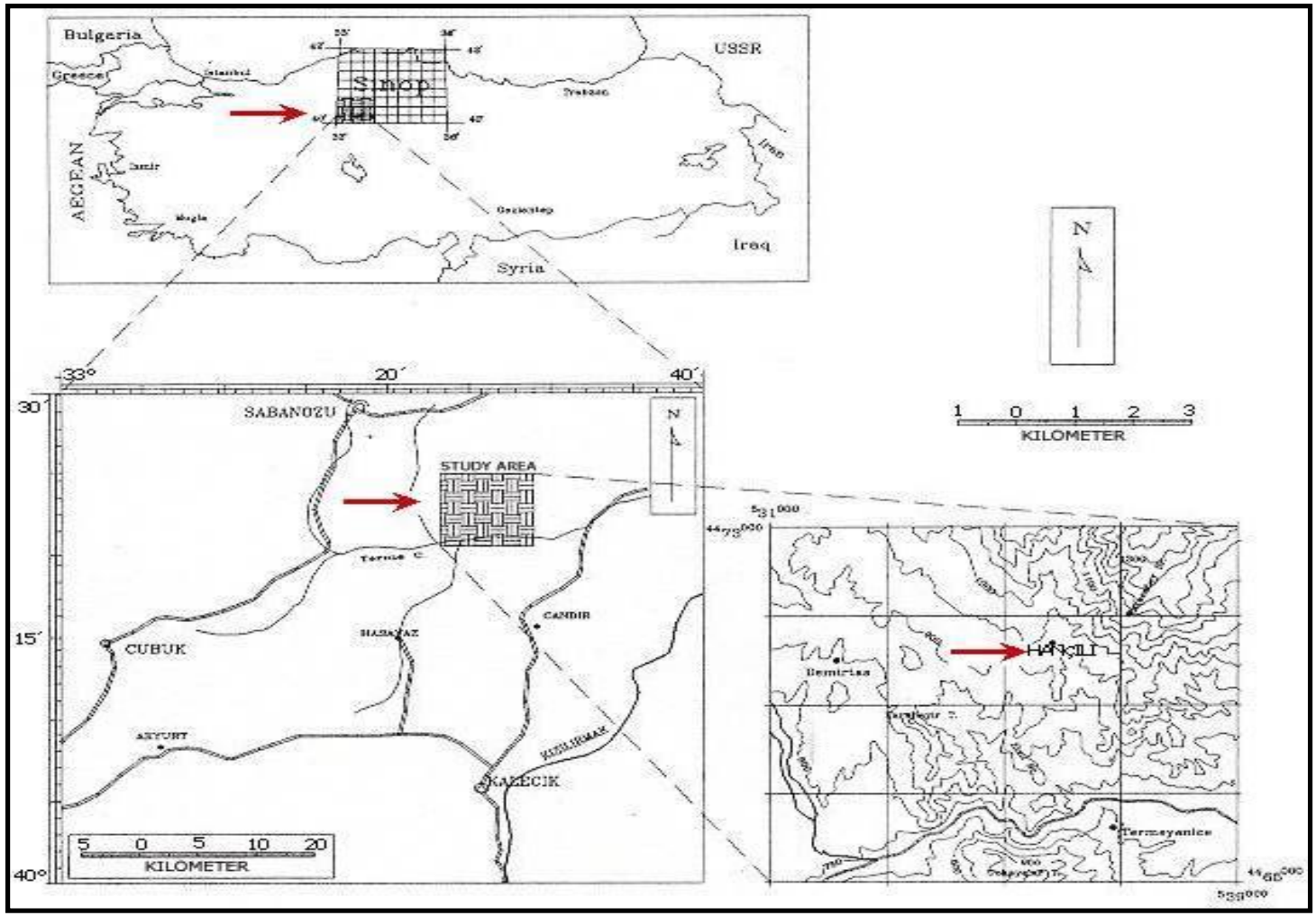


Figure 1.4 Location map of Hançılı Bentonite Clay Used (Güngör, 1992)

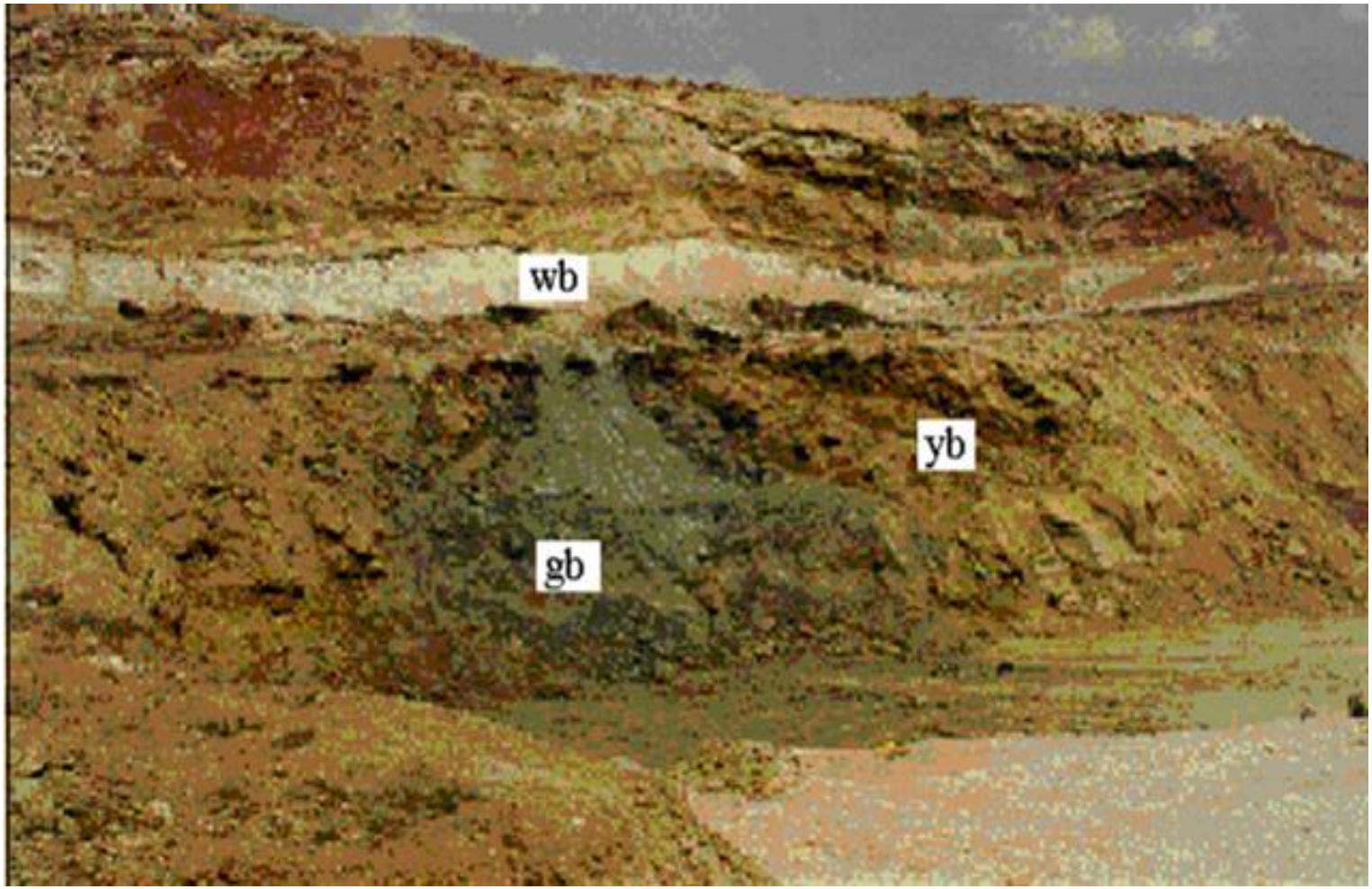


Figure 1.5 View of Hançılı Bentonite Clay
(**wb :** white bentonite , **yb :** yellow bentonite, **gb:** green bentonite)

1.3 Organically Modified Clays (ORGANOCLAYS)

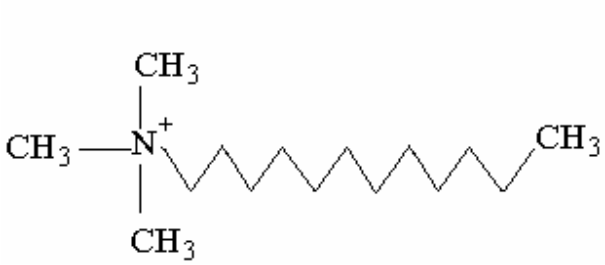
As it is indicated previously, clay minerals (and also zeolites) have negatively charged surfaces which are occupied by the exchangeable cations of alkali and alkaline earth metals, which give them a strong affinity for cationic surfactants. As these exchangeable cations have high hydration energies and layers of water molecules associate with them, clay mineral surfaces also possess a hydrophilic character. When these cations are replaced by organic cations, producing an organoclay structure, the clay becomes hydrophobic in character and can be used to remove hydrophobic contaminants from water (Li *et al.,* 2001).

Organoclays are often prepared using quaternary ammonium cations of the general form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR`]^+$ where R and R` are hydrocarbon groups.

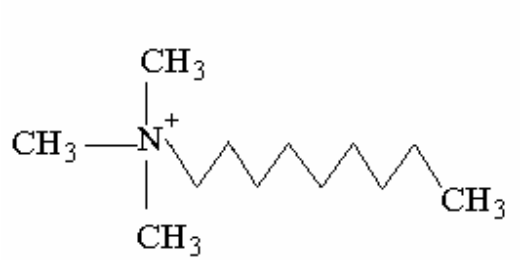
Depending on the molecular sizes of R and R`, organoclays display distinctive sorptive properties and abilities. The most commonly used quaternary ammonium cations are as follows:

- HDTMA$^+$, hexadecyltrimethylammonium ion **(R = $C_{16}H_{33}$)**

- DDTMA$^+$, dodecyltrimethylammonium ion **(R = $C_{12}H_{25}$)**



- NTMA$^+$, nonyltrimethylammonium ion **(R = C_9H_{19})**



In the studies, HDTMA$^+$ tail group has found to have higher affinity for the exchange sites on clays relative to other surfactants (Haggerty and Bowman, 1994; Li, 1999). Therefore HDTMA$^+$ is the most frequently used surfactant in the research.

In the earlier studies of Zhaohui Li in 1999, the degree of HDTMA$^+$ addition was limited to the cation exchange capacity of the clay being modified, where HDTMA$^+$ replaces the charge-balancing cations on the clay surface creating a monolayer as follows:

Clay-M + HDTMA$^+$ = Clay-HDTMA + M$^+$

where M^+ is the metal cation and the sorption of $HDTMA^+$ by clay minerals was attributed to cation exchange as visualized in Figure 1.5 (Li, 1999).

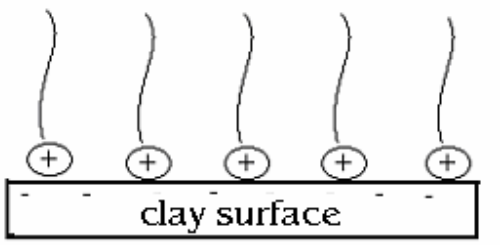


Figure 1.6. Initial monolayer formation when the amount of input $HDTMA^+$ is less or equal to CEC of clay mineral (Li,1999)

Several studies were conducted on the sorption of cationic surfactants to clay surfaces together with the sorption studies of organic solutes like perchloroethylene (PCE), napthalene, benzene. Sorption of organic compounds to organoclay samples were attributed to adsorption and partition (Pease, Sparks, Zhang, 1990; Lee, Crum, Boyd., 1989; Zhu, Baoling, Shen, 2000; Lee, Choi, Park, 2002;).

When excess $HDTMA^+$ is present, the degree of adsorption increases due to hydrophobic interactions among tail groups. As the amount of surfactant added reaches to twice of clay's CEC, a complete surfactant bilayer forms on the clay surface. This reverses the originally negatively charged clay surface into a positively charged one (Figure 1.7).

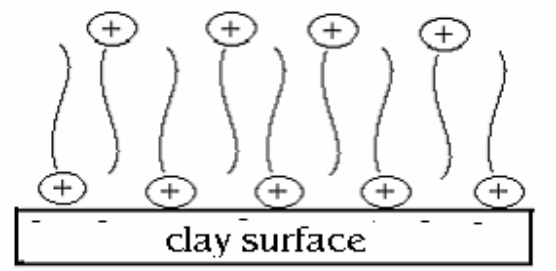


Figure 1.7 Bilayer formation when the amount of input $HDTMA^+$ is nearly twice of CEC of clay mineral (Li, 1999)

Later studies with organoclays and organozeolites prepared as described above, showed that they sorb not only nonpolar organic species but also oxyanions such as nitrate, chromate, arsenate, sulphate (Li, 1999). Sorption of inorganic contaminants such as chromate, nitrate, and arsenate by organoclays has been extensivley studied by Li and Bowman, 2001; Bowman *et al.*, 2000.

1.4 Sorption Process

Sorption in general can be defined as the process in which mass transfer occurs by the actual removal of the dissolved substances from a liquid phase to the solid phase. The interface of a solid represents the interface between the solution phase and the mineral crystal. The nature of that interface depends on the both the crystal phase and the solution.

Various types of sorption processes which take place can be classified as given below (Voyutsky, 1978).

i. **Physical Adsorption :**

Physical adsorption occurs due to non-specific forces of attraction between the dissolved substance and the solid phase. This process is rapid, reversible, relatively independent of temperature and also independent of the concentration of adsorbate and in many cases also of the mineralogical composition of the solid sorbent.

No chemical bonds are formed during physical adsorption; attraction between the adsorbate and adsorbent exists by the formation of intermolecular electrostatic forces, such as London dispersion or van der Waals forces from induced dipole-dipole interactions, or may be dependent on the physical configuration of the adsorbent such as the porosity of activated carbons.

The presence of complexing agents and the pH of the solution have a large influence on physical sorption (Voyutsky, 1978).

When the solid phase is clay mineral surface, the preference of organic cations over alkali and alkaline earth cations on 2:1 layer silicate surfaces is attributed to the combined action of electrostatic and non-Coulombic forces. In the previous studies it was found that the Gibbs free energy for the cation exhange reaction on clay minerals increases as the chain length of the alkyl chains increases.

The additional stabilization energy gained with increasing chain length was attributed to van der Waals interaction between the alkyl chains and the clay surface (Jonhston, 1996).

ii. Electrostatic Adsorption :

This is due to Coulombic forces of attraction between charged solute species and the solid matrix. Ion exchange in which an ion from the aqueous phase is substituted for an ion with the same charge on the surface of the solid phase is an example of electrostatic adsorption process (Borretzen, Salbu, 2005). Electrostatic adsorption is a rapid, largely reversible, somewhat dependent on temperature, and strongly dependent on the composition of the sorbent as well as on the ionic strength of the solution.

iii. Chemisorption :

Chemisorption involves the transfer of electrons between the adsorbent and the adsorbate with the formation of chemical bonds, by chemical reaction, between two species causing adhesion of the adsorbate molecules.

Chemisorption is a concentration and temperature dependent process, and is characterized by high adsorption energies.

The reaction is likely to be slow, and less readily reversible, the equilibrium takes longer time to achieve (Borretzen, Salbu, 2005).

iv. Chemical Substitution :

This process is due to the action of specific chemical forces involving chemical bonding. This is a slow, partially irreversible, largely solute selective process. It depends on the concentration of solute, temperature as well as the composition of the solid matrix (Voyutsky, 1978).

1.5 Evaluation of the Sorption Data

In the evaluation of the data obtained, percent uptake value (% uptake) and/or distribution ratio (R_d) used is as follows:

1.5.1 Percent Uptake Value (% Uptake)

The percent uptake value is the amount of adsorbed ion per hundred grams of clay sample. It is usually expressed in mmol/100 g of clay and determined as indicated below.

The amount of sorbed ion on adsorbent is calculated by the difference between the initial (added) ion concentration and the final concentration taking into account the volumes of the initial and final solutions.

This uptake value is usually expressed for hundred grams of clay, and formulated below.

% Uptake : (($M_1.V_1$- $M_2.V_2$) / Amount of clay used, g) x 100

where,

M_1 : molarity of the initial solution
M_2 : molarity of the resulting solution (after treatment)
V_1 : volume of the initial solution (mL)
V_2 : volume of the supernatant after treatment (mL)

1.5.2 Distribution Ratio Concept (R_d)

The distribution ratio is a parameter that is often used to quantify the sorption of a substance in a system under given conditions. This coefficient can be easily calculated from the sorption experiments and represents the results obtained.

The concentration dependent distribution ratio, R_d is defined as follows :

$$R_d = \frac{[C]_s}{[C]_L}$$

where,

$[C]_S$: Concentration of the solute in the solid phase after sorption (mmol / g)

$[C]_L$: Concentration of the solute in the solution after sorption (mmol/mL)

The distribution ratio (R_d) is a good indicator of the relative sorption capacity of various rocks and minerals but it must be emphasized that measured sorption characteristics for a substance are related to a large number of chemical and physical parameters, such as :

- Composition of the aqueous phase (concentrations of the species present in the system, pH of the system)
- Composition of the solid phase (minerology and chemical characteristics, surface properties, crystallinity, etc.)
- Other parameters such as temperature and contact time.

In general, the distribution ratio increases with the contact time, due to the fact that new surfaces become available for sorption in the solid phase. Thus two different reactions can be distinguished. A rapid surface reaction is followed by a slower, diffusion controlled volume dependent reaction process (Voyutsky, 1978; Hatipoğlu, 1992).

1.6 Isotherm Models

The distribution ratio is the parameter that represents the results obtained from sorption experiments, but this value is not constant since it is a function of a number of parameters such as concentration of the solute and temperature.

Adsorption isotherm models are used to describe the dependence of distribution coefficients on such parameters.

The Langmuir and Freundlich isotherms are the frequently used models that describe the dependence of distribution ratio on concentration.

1.6.1 The Langmuir Isotherm

The Langmuir isotherm is valid when all the adsorption sites on the solid are identical and it implies the saturation condition with all the sites occupied by the adsorbate. It is applicable for electrostatic and chemisorption reactions. The number of surface sites available for sorption is limited and must be specified at the outset (Borretzen, Salbu, 2005). In the Langmuir isotherm, the adsorbed cations are assumed to interact only with the adsorbent but not with each other. The Langmuir equation has the form:

$$\mathbf{C_s = K_L.S_m.C_L / 1+ K_L.C_L}$$

where C_s is the amount of sorbed solute on solid at equilibrium (mmol/kg), C_L is the equilibrium concentration of solute (mmol/L), S_m is the sorption maximum (mmol/kg), and K_L is the Langmuir coefficient (L/mmol), reflecting the affinity of the solute to the surface. Thus, when C_s is plotted against C_s/C_L a linear relationship should indicate the existence of a Langmuir type of sorption.

In this case the slope of the line will be equal to $1/K_L$ and the intercept will be S_m. The following equation can be written in order to determine Rd values (Li, 1999; Li and Bowman, 1997; Li *et al.*, 1998).

$$\mathbf{R_d = K_L.S_m / 1+ K_L.C_L}$$

1.6.2 The Freundlich Isotherm

The Freundlich isotherm is valid when there are various kinds of sorption sites. At lower concentrations the easier sites tend to be occupied first, then at higher concentrations the more difficult sites will be used in the process. It is applicable for physical sorption processes. The Freundlich equation is given by the following equation:

$$\mathbf{X = K . C^{N}}$$

where X is the amount of solute adsorbed per unit weight of solid (g/g),

C is the equilibrium solution concentration of solute (g/mL), and K and N are the isotherm constants which are independent of the nature of the mineral.

The Freundlich relationship can be made linear by taking the logarithms of both sides of equation.

$$\log X = \log K + N. \log C$$

When Freundlich isotherm is valid plotting log X versus log C yields a straigth line with slope N and intercept log K. Rd can be calculated for any concentration using the equation below (Li, 1999).

$$R_d = K. C^{N-1}$$

1.7 Toxicology and Removal of Oxyanions

Anions are mobile species in soils and ground water as most of the natural materials have net negative surface charges.

A number of oxyanions such as nitrate, chromate, sulphate and arsenate can be toxic to humans and wild life at μg/L to mg/L concentrations, thus their removal from contaminated water systems are very important.

Among the oxyanions mentioned, NO_3^-, occurs in the environment due to contribution of soil mineralization and atmospheric deposition of nitrogen. Nitrate (NO_3^-) itself is considered to be of low toxicity but the its reduction results in nitrite and other toxic compounds. Nitrite causes the oxidation of hemoglobin to methemoglobin which is unable to transport oxygen from lungs to tissues (Fedorak, Eckford, 2002).

Boron is an important element that is essential for plant growth but boron concentrations in excess of 2.0 mg/L in irrigation water is deleterious to certain plants. There is evidence that some plants are adversely affected by concentrations as low as 1.0 mg/L (or even less in commercial greenhouses). The ingestion of large amounts of boron can affect the central nervous system, and protracted ingestion may result in a clinical syndrome known as borism (Apha, Awwa and Fsiwa; 1955).

Ions of chromium (Cr^{3+},CrO_4^{2-}) are frequently detected in groundwater and soil contaminants. Naturally, chromium exists in two common states; Cr^{3+} and Cr^{6+}. In the reduced Cr^{3+} state, chromium exists either as $Cr(OH)_3$ or as stoichiometric $Cr_{0,25}Fe_{0,75}(OH)_3$ when iron is present in the system as reductant. Due to its low solubility, Cr^{3+} occurs as a sorbed phase bound to soil and is not readily adsorbed by plants or translocated in the food chain. Thus, it is less mobile and less toxic. In contrast, under oxidized conditions and neutral to alkaline pH medium, chromium exists mainly as chromate which is quite mobile and more toxic.

Chromate (CrO_4^{2-}) is an anionic contaminant often associated with industrial and power generation wastes that are disposed to the land surface (Zachara *et al.*,1988). For the purpose of chromate remedition in groundwater and soil, efforts have been made to reduce Cr^{6+} to Cr^{3+} via in situ chemical reduction. This process produces less soluble and less mobile species, and enhances the sorption possibility to solid surfaces via complexation or ion exchange processes.

1.8 Aim of the Study

In this study, the preparation of an organoclay from a widely abundant local clay, Hançılı Bentonite, by using a proper cationic surfactant in order to modify its surface characteristics was aimed firstly.

Then the organoclay prepared was tested for the successful removal of some oxyanion contaminants such as nitrate and chromate from polluted water.

The enrichment of boron species in the form of borate using organoclay prepared was also aimed.

CHAPTER II

EXPERIMENTAL

2.1 Raw Material : Hançılı Bentonite and Sample Preparation

Hançılı Bentonites used in this study were obtained from Geological Engineering Department of METU. The bulk clay samples were grinded, sieved and samples with particle size smaller than 170 mesh were oven dried at 60 ºC for two days. Then, they were stored in a desiccator prior to use in experiments.

In additon to the local clay used for modifications, two reference clays of the Clay Minerals Society, with well described properties, were used for comparison purposes; KGa-1 : Kaolinite of Tuscelosa formation, USA and SWy-1 : Wyoming Bentonite of Newcastle formation, USA.

2.2 Characterization of Hançılı Bentonites

2.2.1 Cation Exchange Capacity (CEC)

Cation exchange capacites of reference clays KGa-1 and SWy-1 are obtained from literature (Clay Minerals Society). CEC of Hançılı Bentonite was determined in a previous study in our group using various techniques including ammonium acetate method, methylene blue adsortion test, silver-thiourea method, silver nitrate method (Çetin, 2002). Since silver-thiourea method was decided as the method that gave the accurate and definite results in the previous study, the CEC value of Hançılı Bentonite determined by this method was considered for further experiments.

2.2.2 X-Ray Powder Diffraction Measurements(XRD)

X-Ray powder diffraction analyses of powdered Hançılı Bentonite samples were carried out using a Philips PW 3710 X-Ray powder diffractometer at the General Directorate of Mineral Research and Exploration (MTA). Cu K_{α} anode at a scan speed of 3º per minute was used during the studies.

2.2.3 X-Ray Fluorescence Measurements (XRF)

The XRF analysis of the Hançılı Bentonite samples were performed with a high performance Oxford ED-2000 XRF system located at Ankara Nuclear Research and Training Center. Sample pellets were positioned in front of a Si (Li) detector and irradiated with X-rays originating from an Rh target. The tube power was a 50 W and the maximum current was 1000 μA. Eight standards were used for calibration. Samples were used during the measurements and the spectra were obtained and analysed using Oxford Xpert Ease software.

2.2.4 Fourier Transform Infrared Analysis (FTIR)

In the infrared analyses, firstly powdered bentonite samples which were redried at 50°C in order to remove excess moisture were used. 0.001 g of bentonite clay samples were mixed with 0.1 g of spectral grade KBr and grinded using an agate mortar and pestle until a homogeneous mixture was obtained. The mixture was then pressed into a pellet in eigth metric tones pressure. Infrared analyses were carried out by using a Mattson 1000 FTIR spectrometer available in Chemistry Department, METU.

2.3 Chemicals and Reagents

2.3.1 Chemicals

- Aerosol OT (Dioctyl sodium sulfosuccinate)
- Ammonium Acetate, NH_4OOCCH_3
- Azomethine-H,
  8-hydroxy-1-(salicyldeneamino)-3,6-napthalenedisulfonic acid
- Boric Acid, H_3BO_3
- Brucine dihydrate, $C_{23}H_{26}N_2O_4.2H_2O$
- Chromium Chloride, $CrCl_3.6H_2O$
- Citric acid (monohydrate)
- 1,2-dichloroethane ($C_2H_4Cl_2$)
- Eosin Yellowish Dye
- Ethylenediaminetetraacetic acid disodium salt, EDTA-$(Na)_2$
- Glacial Acetic Acid, CH_3COOH
- Hexadecyltrimethylammonium bromide (HDTMA-Br)
  ($C_{19}H_{42}NBr$)
- Hydrochloric acid, Merck extra pure (35%), density : 1.19 g/mL.
- Hydrogen peroxide, H_2O_2 (3.0%)
- L-Ascorbic Acid
- Luminol (Aldrich Chem. Company)
- Potassium Chromate, K_2CrO_4
- Potassium Nitrate, KNO_3

- Silver Nitrate, $AgNO_3$
- Sodium Chloride, NaCl
- Sodium Hydroxide, NaOH
- Sodium Sulfite, Na_2SO_3
- Sodium Tetraborate Decahydrate, $Na_2B_4O_7.10H_2O$
- Sulfanilic Acid, $C_6H_4(NH_2)(SO_3H)(1,4)$
- Sulfuric Acid, H_2SO_4

All chemicals were obtained from E. Merck A.G. except luminol. Deionized water obtained from an Elga Water Purification System in our laboratory was used for the preparation of all sample and standard solutions.

2.3.2 Reagents

Stock HDTMA-Br Solution, 1.6 x10^{-2} M : 5.824 g of HTDMA-Br was dissolved in deionized water and completed to 1000 mL.

NaCl Solution, 1.0 M : 5.85 g of NaCl was dissolved and completed to 100 mL deionized water.

Stock KNO_3 Solution, 1000 ppm: 0.4078 g of KNO_3 was dissolved and diluted to 250 mL with deionized water.

KNO_3 Solution, 100 ppm: Prepared by dilution of 10 mL of 1000 ppm KNO_3 stock solution to 100 mL.

pH 4.5 Buffer : Prepared by dissolving 25 g of citric acid (monohydrate) in 100 mL of deionized water and pH was adjusted to 4.5 with 10 M NaOH.

Eosin Y indicator : Prepared by dissolving 50 mg eosin yellowish dye in 100 mL deionized water.

Brucine Sulfanic Acid : In the preparation of brucine sulfanic acid reagent, 1.0 g of brucine and 0.1 g sulfanilic acid were dissolved in 70 mL hot water.

H_2SO_4 solution: H_2SO_4 solution was prepared by adding 500 mL of concentrated H_2SO_4 into 75 mL of water.

Cr^{3+} solution (1000 ppm) : Cr(III) solution was prepared dissolving 0.512 g of $CrCl_3.6H_2O$ in 100 mL of 0.5 M HCl.

Cr^{6+} solution (1000 ppm) : Cr(VI) stock solution was prepared dissolving 0.374 g K_2CrO_4 in 100 mL deionized water.

Buffer-Masking Solution: 250 grams of ammonium acetate and 15 grams of disodium salt of ethylenediamine tetraacetic acid (EDTA-$(Na)_2$)

were dissolved in 400 mL of deionized water and then 125 mL of glacial acetic acid was added to this mixture slowly and then the resulting solution was mixed throughly.

Azomethine-H Solution: 1.0 gram of L-ascorbic acid was dissolved in 100 mL of deionized water and 0.45 grams of Azomethine-H was dissolved in this solution.

2.4 Preparation of Organoclays

The organoclay samples were prepared from reference clays and Hançılı Bentonite clay by the addition of HDTMA-Br, hexadecyltrimethyl-ammonium bromide) solution. The amount of surfactant added were twice of the CEC of the clays used. The clay-$HDTMA^+$ mixtures were then shaken laterally at 250 rpm and 25°C for 24 hour. After centrifugation, the supernatant solutions were removed and analyzed for equilibrium $HDTMA^+$ concentration using the method of Furlong and Elliker described in section 2.4.1. Then the organoclay samples were filtered and washed several times with deionized water, dried and stored for use in oxyanion sorption experiments. The preparation of organoclay sample is also explained in the following flow chart.

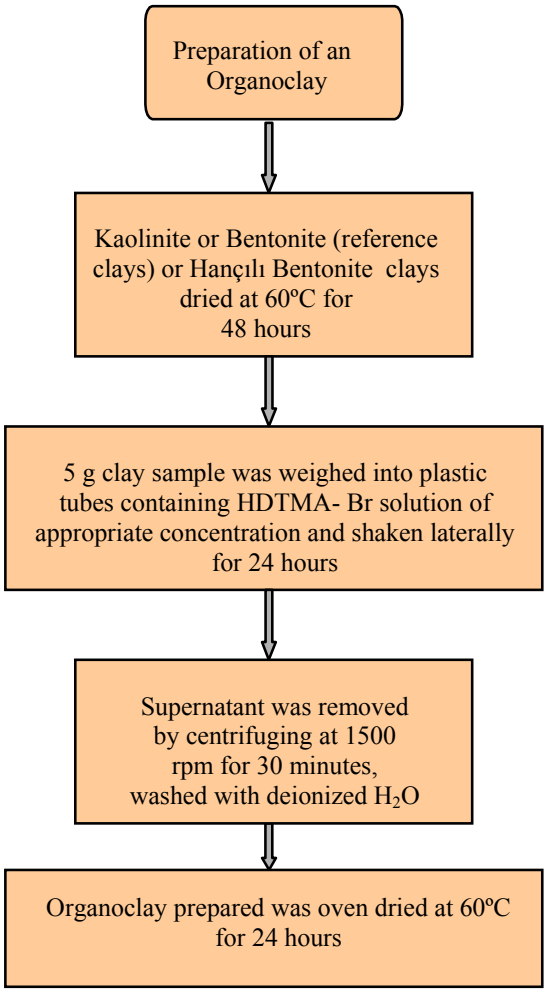


Figure 2.1 Flow chart for the preparation of organoclay

2.4.1 Determination of $HDTMA^+$

In order to determine the quantity of $HDTMA^+$ sorbed by clay samples; concentration of $HDTMA^+$ left in supernatant solutions were determined using a titration procedure developed by Furlong and Elliker (Furlong and Elliker, 1952).

5 mL of surfactant solution (containing HDTMA-Br) is placed into test tube containing 2 mL of dichloroethane, 0.5 mL of pH 4.5 buffer, and 0.1 mL of eosin Y indicator, which were prepared as indicated in section 2.3.2. Before titration, the test tube is vigorously shaken to facilitate the extraction of the quaternary amine from aqeous phase to organic dichloroethane phase. A pink to red color in the dichloroethane phase indicates the presence of a quaternary amine. The solution is then titrated with standard solution of Aerosol OT (dioctyl sodium sulfosuccinate) to a colorless end point.

In this method, a complex formation between $HDTMA^+$ and eosin Y indicator is formed and the color change from pink to red occurs. During the titration with Aerosol OT solution, the complex is destroyed as a result of the reaction between HDTMA-Eosin Y complex and Aerosol OT, the solution becomes colorless.

2.4.2 Determination of Bromide

Another way of determining of $HDTMA^+$ concentration left in supernantant solution in batch experiments is to measure the Br^- concentration released to the solution when $HDTMA^+$ is sorbed on clay surface. For this purpose a HPLC (High Performance Liquid Chromatography) with a Jasco Model 870-UV Spectrophotometric detector and Waters M-6000 A Model HPLC pump was used.

A calibration curve for bromide determination was prepared using four different standard solutions with Br^- concentrations ranging between 1x 10^{-4} and 1x 10^{-3} M. For the preparation of standards and analytical grade KBr was used. All solutions and standards were prepared with deionized water. Then, the bromide concentrations of samples were determined using HPLC and employing the calibration curve prepared.

2.5 Batch Sorption / Desorption Experiments

In sorption experiments, for each % uptake or R_d determination, precisely weighed amount of organoclay prepared (in the range of 100 mg) was shaken laterally with known amount of oxyanion solution of interest in the range of 5-10 mL volumes for about 8 hours. After separation of two phases by means of centrifugation and decantation, the change in the concentration of oxyanion in the solution was determined using the procedures described in the following sections.

In the desorption experiments, procedure given above was repeated using presicely weighed oxyanion treated organoclay samples (in the range of 100 mg). They were shaken with 10 mL of deionized water up to 12 hours. After the separation of two phases by means of centrifugation and decantation, the amount of oxyanion released to the solution was determined. Experiments were carried out using dublicate samples for each point of interest.

2.6 Nitrate-Organoclay Interactions

Known amount of organoclays (approximately 100 mg) prepared from Hançılı Bentonite and those from two reference clays KGa-1 (kaolinite) and SWy-1 (montmorillonite) were shaken with 10 mL of known concentrations of KNO_3 solutions in the range of 1.0×10^{-4} M to 3.0×10^{-3} M at 250 rpm and at room temperature for 24 hours. For comparison unmodified (raw) Hançılı bentonite clay was also treated under the same experimental conditions for measuring its nitrate sorption capacity. Nitrate determinations at the supernatant solutions were carried out using the procedure given in the following section.

2.6.1 Nitrate Determination

The '**brucine method'** (Jenkins and Medsken, 1964) was used for the determination of nitrate concentration in the solution of interest. In this method; 5 mL of sample, 5 mL of standards (10-50 ppm) and 5 mL of blank solutions were taken into separate tubes. And 1 mL of brucine sulfanic acid reagent prepared as indicated in section 2.3.2 was added to each tube. 10 mL of H_2SO_4 solution was put into seperate beakers and the tubes containing sample, standards and blank were transferred to the beakers. The solutions were left in dark for 10 minutes. Then the solutions were transferred into test tubes containing 10 mL of water and again left in dark for 20-30 minutes. Finally the absorbance of solutions were measured at 420 nm using Shimadzu UV-160 UV-Visible spectrophotometer applying the calibration curve obtained form standards prepared in the same way (Tekin, 2004).

2.7 Borate-Organoclay Interaction

In order to determine the sorption ability of boron species on organoclay samples, two different boron compounds; namely boric acid (H_3BO_3) and borax (Sodium tetraborate decahydrate, $Na_2B_4O_7.10H_2O$) were used as adsorbents.

In one set of experiments, 10 mL of 2.0 x 10^{-3} M boric acid solutions at either pH: 8 or 9 or 10 were mixed with 100 mg of unmodified and

modifed bentonite samples for 24 hours at 250 rpm and 25 ºC. There was no change in the pH values of the solutions after 24 hour shaking.

In the second approach, 10 mL of $4x10^{-3}$ M borax solution was mixed with 100 mg of unmodified and modified bentonite samples. The experiment was run in dublicates. Then these samples were shaken at 250 rpm and 25 ºC for 24 hours. The amount of sorbed borate ($B_4O_7^{2-}$) species was determined from the difference between the initial and final concentrations. The calibration curve used for the determinations was obtained using five standard solutions from 1.0×10^{-5} M to 6.0×10^{-5} M. In order to determine the borate concentration Azomethine-H method explained in the following section was used (Section 2.7.1).

In order to determine whether lower borate concentration affects the sorption or not, 1.0×10^{-4} M of borate solution was added to 100 mg of modified and unmodifed bentonite samples. The resulting borate concentration after 24 hour shaking at 250 rpm was determined.

Then 10 mL of borax solutions of $1.0x10^{-4}$ M at pH values 5, 7, 8, 9 and 10 were mixed with 0.1 g of unmodified and modified bentonite samples for the determination of effect of pH in the sorption phenomena in the case of borax. The pH adjustments were again made using NaOH. The same procedure with boric acid was followed. All experiments were run in dublicates.

The desorption experiments were conducted for the determination of stability of borate-organoclay interaction. Known amounts of organoclay samples (100 mg) were shaken with $1.0x10^{-4}$ M borate solution in the previously determined conditions. The sorbed borate amount was determined again using colorimetric Azomethine-H method of Gupta and Stewart (Gupta and Stewart, 1975). Then the solutions were filtered and dried. After the grinding process of organoclay sample treated with borate, 100 mg of organoclay samples were mixed with 10 mL of water and the borate concentration in the supernatant was determined with time intervals in two hours shaking.

2.7.1 Borate Determination, the Colorimetric Azomethine-H Method

Azomethine-H (monosodium salt hydrate) method was used for the determination of boron species as indicated in the previous studies in literature (Keren and Gast, 1981, Keren and Talpaz, 1984). In this method, 2 mL of buffer-masking solution was added into 1 mL of supernatant solution and mixed. Then 2 mL of Azomethine-H solution was added to this solution and mixed. The resulting solution was left for 30 min. Finally, the absorbance of the samples were measured at 420 nm using Shimadzu UV-160 UV Visible spectrophotometer. The same procedure was applied for each standard and all calibrations were done with six standards.

As it is known that above pH: 7 boric acid is in the form of $B(OH)_4^-$; the boric acid solutions at different pH levels above 7.0 were mixed with unmodified and modified bentonite samples at the same conditions indicated above. Fistly, the validity of Azomethine-H method was checked for pH values above 7.0. The concentrations of prepared 2.0 x 10^{-3} M boric acid solution at pH : 8, 9, and 10 were determined using Azomethine-H method. The pH of the solutions were adjusted using NaOH. The concentrations were determined to be $2.1x10^{-3}$, $1.9x10^{-3}$,and $1.9x10^{-3}$ M respectively.

2.8 Chromate-Organoclay Interaction

Organoclay samples prepared from Hançılı bentonite and reference clays together with unmodified local clay samples were treated with solutions of known initial concentrations of chromate within the range of $1.0x10^{-4}$-4.0×10^{-4} M using lateral shaking at 250 rpm for the 24 hours. The amount of clays used for this experiment was approximately 100 mg for each. Final chromate concentrations in the supernatant solutions were determined by Flame Atomic Absorption Spectrometry (FAAS) as described in the following section (Section 2.8.1).

The effect of pH on chromate sorption was also investigated by another series of experiments. 10 mL of 1.0×10^{-3} M chromate solution were added to 100 mg of organoclay samples, the pH of the solution was adjusted to different pH values between 3.0-9.0 using NaOH and HCl.

After 24 hours of shaking at 250 rpm, the chromate concentrations of the supernatant solutions were determined by FAAS.

2.8.1 Chromate Determination

PU 9200 Model Flame Atomic Absorption Spectrometry (FAAS) was used for chromium measurements at 357.9 nm resonance line of chromium with a bandpass of 0.5 nm. The results in FAAS were obtained by an Epson FX-850 printer coupled to the spectrophotometer. For atomization; fuel rich air-acetylene flame with a 50 mm burner slot was used. Instrumental parameters for chromium determination by FAAS are given in Table 2.1.

Table 2.1 Instrumental Parameters Used for the Determination of Chromium in FAAS

Light Source	Chromium Hallow Cathode Lamp
Wavelength	357.9 nm
Band Pass	0.5 nm
Lamp Current	10 mA
Flame	Fuel rich air-acetylene
Burner Slot	50 mm

2.8.2 Sorption Characteristics of Organoclay in Cr(III) and Cr(VI) mixture

In order to check the selectivity of organo-bentonite prepared towards chromium species a batch sorption experiment was carried out with a mixture containing Cr(III) and Cr(VI) with initial concentrations of 3.27 $x10^{-4}$ M for each ion by mixing proper amount of solutions.

Cr(III)-Cr(VI) mixed solution was then prepared by mixing from the stock solution of each species. 0.01 M luminol prepared in 1 M KOH and 1% H_2O_2 was used as stock solution throughout CL measurements. 100 mg of organoclay samples were shaken with 20 mL of mixture solution for 24 hours at 250 rpm. The concentration of Cr(III) and Cr(VI) species were then determined by chemiluminescence (CL) measurements by using Perkin Elmer L550B Luminescence Spectrometer. Emission monochromator was set at 425 nm and the slits were positioned to 20 nm for photomultiplier tube in order to receive all the light coming from the reaction cell. A Perkin Elmer Stirred Cell Holder was used for continuous mixing of solutions during the measurements.

For Cr (III) determination, 2.1 mL of luminol mixture was placed in the cell compartment which was shielded from ambient light by using a black cartoon box. Chemiluminescence measurements were immediately done after the injection of 0.9 mL of Cr(III) solution.

Since light emission from CL system is proportional to the luminol, hydrogen peroxide, and catalyst concentration and Cr(III) behaves as a catalyst so that its concentration is determined directly while Cr(VI) was reduced to Cr(III) using 0.01 M solution of sodium sulfite, Na_2SO_3, prior to its determination (Sürdem, 2004).

As oxidation of luminol by hydrogen peroxide takes place very slowly, a catalyst is needed. Cr(III) has a catalytic effect in this reaction. Cr(VI) does not catalyze the oxidation of luminol by hydrogen peroxide hence it does not give any chemiluminescence signal.

2.9 Chromate and Nitrate Mixture–Organoclay Interaction

In order to determine the sorption behaviour of organoclay sample prepared in a mixture of chromate and nitrate the following experiment was performed.

2.65×10^{-3} M nitrate solution and 1.3×10^{-3} M chromate solutions were prepared from stock solutions of KNO_3 and K_2CrO_4 as indicated in section 2.3.2, respectively. 5 mL of each solution was added to 0.2 g of organoclay sample prepared and shaken for 24 hours at 250 rpm. Then concentrations of nitrate and chromate in the supernatant solution were determined using HPLC and AAS, respectively.

CHAPTER III

RESULTS and DISCUSSION

3.1 Characterization of Hançılı Bentonite

3.1.1 Cation Exchange Capacity

The cation exchange capacities of two reference clay samples; kaolinite (KGa-1), and montmorillonite (SWy-1), and Hançılı Bentonite clay are given in the Table 3.1.

The cation exchange capacities of reference clay minerals were obtained from the data given by Clay Minerals Society and that of Hançılı bentonite was determined in a previous study using the silver-thiourea method (Çetin, 2002).

Table 3.1 Cation Exchange Capacity of Clay Minerals

Clay Mineral	CEC (meq/100 g)
Kaolinite, KGa-1	2-4*
Montmorillonite, SWy-1	70-100*
Hançılı Bentonite	50-70**

* : The Clay Minerals Society

**: Yasin Çetin, Chem 499 Undergraduate Research, 2002.

3.1.2 X-Ray Powder Diffraction Analysis (XRD)

The X-Ray powder diffraction analysis revealed that Hançılı Bentonites consist of mainly dioctahedral smectite which is montmorillonite as seen in the XRD traces in Figure 3.1.a-b. The location of the [060] peak on the X-Ray powder diagram has the reflection at 1.4923. This peak is observed at 1.49 to 1.52 Aº for dioctahedral types of clay minerals whereas it is observed at 1.53 to 1.57 Aº for trioctahedral types (Moore and Reynolds, 1997).

Previous mineralogical and chemical analyses indicate ryholitic and andesitic composition for the precursor volcanic materials which alter to bentonite in the study area (Güngör, 1992). Increased interlayer spacing of the modified Hançılı Bentonite is clearly observed that d_{001} peak of raw Na montmorillonite, d_{001}=12.6033 (Figure 3.1.a), is shifted to d_{001}=18.7853 (Figure 3.1.b) in the case of organoclay which is probably an indication for the formation of the organoclay structure.

This observation also is in accordance with the results found by Lee *et al.* in 2002.

3.1.3 X-Ray Fluorescence Analysis (XRF)

The results of XRF analysis of the raw clay samples which were carried out at Ankara Nuclear Research and Education Center (ANAEM) using a high performance Oxford ED-2000 XRF system are given in Table 3.2. In this table percentages of major elements present are expressed in form of their oxides, except that of Na which could not be determined because of the experimental limitations. As seen, Hançılı Bentonite contains nearly 4% iron oxide. However, this presence does not interfere with the experiments performed as the chemical reduction of oxyanions by ferrous ion or sorption by ferric iron oxides are unlikely (Johnston, 1996). Minor or trace elements present are also given in the Table 3.2 which are presented at ppm levels.

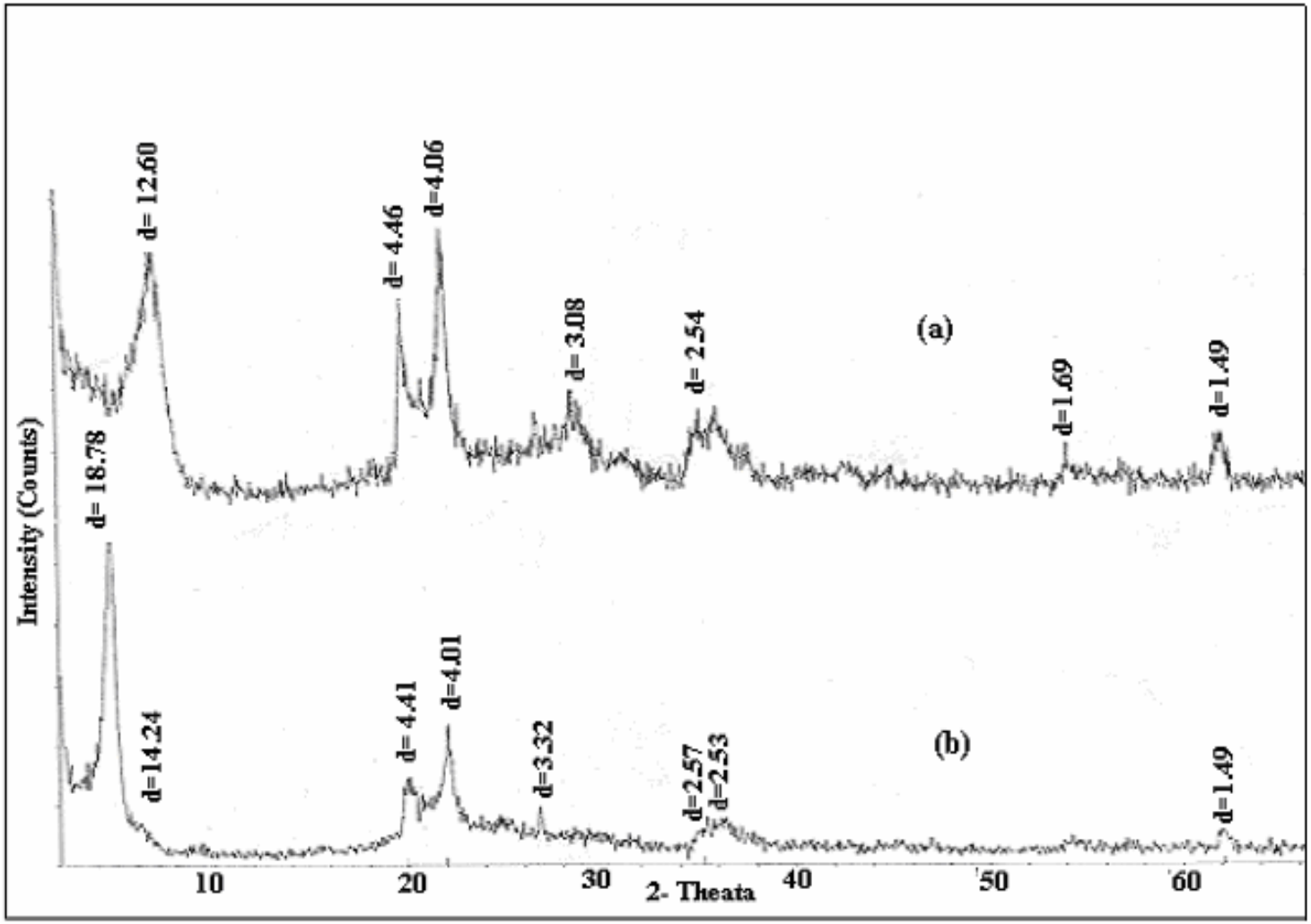


Figure 3.1 X-Ray Powder Diagram of Hançılı Bentonite a) before, b) after the $HDTMA^{+}$ treatment

Table 3.2 Results of XRF Analysis of Hançılı Bentonites

Major Elements (%)		Minor/Trace Elements (ppm)	
MgO	2.91	Sr	207
Al_2O_3	14.5	Zr	169
SiO_2	62.6	Y	73.3
K_2O	0.88	Nb	1074
CaO	1.06	Th	88.0
Cr_2O_3	0.02	La	96.6
MnO	0.01	Ce	39.4
Fe_2O_3	3.57	Pb	25.3
BaO	0.11	Cu	20.6
		Zn	67.2
		Ga	20.9
		V	18.8
		Rb	53.0

As seen, the major element oxides present in the Table 3.2 sum up to 85.66%. Knowing the Hançılı bentonite is a Na-bentonite (Güngör, 1992) one can assume the rest as being Na_2O, which must be present in the amount corresponding to 14.34%. A chemical formula calculation could be performed with this data using the approach of Foster (1962). The data obtained from XRF analysis was used for the calculation of structural formula as follows:

CALCULATION OF STRUCTURAL FORMULA

	% : MW Cat.Val.	Gr.eq. of cat.con.	Cat.val.p.u.cell	Cat.p.u.cell	CHARGE
SiO_2	62.6 : 60.04 – 1.04 x 4	4.16 : 0.12	34.67 : 4	8.668 - 0.668 8.000	- 0.668 *tetrahedral group*
Al_2O_3	14.5 : 101.9 – 0.142 x 6	0.853 : 0.12	7.115 : 3	2.372	
TiO_2	0.24 : 79.9 = 0.003 x 4	0.012 : 0.12	0.1 : 4	0.025	
Fe_2O_3	3.57 : 159.7 – 0.022 x 6	0.132 : 0.12	1.1 : 3	0.367	*octahedral group*
FeO	-				- 2.482
MgO	2.91 : 40.31 = 0.072 x 2	0.144 : 0.12	1.2 : 2	0.6	
MnO	0.01 : 70.93 = 0.0001 x 2	0.0002 : 0.12	0.002 : 2	0.001	
			2.402	3.365	
Octahedral Al cation x 3 = 2.267 x 3 = 6.801 (oct. occupancy)			+ 6.801		
			9.203		
			-12		
			-2.797 (octahedral charge)		
CaO	1.06 : 56.08 – 0.019 x 2	0.038 : 0.12	0.317 : 2	0.159	
Na_2O	14.23 : 61.98 = 0.229 x 2	0.459 : 0.12	3.826 : 1	3.826	+ 4.14 *(interlayer cation charge)*
K_2O	0.88 : 94.20 = 0.009 x 2	0.018 : 0.12	0.150 : 1	0.150	
		5.816 : 44 = 0.132			

$$[(Al^{3+}_{1.1}\,Ti^{4+}_{0.01}\,Fe^{3+}_{0.11}\,Mg^{2+}_{0.3}\,Mn^{2+}_{0.0005})^{-1.24}\,(Si^{4+}_{4.3}\,Al^{3+}_{0.33})^{-0.33}\,O_{10}(OH)_2]^{-1.57}\,(Ca^{2+}_{0.08}K^{+}_{0.07}\,Na^{+}_{1.9})^{+2.07}$$

The result is found to be $[(Al^{3+}_{1.1}Ti^{4+}_{0.01}Fe^{3+}_{0.18}Mg^{2+}_{0.3}Mn^{2+}_{0.0005})^{-1.24}$ $(Si^{4+}_{4.3}\ Al^{3+}_{0.33})^{-0.33}\ O_{10}(OH)_2]^{-1.57}\ (Ca^{2+}_{0.04}K^{+}_{0.07}Na^{+}_{1.9})^{+2.07}$ which is in turn in good agreement with that of a previous study in which is Hançılı Bentonite clay is characterized and the following formula is obtained;
$[(Al^{3+}_{1.3}Ti^{4+}_{0.07}Fe^{3+}_{0.3}Mg^{2+}_{0.3}Mn^{2+}_{0.0005})^{-0.23}(Si^{4+}_{3.9}Al^{3+}_{0.06})^{-0.31}$
$O_{10}(OH)_2]^{0.31}\ (Ca^{2+}_{0.03}K^{+}_{0.07}Na^{+}_{0.27})^{+2.07}$ (Güngör, 1992).

3.1.4 Fourier Transform Infrared Analysis (FTIR)

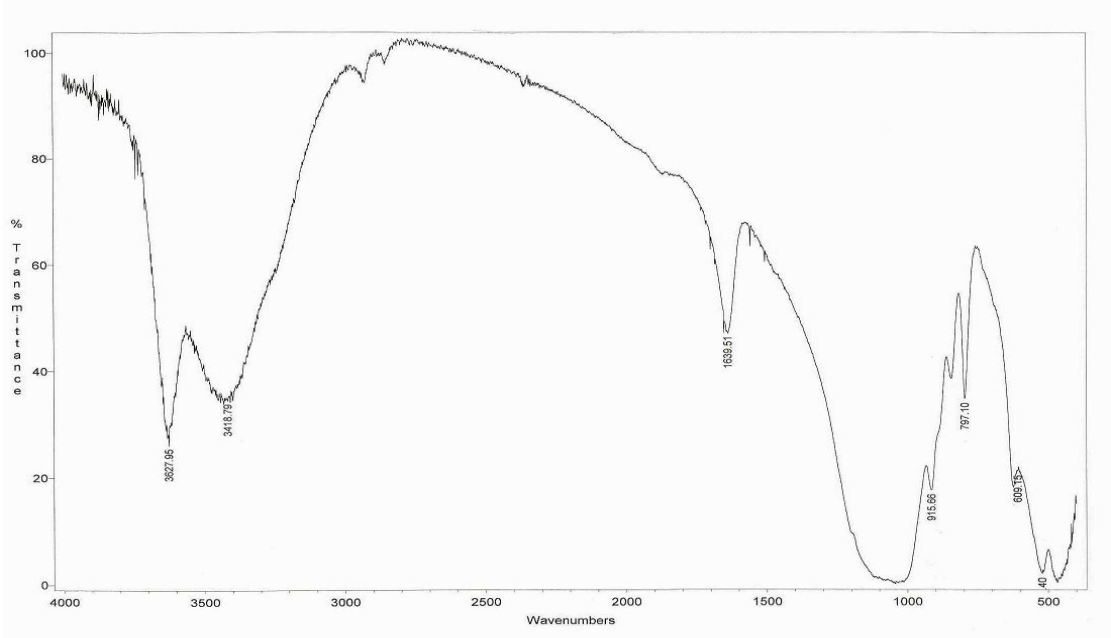
The FTIR traces of raw and organo Hançılı Bentonite are given in Figure 3.2.a-b. The major peaks observed for these are given in Table 3.3. and Table 3.4, respectively.

The O-H stretchings observed at 3630 cm^{1-} in both of the cases supports the dioctahedral structure of Hançılı Bentonite (Jackson, 1975).

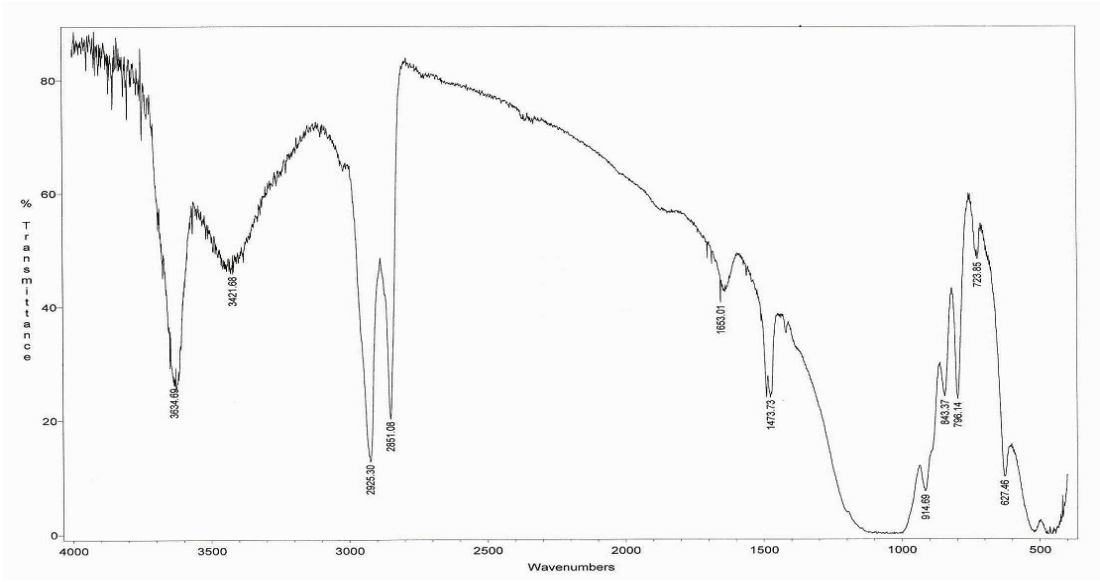
In both raw and modified Hançılı bentonite samples OH deformation bands of Al at 910 cm^{1-}, Al-Mg-OH groupings at 840 cm^{1-}, Si-O stretching at 790 cm^{1-} are observed. Hançılı bentonite gives the OH stretching band at the range between 3618- 3627 cm^{1-} which is in accordance with the previous study in literature (Güngör, 1992).

FTIR spectra of organo-bentonite differs from that of Hançılı bentonite in the C-H stretchings observed at 2850-2925 cm^{1-} and also at 1420 cm^{1-} indicating the presence of one or more alkane groups as seen in Figure

3.2.a-b. These peaks support the organo-bentonite structure in which alkane groups results from $HDTMA^+$ added.



(a)



(b)

Figure 3.2 FTIR Spectra of **a)** Hançılı Bentonite, **b)** Organo-bentonite

Table 3.3 Infrared absorption data for raw Hançılı Bentonite clay sample

Wave Number, cm^{1-}	**Assignment**
3630	OH stretching
3420	Hydration, OH deformation
1630	Hydration, HOH deformation
910	OH deformation, linked to 2 Al^{3+}
840	OH deformation, linked to Al^{3+}, Mg^{2+}
790	Silica
470	AlO stretching

Table 3.4 Infrared absorption data for Organo-Bentonite clay sample

Wave Number, cm^{1-}	**Assignment**
3630	OH stretching
3420	Hydration, OH deformation
2850	Alkanes, C-H stretching
2925	Alkanes, C-H stretching
1620	Hydration, HOH deformation
1470	Alkanes, C-H stretching
910	OH deformation, linked to 2 Al^{3+}
840	OH deformation, linked to Al^{3+}, Mg^{2+}
790	Silica
470	AlO stretching

3.2 Preparation of Organoclays, Sorption/Desorption Characteristics of $HDTMA^+$ ion on Hançılı Bentonite

For the organoclay preparation, samples of Hançılı Bentonite with a particle size of less than 170 mesh were treated with HDTMA-Br solutions of two different concentrations 1.2 x 10^{-2} M and 6 x 10^{-3} M corresponding to 100% (60 mmol/100 g)and 200 % CEC (nearly 120 mmol/100 g) of the clay studied. For these two loadings, the amount of $HDTMA^+$ sorbed with respect to time in a period of 12 hours (720 min.) can be seen in Figure 3.3.

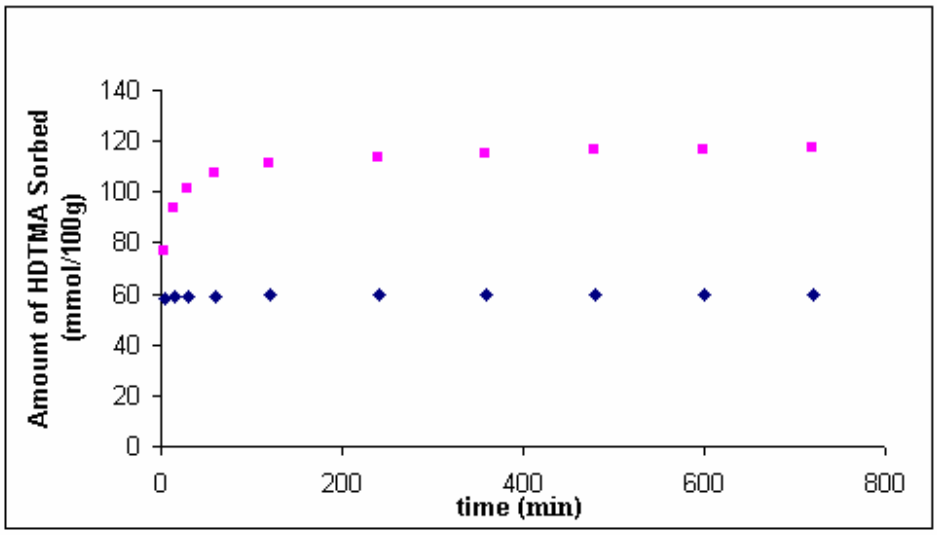


Figure 3.3 HDTMA Sorption on Hançılı Bentonite with respect to time.

♦ : Initial HDTMA input is the same as CEC of the clay (100% CEC)

■ : Initial HDTMA input is twice of CEC of the clay (200 %CEC)

In Figure 3.3 the trend is indicated that when the initial input of $HDTMA^+$ is the same as that of CEC of the clay, which corresponds to

less than a complete monolayer coverage, a simultaneous uptake takes place with a magnitude of 59.6 mmol/100 g. This corresponds to 99.3% of the initial surfactant concentration added. As the initial $HDTMA^+$ concentration is increased to twice of CEC (120 mmol/100 g) of the clay, the sorption process goes through a transition time, reaching to a maximum in around two hours beyond which a plateau is reached indicating a structural rearrangement of the sorbed surfactant molecules. At the plateau, which corresponds to a $HDTMA^+$ loading of 116.8 mmol/100g, the $HDTMA^+$ uptake of the clay reaches to 97.3% of the initial added amount. For comparison, two reference clays, kaolinite (KGa-1) and montmorillonite (SWy-1) were also treated with $HDTMA^+$ solutions containing twice of their CEC values for 24 hours. The uptake values at their saturation plateau, together with that of Hançılı Bentonite are given in Table 3.5.

Table 3.5 $HDTMA^+$ Uptake values for the reference clays and Hançılı Bentonite at the saturation plateau (Initial $HDTMA^+$ was twice of CEC of the corresponding clay)

		HDTMA Uptake Values	
CLAY TYPE	CEC (meq /100g)	This study (mmol/100 g)	Literature (mmol/100 g)
Kaolinite, KGa-1	2-4	5.2 ± 0.5	5.7*
Montmorillonite, SWy-1	70-100	105 ± 0.5	-
Hançılı Bentonite	50-70	116 ± 0.8	-

- : Li and Bowman, 2001

As seen, the uptake values found for, KGa-1, Kaolinite is in accordance with that of Li and Bowman, 2001. The uptake value of the Hançılı bentonite and that of Wyoming montmorillonite is also in comparable magnitudes with each other as expected.

In order to confirm the amount of $HDTMA^+$ uptake of the Hançılı Bentonite clay samples, bromide concentrations, at the plateau, were also measured by HPLC and was found to be 58 mmol/100g clay corresponding to half of the $HDTMA^+$ needed for a bilayer formation, which was found to be 116.8 mmol/100 g. This trend is also in good agreement with those of the result given in literature for the reference clays (Li and Bowman, 2001; Li, 1997).

Although a saturation plateau is reached in nearly two hours as seen in Figure 3.3, eight hours of shaking were adopted in further organoclay preparations for convenience.

In order to check the degree of stability of the prepared organoclay, a batch desorption experiment was performed. $HDTMA^+$ desorption in time is given in Figure 3.4 where the clay was initially loaded up to twice of its CEC initially. The trend observed indicates a two-stage desorption of the surfactant. The first stage is (up to 24 hours) probably corresponding to desorption from the outer layer of the surfactant bilayer while the second one which starts at around 72 hours and continues till 96 hours, corresponds to the desorption from inner layer of the bilayer

which is electrostatically bound to the mineral surface. At the end of seven days of organoclay-water interaction, only a total of 1.1 % $HDTMA^+$ were found to leach, revealing a rather stable organoclay structure in aqueous media, within the period of measurements.

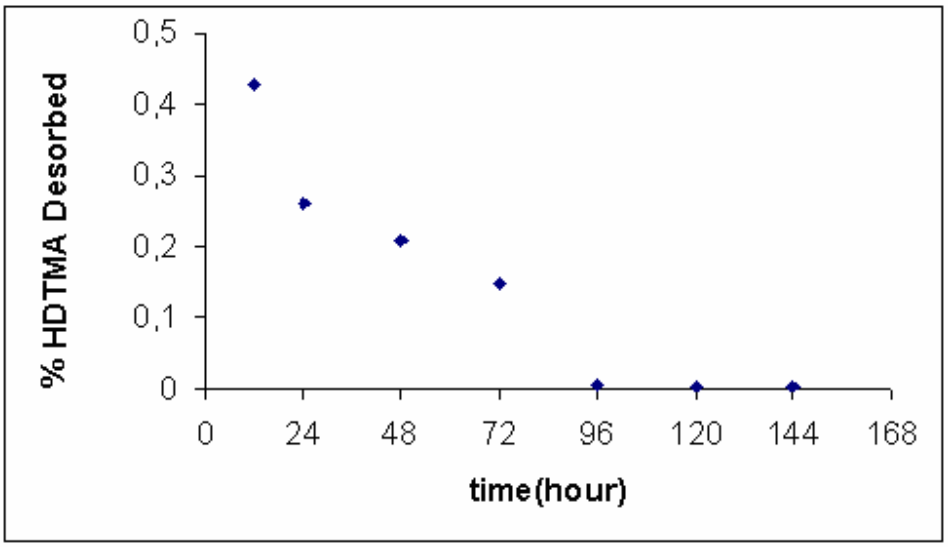


Figure 3.4 Short-term desorption of HDTMA from Hançılı Bentonite in aqeous media (initially loaded to twice of the CEC of the clay).

3.3 Nitrate-Organoclay Interactions

3.3.1 Sorption of Nitrate

Our first aim in nitrate sorption experiments was to find out the degree of nitrate sorption on the organoclay prepared and the time needed to reach a saturation plateau. 0.1 g of organoclays from Hançılı bentonite clays and those from two reference clays KGa-1(kaolinite) and SWy-1

(montmorillonite) were treated with $1.0x10^{-4}$-$3.0x10^{-3}$ M of KNO_3 solutions at a lateral shaking of 24 hours. For comparison unmodified (raw) Hançılı bentonite clay was also tested for nitrate sorption under the same experimental conditions. In Figure 3.5, the nitrate sorption by the organoclay in which an equilibrium is reached in about four hours is given.

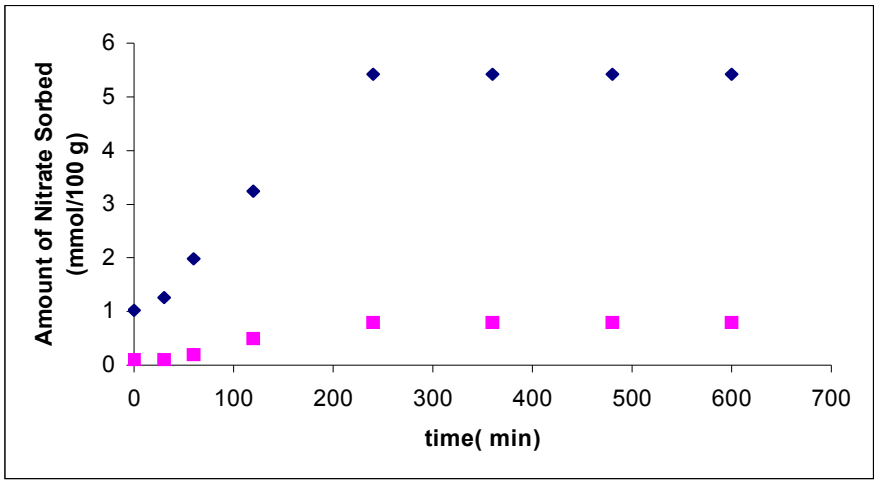


Figure 3.5 Nitrate sorption kinetics on organo Hançılı bentonite

♦ : Organo-bentonite, ■ : Raw bentonite

The nitrate uptake values of local and reference clays at the saturation plateau is given in Table 3.6.

Table 3.6 Nitrate Uptake values of reference and Hançılı bentonite clays at the saturation plateau.

CLAY TYPE	NITRATE UPTAKE (mmol/100 g)			
	UNMODIFIED		MODIFIED	
	This Study	Literature	This Study	Literature
Kaolinite, KGa-1	0.54	0.02*	2.0	2.4
Montmorillonite, SWy-1	2.1		7.4	
Hançılı Bentonite	0.72		8.1	

* : Li and Bowman, 2001

As seen in Table 3.6, after $HDTMA^+$ modification, nitrate sorption of all clay types are increased by several folds, that is, nearly 4.0 fold for modified kaolinite and 3.5 fold for montmorillonite, and about eleven fold increase in the case of modified Hançılı bentonite.

In order to evaluate the nitrate sorption characteristics of the organoclay prepared, known amounts of organoclay samples were treated with KNO_3 solutions of varying initial nitrate concentrations between 0.98-3.2 mM and shaken laterally for a total of eight hours. The trend in time using R_d versus time relationship is shown in Figure 3.6. As seen, for all concentrations studied, an equlibrium is reached at about four hours, and the magnitude of nitrate sorption increases as the initial concentrations increases.

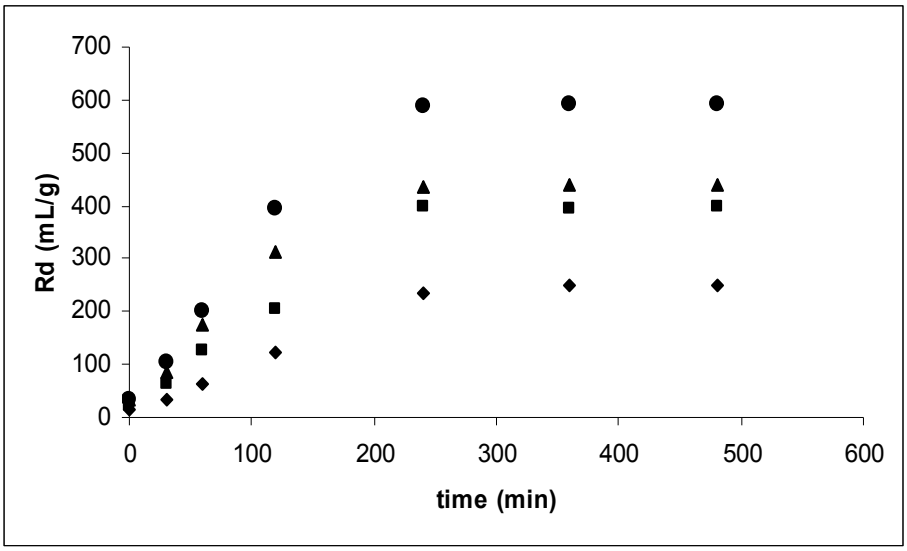


Figure 3.6 Nitrate Sorption Kinetics: The change of R_d with time for HDTMA-modified Hançılı Bentonite. Nitrate concentrations are; ♦ : $9.89x10^{-4}$ M, ■ : $1.73x10^{-3}$ M, ▲: $2.34x10^{-3}$M, ●: $3.24x10^{-3}$M.

The data obtained in this series of experiments were fitted to both Langmuir and Freundlich isotherms. In Figure 3.7 and Figure 3.8, Langmuir and Freundlich fittings are given respectively. The Langmuir and Freundlich isotherm constants obtained are given in Table 3.7.

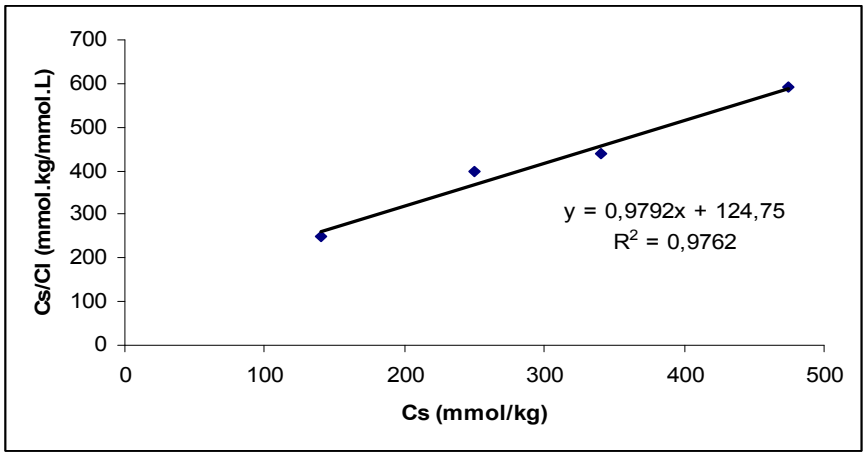


Figure 3.7 Langmuir Isotherm for Nitrate Sorption on Organo-bentonite

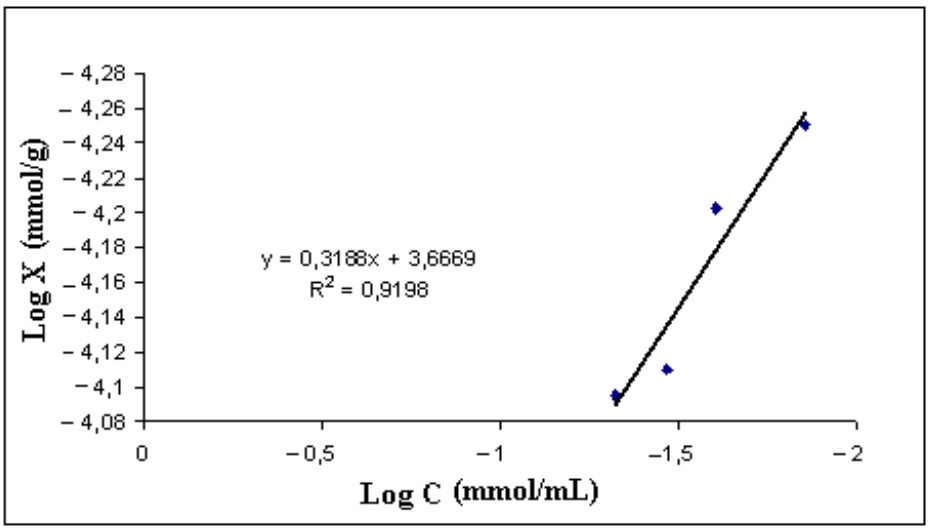


Figure 3.8 Freundlich Isotherm of Nitrate Sorption on Organo-bentonite in which X = amount of solute adsorbed per unit weigth of solid (g/g), C = equilibrium solute solution concentration (g/mL)

Table 3.7 Isotherm Constants Obtained from the Langmuir and Freundlich Fittings

Isotherm Type	Isotherm Constants	Values
Langmuir	Sm (mmol/kg) KL (L/mmol) R	124 1 0.979
Freundlich	K N R	4644 0.32 0.919

From these fittings one can conclude that nitrate sorption on HDTMA-modified Hançılı bentonite is better described by the Langmuir isotherm in which sorption maximum S_m is 124 mmol/kg with a Langmuir coefficient of 1 L/mmol.

Sorption of nitrate by HDTMA-modified clays were attributed to anion exchange in the previous studies (Li, 1999) in which the nitrate ions replace bromide ions associated with the surfactant head groups at the outer layer, can be represented as the following equation. This sorption phenomena on organoclay surface is schematically shown in Figure 3.9.

$$\text{HDTMA-Clay-Br} + NO_3^- = \text{HDTMA-Clay-}NO_3 + Br^-$$

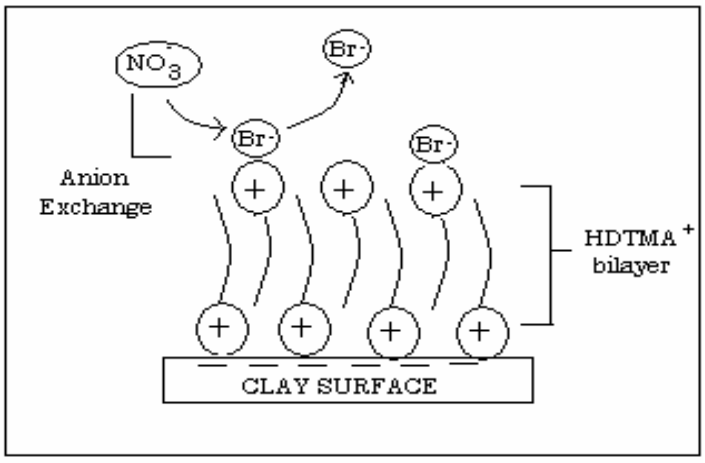


Figure 3.9 Sorption of Nitrate on Organo-bentonite (Li,1999)

In a nitrate sorption experiment when concentration of bromide ions released at saturation plateau were measured with the approach as described in section 2.4.2, it was found that 5.2 mmol of bromide ions

released for each 5.5 mmol of nitrate ions sorbed. This almost 1:1 relationship may also indicate that the retention of nitrate ions by organo-bentonite takes place through an anion exchange mechanism.

3.3.2 Desorption of Nitrate

In order to determine the stability of nitrate sorption on organoclay structure a series of experiments were performed. The organoclay samples were shaken with 10 mL of 4 $x10^{-4}$ M nitrate solutions for 24 hours at 250 rpm. Then nitrate uptake of organoclay samples were determined. The supernatant solutions were decanted and replaced with deionized water. Firstly, the concentration of nitrate for each solution was determined in the deionized water and labeled as the initial nitrate concentration. Then, the nitrate concentration of each solution were determined during the course of shaking for each day. The amount of desorbed nitrate was calculated from the difference between the final and initial concentration at the end of each day.

The maximum nitrate release observed at the end of the first day was 2.25 % of the sorbed nitrate. The amount of nitrate released was decreased day by day. Finally it was concluded that at the end of the sixth day; totally 4.5 % of the initially sorbed nitrate was released. The nitrate concentration remained constant at the supernant solution after the sixth day. In Figure 3.10, the change in the amount of nitrate desorbed for each day was shown.

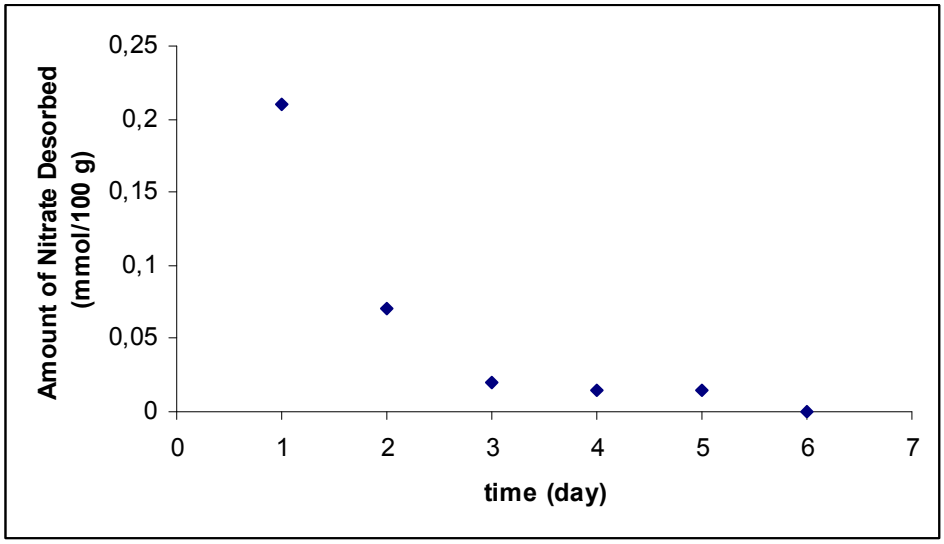


Figure 3.10 Short term desorption of nitrate from organobentonite

3.4 Sorption / Desorption of Borate

3.4.1 Sorption of Borate

There are two types of surfaces in clay minerals; the planar and edge surfaces. The structure of the edge surface is entirely different from that of the planar surface. At the platelets's edges, the tetrahedral silica sheets and the octahedral alumina sheets are distrupted, and primary bonds are broken. At this type of surface the structural ions are not fully coordinated by structural oxygens whereas these ions are fully coordinated on the planar surfaces. Specific adsorption can occur for any anion capable of coordination with the structural cations (Keren and Talpaz, 1984; Keren and Gast, 1983; Keren *et al*.,1981).

Previous studies indicate that borate can be adsorbed on clay minerals and on hydrous oxides of Fe and Al through a mechanism referred to as ligand exchange, whereby the adsorbed species displace OH^- (or H_2O) from the surface and form partly covalent bonds with the structural cations (Mezuman and Keren, 1981).

As indicated earlier, first experiments were based on the determination of the form the boron species that was most adsorbed by organoclay sample. In literature it was indicated that boric acid (H_3BO_3) can sorb on natural clay surface via ligand exchange as stated above. In the beginning of this study with boron species it was thought that boric acid can be sorbed on organoclay via both ligand and ion exchange, since boric acid is in the form of $B(OH)_4^-$ Thus; first experiments were conducted with boric acid. The results are given in Table 3.8.

Table 3.8 Borate Sorption by modified and unmodified clay samples when 2.0×10^{-3} M H_3BO_3 was used as adsorbate

CLAY TYPE	pH	AMOUNT OF BORATE SORBED (mmol/100 g)	Percentage of Sorbed Borate
Modified Bentonite	8	2.2 ± 0.1	11
Unmodified Bentonite	8	6.8 ± 0.3	33
Modified Bentonite	9	3.1 ± 0.2	15
Unmodified Bentonite	9	4.5 ± 0.3	23
Modified Bentonite	10	2.3 ± 0.1	12
Unmodified Bentonite	10	2.6 ± 0.1	14

The percentage of sorbed borate in Table 3.8 is the ratio of the boric acid sorbed to that of initial boric acid amount introduced. As seen from the Table 3.8, sorption capacity of unmodified bentonite is higher, between the pH : 8-10. It can also be seen that the sorption of boric acid by unmodified bentonite decreases with increasing pH, whereas no significant change was observed in the case of modified bentonite. The amount of sorbed boric acid was higher for unmodified bentonite. Although being negatively charged in this pH range (in the form of $B(OH)_4^-$), the expected ion exchange phenomena between the Br^- and $B(OH)_4^-$ ions was not observed on the contrary to nitrate ion. The boron hydrolysis reaction is as follows :

$$B(OH)_3 + 2\,H_2O = B(OH)_4^- + H_3O^+$$

The pK_a value for this reaction is 9.23 at 25 ºC.

The expected trend was increasing boric acid sorption by organoclay with increasing pH. In the case of unmodified bentonite at pH: 8 was the maximum sorption point as expected. It can be explained as follows:

According to the reaction given above when pH is below 7.0, $B(OH)_3$ predominates and the adsorption is small because the affinity of unmodified clay for this species is small. As the pH increased, the $B(OH)_4^-$ concentration increased rapidly and so boron adsorption

increased. At pH:10, OH^- species dominates and adsorption of boron gets smaller due to the competition of OH^- for the same adsorption sites.

In the second part of experiments sodium tetraborate decahydrate, $Na_2B_4O_7.10H_2O$, was used as adsorbent. Sodium tetraborate was selected since boron species has same charge (-3) as it has in boric acid and again in aqeuous solution it gives negatively charged borate ion $B_4O_7^{2-}$.

Table 3.9 Amount of Borate Sorbed by modified and unmodified clay samples when $4.7x10^{-3}$ M $Na_2B_4O_7$ was used as adsorbent

Clay Type	Amount of Borate Sorbed (mmol/100 g)	%
Modified Bentonite	4.4 ± 0.5	11
Unmodified Bentonite	2.4 ± 0.2	5

The results in Table 3.9 indicate that sorption capacity of organo-bentonite sample is higher than the raw bentonite. But in the case of modified bentonite the percentage of adsorbed borate was only 11% of the added amount that is not enough for the enrichment process. It was thought that this low sorption may result from interaction between the borate ions in aqeous media, as a result of high concentration, thus another experiment with lower borate concentration from 10^{-3} to 10^{-4} M was conducted.

When the added borate concentration was $1.0x10^{-4}$ M, the following results were obtained (Table 3.10)

Table 3.10 Amount of Borate Sorbed by modified and unmodified clay samples when borate concentration added was $1.0x10^{-4}$ M

Clay Type	Amount of Borate Sorbed (mmol/100 g)	%
Modified Bentonite	0.201± 0.002	16
Unmodified Bentonite	0.020± 0.005	2

Again it was revealed that sorption capacity of modified sample was higher than the unmodified form. But the percentage of sorbed borate was still low being only 16% for the modified bentonite.

$1.0x10^{-4}$ M borate solutions prepared from $Na_2B_4O_7$ with different pH values were investigated in order to determine the effect of pH on borate sorption. Five solutions with different pH's were mixed with modified and unmodified bentonite samples and shaken at 250 rpm for 24 hours. The pH values were adjusted using NaOH and HCl. At the end of 24 hour shaking there was no change in pH values of the borate solutions added. The results are given in the following figure (Figure 3.11).

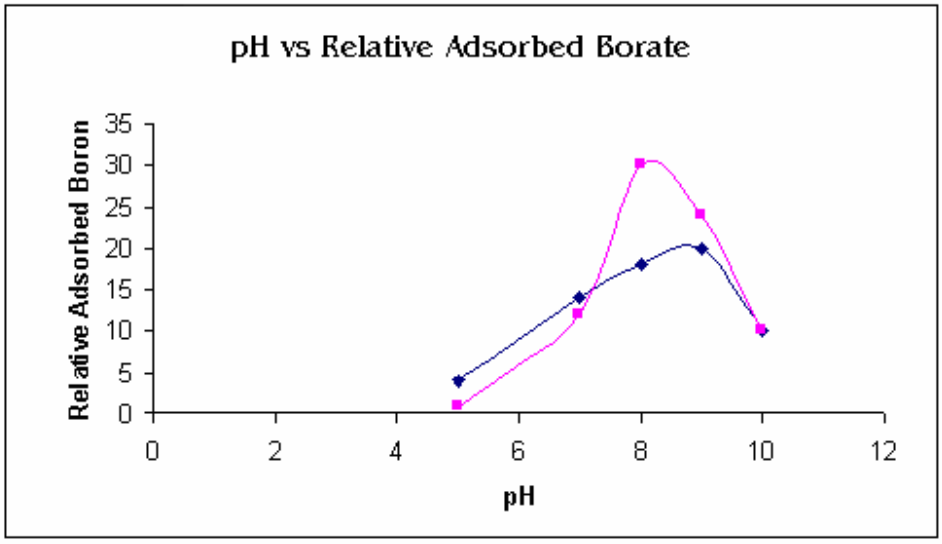


Figure 3.11 The Effect of pH on Borate Sorption

♦ : Raw Bentonite

■ : Organobentonite

It was determined that sorption maximum was obtained around pH: 9.0 for unmodified bentonite whereas it is around pH:8.0 in the case of modified bentonite.

As a result, it can be said that borate ion, $B_4O_7^{2-}$ can be sorbed on modified bentonite surface via ion exchange whereas $B(OH)_4^-$ ion can sorb only via ligand exchange. In the case of $B_4O_7^{2-}$ ion the low sorption can be explained by the size of this ion.

3.4.2 Desorption of Borate

In order to determine the stability of borate-organoclay interaction; desorption experiments were performed. It was concluded that when organoclay sample to which borate ions were adsorbed was not stable in aqeous medium. The borate ions leave the organoclay surface when they interact with water.

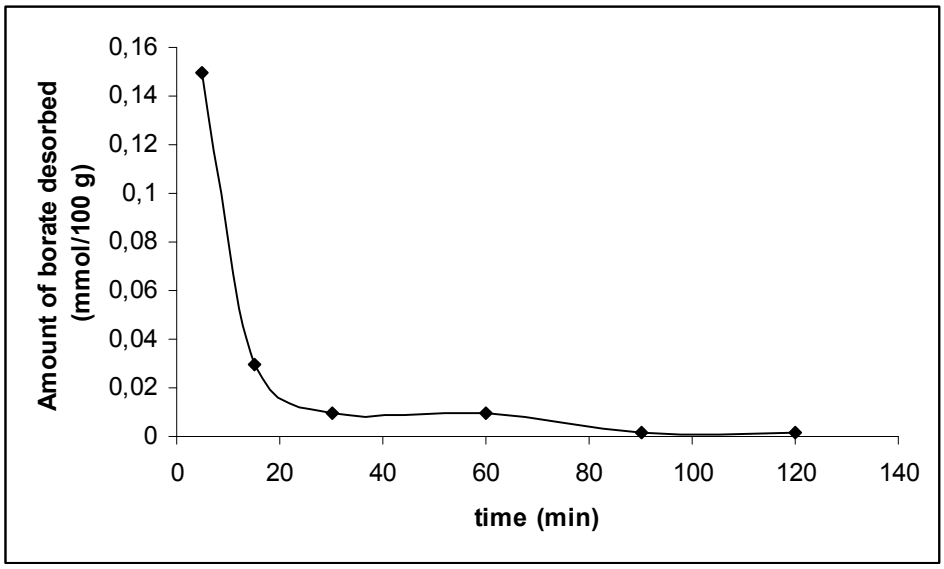


Figure 3.12 Short term desorption of borate from organobentonite

As seen in Figure 3.12; as soon as organoclay-borate samples were mixed together it was revealed that 75% of the sorbed borate left the organoclay structure within five minutes. In thirty minutes desorption becomes constant and by the end of the two hours the amount of the borate in supernatants were determined to be 90 % of the sorbed amount.

3.5 Chromate-Organoclay Interactions

As in the case of previous sorption experiments, organoclay samples prepared from Hançılı bentonites, KGa-1 (kaolinite), SWy-1 (montmorillonite) together with unmodified clay samples were treated with chromate solutions of known initial concentrations. The aim was to explore and compare the chromate uptake capacity of organoclays, time needed to reach an equilibrium and optimum shaking time for further studies.

The chromate sorption trend of modified and unmodified samples of Hançılı bentonite is given in Figure 3.13. The untreated samples show a minimal sorption capacity as indicated above. In case of modified Hançılı bentonite samples, an equilibirium is obtained within three hours of shaking time. However, in order to be on the safeside an eight hours of shaking time was adapted for further experiments. No pH adjustment was done for this set of experiments where the pH of the initial chromate solutions is found to be between 6.5-7.0, where CrO_4^{2-} predominates (Haggerty and Bowman, 1994).

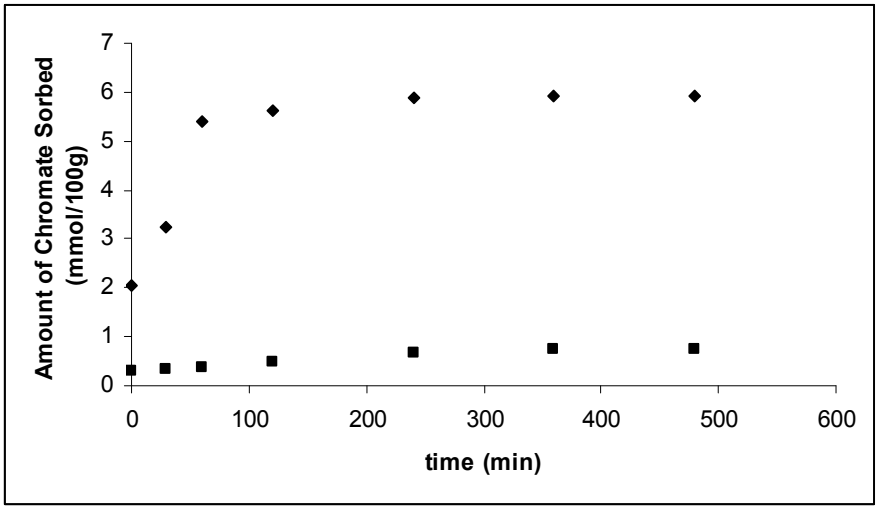


Figure 3.13 Sorption of Chromate on unmodified and organobentonite, initial concentration of chromate solution: 2.0×10^{-3} M.

♦ : Organo-bentonite

■ : Unmodified bentonite

The chromate uptake values by modified and unmodified clay samples at the end of a 24 hours of shaking period are given in Table 3.11.

Table 3.11 Chromate uptakes of reference clays and organobentonite

CLAY TYPE	CHROMATE UPTAKE (mmol/100 g)			
	UNMODIFIED		MODIFIED	
	This Study	Literature	This Study	Literature
Kaolinite, KGa-1	0.06	0.0089* 0.03**	1.32	1.3
Montmorillonite, SWy-1	0.96		8.96	
Hançılı Bentonite	0.71		6.51	

* : Li and Bowman, 2001 ** : Zachara et al., 1988

As seen in Table 3.11 the chromate sorption increases about 9-fold for montmorillonite SWy-1 and Hançılı bentonite compared to those of raw clays while there seems to be 22-fold increase in case of kaolinite KGa-1. For the raw kaolinite uptakes there seems to be a rough correlation with those of literature while the values for modified kaolinite is in very good agreement with that of literature (Zachara *et al.*, 1988).

For the investigation of sorption characteristics a series of sorption experiments were carried out with solutions of varying initial chromate concentrations between 0.79-3.01 mM. R_d versus time trend of these experiments carried out at different concentrations is given in Figure 3.14. Clearly, as the initial concentration increase R_d values also increase. These data are fitted to both Langmuir and Freundlich isotherm models. The plots obtained are given in Figures 3.15 and 3.16, the isotherm constants obtained from these fittings are presented in Table 3.12.

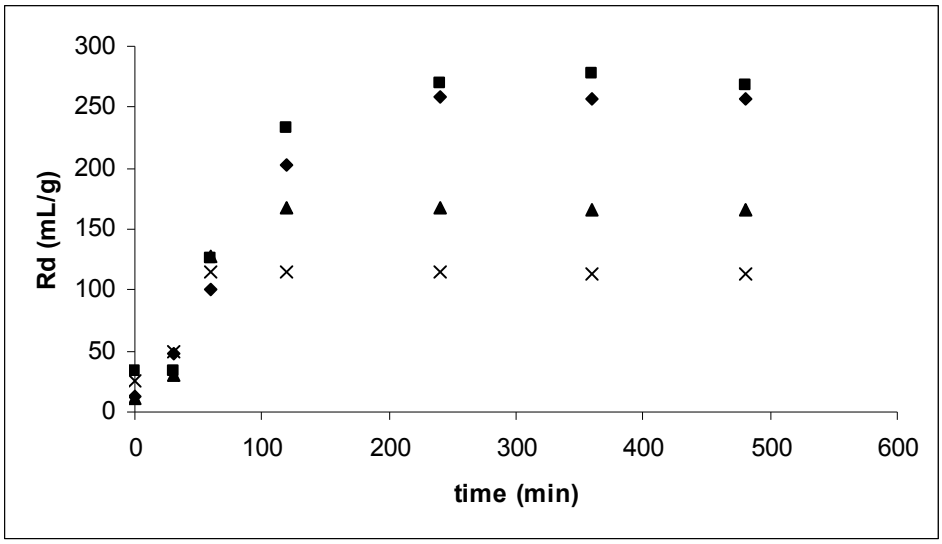


Figure 3.14 Chromate Sorption Kinetics: The change of R_d with time for HDTMA-modified Hançılı Bentonite. Amount of Chromate added; ■ : $3.01x10^{-3}$ M, ◊ : $2.62x10^{-3}$ M ▲: $1.70x10^{-3}$ M, , * : $7.92x10^{-4}$ M,

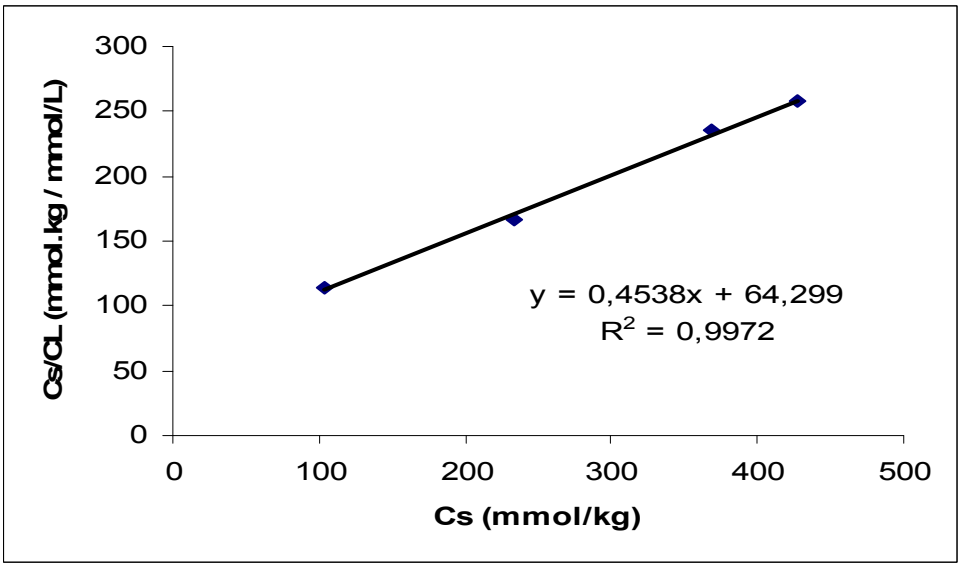


Figure 3.15 Langmuir Isotherm of Chromate Sorption on Organo-bentonite

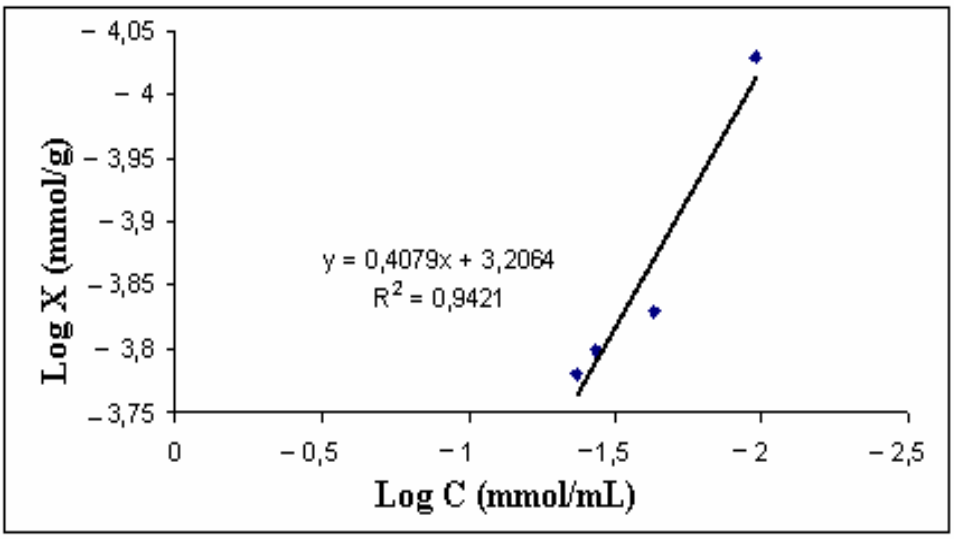


Figure 3.16 Freundlich Isotherm of Chromate Sorption on Organo-bentonite

Table 3.12 Isotherm Constants Obtained for the Sorption of Chromate on Organo-bentonite

Isotherm Model	Isotherm Constants	Values
Langmuir	Sm (mmol/kg) KL (L/mmol) R	64 2 0,997
Freundlich	K N R	1608 0.41 0.942

As in the case of nitrate sorption, chromate sorption of Hançılı bentonite is best described by the Langmuir isotherm with a sorption maximum at 64 mmol/ kg and with the correlation coefficient of 2 L/mmol that indicates the affinity of chromate to the bentonite surface.

Previous studies indicated that sorption of chromate by surfactant modified clay minerals was due to surface anion exchange and the anion exchange reaction of chromate replacing bromide on the surface which can be written as follow;

$$HDTMA\text{-}Clay\text{-}Br + CrO_4^{2-} \longrightarrow (HDTMA\text{-}Clay)_2\text{-}CrO_4 + 2\ Br^-$$

The sorption process can be visualized as follows (Figure 3.17)

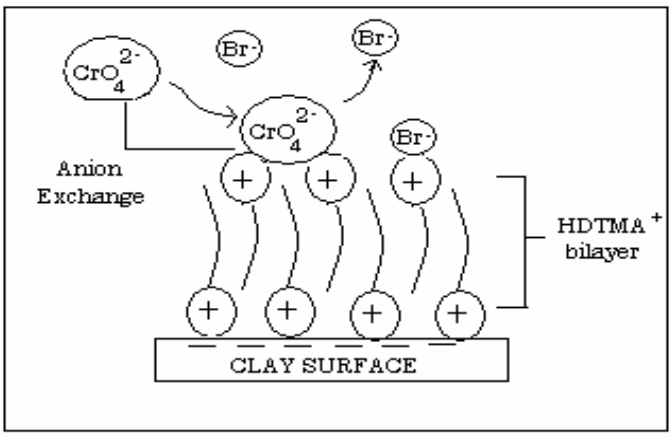


Figure 3.17 Sorption of Chromate on Organo-bentonite (Li, 1999)

This linear trend was also confirmed by an experiment where 5.80 mmoles of bromide were released for 3.84 mmoles of chromate sorbed.

Therefore we can conclude that the anion exchange is the main mechanism for chromate retention by organo-bentonite.

3.5.1 The Effect of pH on Chromate Sorption by Organoclay

The results of experiments carried out to investigate the effect of different pH values on chromate sorption are given in Table 3.13.

Table 3. 13 The effect of pH on chromate sorption by organoclay with an initial chromate concentration, $1.0x10^{-3}$ M.

pH of the SOLUTION	CHROMATE UPTAKE (mmol/100 g clay)	PERCENTAGE OF SORBED CHROMATE
3.0	9.61	90 %
5.0	7.43	81 %
7.0	4.47	51 %
9.0	4.38	49 %

As seen chromate sorption is the highest in acidic medium. As the pH is decreased chromate uptake of organo-bentonite increased. This result may be explained considering the fact that in the pH values below 6.51 chromate is in the form of CrO_4^{2-} and $HCrO_4^-$, that is; there are negatively charged ions in the medium which enhances the sorption onto positively charged organo-bentonite surface.

As the pH is increased then, the OH^- ion becomes dominant species in the medium. The chromate sorption by organo-bentonite decreases due to competition between OH^- and CrO_4^{2-} ions.

3.5.2 Desorption of Chromate

In the chromate desorption experiments; the same method with nitrate desorption was followed. Firstly organoclay samples were shaken with 4×10^{-4} M chromate solutions and uptake values were determined. Then, the supernant solutions were replaced with deionized water and chromate concentrations were determined for each day. As can be seen from Figure 3.18; the maximum chromate release was again observed at the end of the first day.

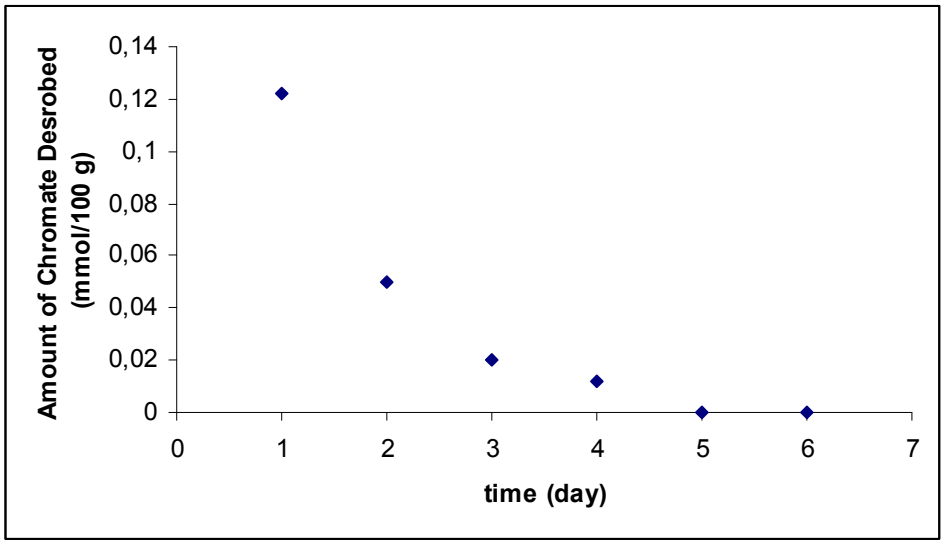


Figure 3.18 Short Term Desorption of Chromate from organobentonite

The total amount of chromate desorbed in six day period was found to be nearly 3.3 % of the sorbed amount. At the end of the desorption experiments it was revealed that chromate-organoclay structure is more stable than nitrate-organoclay structure. Although the amount of ion

added to organoclay samples was nearly same in both nitrate and chromate cases, the amount of sorbed chromate ion was more than nitrate ion. But the desorbed chromate ion was less than nitrate ion. In both nitrate and chromate cases maximum ion release was observed as soon as organoclay-ion structure interacts with water.

3.5.3 Retention in Cr(III) and Cr(VI) mixture

In order to confirm the selectivity of organo-bentonite prepared for Cr^{6+} a batch experiment was carried out with a mixture containing Cr^{3+} and Cr^{6+} (in the form of CrO_4^{2-}) with an initial concentration of $3.27x10^{-4}$ M for each ion. As given in the experimental section the concentrations of Cr^{3+} and Cr^{6+} species were determined by chemiluminescence measurements. Results are given in Table 3.14.

Table 3.14 Amount of Chromium species added and sorbed in a mixture of CrO_4^{2-} and $CrCl_3$.

	Cr(VI)	Cr(III)
Amount of Ion Added (mmol/100 g)	3.27	3.27
Amount of Ion Sorbed (mmol/100 g)	1.98	0.48

As seen organo-bentonite samples absorb Cr^{6+} with a degree reaching to 63% of the inital added amount while Cr^{3+} sorption is only about 14% indicating a higher selectivity for Cr^{6+} as expected due to the possibility

of CrO_4^{2-} - Br^- exchange processes taking place at the tail groups bounded to the organoclay surface.

3.6 Chromate and Nitrate Mixture–Organoclay Interaction

In order to balance the charge equivalence between chromate (CrO_4^{2-}) and nitrate (NO_3^-) ions; solutions of these ions were added in the concentration ratio of 1:2. It was revealed that while only 15% of the initial added chromate was sorbed by organoclay sample, it was 67% for the nitrate case. Organo-bentonite structure shows higher affinity for nitrate ion than chromate ion as seen in Table 3.15.

Table 3.15 Amount of Ions Sorbed by Organoclay in a Chromate-Nitrate Mixture

NITRATE- CHROMATE MIXTURE		**Percentage of Ion Sorbed**
Initial Concentration of Chromate Added	1.30×10^{-3} M	15 %
Final Concentration of Chromate after shaking	1.11×10^{-3} M	
Initial Concentration of Nitrate Added	2.65×10^{-3} M	67%
Final Concentration of Nitrate after shaking	8.80×10^{-4} M	

CHAPTER IV

CONCLUSION

In this study, an organoclay was prepared using a local clay, Hançılı Bentonite from Kalecik, Hançılı region in Turkey.

At first, the characterization of Hançılı Bentonite clay sample was performed using XRD, XRF and FTIR analyses. As a result of X-Ray powder diffraction trace obtained, Hançılı Bentonite clay was determined to be Na-bentonite and dioctahedral smectite type of clay consisting mainly montmorillonite clay mineral. The expected chemical formula was obtained using the results of XRF analysis. The FTIR spectra of samples support the dioctahedral structure of Hançılı Bentonite clay.

The sorption of cationic surfactant, $HDTMA^+$, by Hançılı Bentonite clay was studied for both the initial $HDTMA^+$ input is the same as CEC of the clay and twice of the CEC of the clay. More than % 97 of the initial added $HDTMA^+$ amount were appeared to be sorbed by Hançılı Bentonite in both cases. When the initial input of $HDTMA^+$ is the same as that of CEC of clay, corresponding to less than a complete monolayer coverage, a simultaneous sorption of $HDTMA^+$ takes place. As the initial

added $HDTMA^+$ amount is increased to twice the CEC of the clay, the sorption maximum is obtained in around two hours time indicating a structural rearrangement of $HDTMA^+$ molecules forming a bilayer structure. This bilayer formation was supported by also released Br^- measurements. The bromide ion amount released was found as half of the $HDTMA^+$ needed for a bilayer formation. For comparison, two reference clays; Kaolinite, KGa-1, and Wyoming Montmorillonite, SWy-1, were also used for $HDTMA^+$ sorption. The results obtained were in accordance with that of Li and Bowman, 2001.

The short term desorption studies revealed that at the end of seven days of organobentonite-water interaction, only 1.1% of $HDTMA^+$ were found to leach, indicating a stable organobentonite structure in the aqeous medium.

The organobentonite sample prepared was tested for the removal of anionic contaminants, such as nitrate and chromate. The organobentonite was also tested for the enrichment processes in case of borate species.

The nitrate sorption of Hançılı Bentonite clay increased eleven fold in its modified form. The sorption of nitrate by organobentonite is well described by the Langmuir isotherm in which sorption maximum at S_m is found to be 124 mmol/kg with a Langmuir coefficient 1.0 L/mmol. The sorption of nitrate by organobentonite was attributed to anion exchange

in which the nitrate ions replace bromide ions, the ratio of the bromide ion released to nitrate ions sorbed was found to be 1:1.

As a result of the short term desorption studies, it was observed that organobentonite-nitrate structure was stable in aqeous media. Totally 4.5 % of the initially sorbed nitrate was released at the end of sixth day.

The amount of borate ions sorbed by organobentonite sample was not sufficient for the enrichment purposes. It was revealed that the maximum borate sorption, in the form of $B_4O_7^{2-}$, by organobentonite, occurs at around pH =8.0. The amount sorbed was nearly 30 % of the initial added borate ion. The maximum sorption was obtained at pH=9.0 and the sorbed amount was only 15% of the initial added amount where the borate ion was in the form of $B(OH)_4^-$.

As a result of sorption studies with borate ions, it may be concluded that $B_4O_7^{2-}$ can be sorbed on organobentonite surface via ion exchange whereas $B(OH)_4^-$ ion can be sorbed only via ligand exchange. The low degree of sorption of $B_4O_7^{2-}$ by organobentonite may be explained by the larger size of this ion.

In the desorption studies with borate ions, it was seen that as soon as organobentonite-borate samples were mixed with water, %75 of the sorbed borate were released. At the end of the two hours this released

amount reached to % 90 revealing that the organobentonite-borate structure was not stable in aqeous media.

The studies with chromate ion indicated that the chromate sorption increased about nine fold for Hançılı Bentonite in its modified form. The chormate sorption by organobentonite is well described by the Langmuir isotherm with a sorption maximum at 64 mmol/kg and with the correlation coefficient of 2 L/mmol.

The sorption of chromate by organobentonite was attributed to anion exchange in which chromate ion replaces bromide ions. The studies in which the bromide ion released indicated that the ratio of bromide ion released to chromate ion sorbed was 1:2. The chromate sorption on organobentonite increased with decreasing pH values. The chromate sorption was maximum in acidic medium since CrO_4^{2-} and $HCrO_4^-$ are the dominant species at this pH. The OH^- ion becomes dominant in basic medium, and due to competition between OH^- and CrO_4^{2-}, the degree of sorption decreases with increasing pH.

The short term desorption studies with chromate revealed that the resulting organobentonite-chromate structure was stable. The total amount of chromate leached in a six day period was found to be nearly 3.3% of the sorbed amount.

The organobentonite sample shows higher affinity for Cr(VI) than for Cr(III) when these two ions are present together. While the amount of sorbed Cr(VI) was found to be 63% of the added amount, it was only 14% for Cr(III) ion indicating higher selectivity for Cr(VI) due to the CrO_4^{2-} - Br^- echange process taking place on the organobentonite surface.

The organobentonite sample shows higher affinity for nitrate ion than chromate ion. In a solution containing both nitrate and chromate ions, only 15% of the initial added chromate sorbed while it was 67% with nitrate. This phenomena may be explained by the ion exchange process occurring. The nitrate ion replaces one bromide ion on the organobentonite surface, on the other hand, the chromate ion, being larger and charged as -2, replaces two bromide ions.

The following statements can be drawn from the investigations carried throughout this study;

- Negatively charged clay mineral surfaces reverse into positively charged ones at a surfactant concentration that is 200% of clay's CEC.

- More than 97% of HDTMA can be sorbed on our local clay.

- Organoclays thus prepared are stable in aqeous medium.

- Chromate and nitrate uptakes of organoclay prepared is at least 7-8 times greater that of natural clay, the resulting organoclay-ion complexes are stable.

- Organoclay prepared shows selectivity towards Cr (VI) in a mixture of Cr (III) and Cr(VI).

- Organoclay prepared shows higher affinity for nitrate ion in a nitrate-chromate mixture.

- Organoclay prepared is not suitable for enrichment of borate species since it shows low affinity for this ion.

- The results demonstrate that properly prepared organoclay can be used as an effective sorbent for oxyanions such as nitrate and chromate.

A future study could be the application of this modified clay for some other potentially toxic anions as well as their mixtures from aqeous systems.

CHAPTER V

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