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ADSORPTION PROPERTIES OF INORGANO-ORGANO BENTONITE

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ÖZET

INORGANO – ORGANO BENTONİTİN ADSORPSİYON ÖZELLİKLERİNİN SAPTANMASI

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Bu tezde Inorgano (al-pillared), organo ve inorgano-organo bentonitin adsorpsiyon özellikleri incelenmiştir. Çalışma başlıca iki bölümden oluşmaktadır: birinci bölüm modifiye bentonitlerin hazırlanması ve ikinci bölüm ise hazırlanan bentonitlerin gliserinin renginin ağartılmasında kullanılmasıdır.

Deneysel çalışmaların ilk bölümünde Al-pillared-, organo-, ve inorgano organo bentonitler mikrodalga yöntemiyle hazırlanmıştır. Al-pillared bentonitler, başlangıc [Al^{+3}] derişimi 0.1, 0.15, ve 0.2 M olacak şekilde hazırlanmıştır. Organo bentonitlerin hazırlanışında, kilin katyon değişim kapasitesinin (CEC) % 100'üne eşdeğer miktarlarda Hexadecyltrimethylammonium bromide (HDTMAB) kullanılmıştır. Numuneler kurutucu, dondurarak kurutma ve mikrodalga yöntemleri ile kurutularak, kurutma şeklinin kilin yapısına ve ağartma kapasitesine olan etkisi incelenmiştir. Inorgano-organo bentonitler [Al^{+13}] ve HDTMAB kullanılarak modifiye edilmiştir. Numune hazırlama sırasında başlangıç [Al^{+3}] derişimi 0,1 M ve yüzek aktif maddenin miktarı 4 mmol/ kil olarak alınmıştır

İkinci bölümde, hazırlanmış olan Al-pillared, organo ve inorgano-organo bentonitlerinin ağartma etkinliğine zaman, sıcaklık ve adsorbent miktarı gibi parametrelerin etkisi incelenmiştir.

Anahtar sözcükler: Organo bentonit, Al-destekli bentonit, inorgano-organo bentonit, biyodizel, gliserin, ağartma

ABSTRACT

ADSORPTION PROPERTIES OF INORGANO-ORGANO BENTONITE

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MSc in Chemical Engineering

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In this work, the adsorption properties of modified clays, inorgano (Al-pillared), organo, inorgano-organo, were investigated using distilled glycerine. The study mainly consists of two parts: first, preparation of modified bentonites and second, bleaching of distilled glycerine by modified bentonites.

In the first part, Al-pillared, organo-, and inorgano-organo bentonites were prepared by microwave irradiation method. During the synthesis of Al-pillared clay, amount of aluminium used in the preparation was taken 0.1, 0.15 and 0.20 M Organo clays were synthesized by using Hexadecyltrimethylammonium Bromide

(HDTMAB). The amount of HDTMAB used was in amount equivalent to 100% of the cation exchange capacity (CEC) of clay. Organo clays were dried under three different drying conditions; oven, microwave, and freeze drying and so it was observed the effect of drying conditions on the structure and adsorption behaviour of the adsorbents. Inorgano-organo bentonites were modified with polyhydroxialuminum and alkylammonium cations. During the synthesis of inorgano-organo clay, 0.1M [Al^{+3}] initial concentration and HDTMA in amount such that the ratio of HDTMA to clay to be 4.0 mmoles/gram.

In the second part, the adsorbents prepared were used to investigate the effect of temperature, time of contact, and adsorbent amount.

Keywords: Bentonite, organo bentonite, Al-pillared bentonite, inorgano-organo bentonite, inorgano-organo bentonite, biodiesel, glycerine, bleaching

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LIST OF SYMBOLS

BE	Bleaching Efficiency, %
CEC	Cation exchange capacity (meq/100g clay)
FD	Freeze Dried
HDTMAB	Hexadecyltrimethylammonium Bromide
MONG	Matter Organic Non-glycerol
MW	Microwave
MWD	Microwave Dried
OD	Oven Dried
PILC	Pillared interlayered clay
RS	Removal of Soap, %

1.0 INTRODUCTION

Due to the limited capacity of fossil fuels and their environmental impacts, the production of renewable and environmentally friendly fuels is an active area of research. Although they are about 2.3 times more expensive than the fossil fuels at the moment [Kondili and Kaldellis, 2007], the use of sustainable raw materials, vegetable oils and animal fats, and their lower emissions [Gerpen, 2005] make the biofuels the alternatives to the classical fuels. The economy of biodiesel production is greatly affected by the sale of glycerine and right-sized biodiesel plant will win with more feasible project economics by the sale of this product. Therefore, the biodiesel manufacturers should also consider glycerine quality even it means additional cost. Thus at this time, biodiesel like other biofuels is not economically competitive with the fossil fuels and technological development is needed to bring the production cost of biodiesel down. Among the precautions to be taken for this aim, the reduction of the cost of refinery of crude glycerine seems more convenient than others since it is possible without making any drastic change in the equipment and process.

Glycerine recovery process includes neutralization, stripping, distillation, and bleaching units. Bleaching is an important process in the production of technical glycerin. Bleaching involves the removal of colored pigments and other impurities such as soaps and catalysts by adsorption with bleaching adsorbents. Activated carbon, silicon-based adsorbents, hectorite-based activated clays, and organo-cationic clays are the groups of adsorbents most often studied for removing colorants from oils. [Caglayan et al., 2005]

Due to its high surface area, activated carbon is commonly used bleaching adsorbent however it is very expensive.

Clay minerals especially smectites are generally modified by applying a known type of activation, i.e., acidic, cationic, anionic, organo-cationic, or thermal, to form new active sites and/or to rainforce existing ones. Smectites are used in the modification because of their high cation exchange capacity, swelling capacity, high surface area, and resulting high sorption capacities.

In this study, the bleaching properties of crude clay, Al-pillared clays, organo clays and inorgano-organo clays were studied as alternatives to activated carbon.

All types of modified clays were prepared by the microwave irradiation which is an energy-intensive and the decreasing time-consuming method [Baldassari et al., 2006]. During the synthesis of Al-pillared clay, amount of aluminum used in the preparation was changed and so it was observed the effect of this change on the structure and bleaching behavior of the adsorbents.

Organo clays were synthesized by the exchange of neutralizing cations with alkylammonium cations of Hexadecyltrimethylammonium Bromide (HDTMAB). HDTMAB was used in amount equivalent to

100% of the cation exchange capacity (CEC) of clay. Organo clays were dried under three different drying conditions; oven, microwave, and freeze drying.

Inorgano-organo clays which were clay mineral modified with polyhydroxialuminum and alkylammonium cations. During the synthesis of inorgano-organo clay, 0.1M [Al^{+3}] initial concentration and HDTMA in amount such that the ratio of HDTMA to clay is 4.0 mmoles/gram were used.

The textural characteristics of the materials obtained were studied by XRD, FTIR, SEM, BET and DSC analyses. The effect of temperature, contact time, the amount of adsorbents was determined. Glycerine colors were measured by Lovibond PFX880 Tintometer in a red and yellow color scale.

All of the adsorbents showed different BEs. As the maximum BEs of the adsorbents was compared, Oven Dried Organo Clay has maximum bleaching efficiency with 54.7 % red and 67.4 % yellow values.

It was found that the mixture of 1% of activated carbon and %1 of microwave dried organoclay is effective as 3% of activated carbon for 50°C and 1 hour contact time. Thus, a 60% reduction obtained in the amount of activated carbon points that the method proposed has the potentialities to evaluate a more feasible process economics.

2.0 LITERATURE REVIEW

Glycerine recovery process includes neutralization, stripping, distillation, and bleaching units. Every unit operation in the refining process has its own complexity, and unique importance in achieving finished product quality. This project focuses on the bleaching stage of the process.

2.1 Bleaching

Bleaching is a very important step in oil and fat processing. In early days the process was thought to remove only coloured pigments, but more modern schools of thought consider the process to be much more than this. The process involves the removal of coloured materials and other impurities by adsorption with bleaching adsorbents. The process would be better termed "adsorptive cleansing". [www.nzic.org.nz/ChemProcesses/food/6G.pdf]

Bleaching is also an essential process in the production of technical glycerine with the required colour, properties desired by consumers. The purpose is the removal of MONGs (Matter Organic Non-glycerol), trace metals, color pigments, free faty acids and other breakdown products in the glycerine by adsorption on the active surface of the bleaching adsorbents to improve colour and stability of the final glycerine. [Kaynak et al., 2004]

After the bleaching process, color of fats are usually described using the Lovibond 5.25 – inch scale, correctly known as the American Oil Chemists' Society (AOCS) Wesson color but also as AOCS Lovibond color or just Lovibond color.[Edward, 1996]

Bleaching can made by different methods and different adsorbents to obtain technical glycerine. The most important adsorbent used in bleaching fats and oils is bleaching earth or clay. The raw materials for these adsorbents are bentonites or montmorillonite which have been treated with organics and inorganics to yield very effective bleaching materials.

2.2 Bleaching Methods

During the bleaching process adsorption is occurring via many different mechanisms. Bleaching mechanism by which the sorbent locks onto a contaminant can occur three different ways:

- Physically through surface attraction involving Van Der Waals forces
- Chemically by chemical or ionic bonds to the surface of the clay
- By molecular sieves which trap contaminants under pressure inside the pores of the clay during filtration

Bleaching process is carried out in batch and continuous operations at atmospheric pressure or under vacuum.

In batch bleaching, a quantity of sample is pumped to a tank equipped with an agitator and steam coils. The sample is heated to optimum temperature when the agitator running. The desired quantity of bleaching adsorbents is then pulled into the sample. At the end of the bleaching time, sample and adsorbent mixure is pumped to a filter where the adsorbents are removed. Bleached sample is sent to a storage tank.

Continuous bleaching methods have been used, such as using a single large vacuum tank, a single large atmospheric tank, and multiple tanks where the sample is pumped from one to another. The tank capacity must be large enough.

2.3 Adsorption

Bleaching by adsorption is used to improve the colour of the oil, remove impurities such as soaps and catalysts and to remove metallic compounds and prooxidants.

The unbalanced forces at the phase boundary cause changes in the number of molecules (atoms, ions) to occur on the boundary surface as compared with the corresponding numbers within the neighbouring phases. This change in concentration at the surface is referred to as adsorption, and may be a physical process (physisorption) taking place due to van der Waals forces, hydrogen bonding, etc.., or it may be due to chemical processes and to the formation of chemical compounds (chemical adsorption or chemisorption). As a result of these processes, the balance of forces at the interface is partly or fully restored.

Adsorption is dependent not only on the surface charge, but also on the surface area. The amount of material adsorbed is directly proportional to the specific surface. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation [www.aquatechnologies.com/info_bentonite_clay.htm]. Adsorption processes are usually classified according to the kind of phases constituting the interface, and according to the type of forces. Depending on the type of phases in contact, we can consider the process of adsorption in the following systems:

1. Liquid / Gas
2. Solid / Gas
3. Solid / Liquid
4. Liquid/Liquid

2.4 Bleaching Adsorbents

Bleaching involves the adsorption of color pigments by bleaching adsorbents. The classification of adsorbents into polar and non-polar proves unsatisfactory when the nature of adsorption forces is considered. By introducing suitable functional groups on to the surface of a polar silica gel we can change its adsorption properties over a wide range. These properties may become analogous to those of non-polar adsorbents when the active OH groups at the gel surface are substituted by non-active groups. It is therefore more reasonable to classify adsorbents according to their surface chemical character, account being taken of the electronic charge distribution on their surface.

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called "hydrophilic" and aluminosilicates such as zeolites, clays, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, nonpolar adsorbents are generally "hydrophobic". Carbonaceous adsorbents, polymer adsorbents and silicalite are typical nonpolar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water.

The most frequently used adsorbents used for glycerine bleaching are natural earth, activated carbon and activated earth. They differ in bleaching performance. Bentonite minerals have limited sorptive properties in the natural state and require chemical treatment to create the surface area and porosity needed for bleaching.

2.4.1 Activated Carbon

The most common adsorbent is Activated Carbon. Activated carbon is the generic term used to describe a family of carbonaceous adsorbents with a highly crystalline form and extensively developed internal pore structure. A wide variety of activated carbon products is available exhibiting markedly different characteristics depending upon the raw material and activation technique used in their production. Activated carbons have a higher bleaching efficiency than natural clays. Activated Carbon is produced specifically so as to achieve a very big internal surface. The volume of pores of the activated carbons is generally greater than 0.2 ml g^{-1}. The internal surface area is generally greater than 400 m^2 g^{-1}. The width of the pores ranges from 0.3 to several thousand nm.

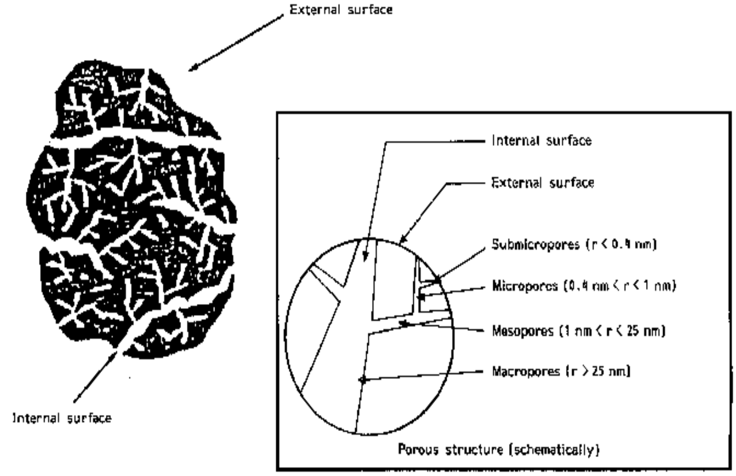


Figure 2.1: Schematic activated carbon model

All activated carbons are characterized by their ramified pore system within which various mesopores (r = 1-25 nm), micropores (r = 0.4-1.0 nm) and sub micropores (r < 0.4 nm) branch off from what we call macropores (r > 25 nm). [Henning and Schäfer]

This big internal surface makes active carbon ideal for adsorption. Active carbon comes in two variations: Powder Activated Carbon and Granular Activated Carbon. These materials can adsorb a wide variety of substances. Active carbon can adsorb the following soluble substances:

- Adsorption of organic, non-polar substances such as:
    - Mineral oil
    - BTEX
    - Poly aromatic hydrocarbons (PACs)

  - (Chloride) phenol
- Adsorption of halogenated substance: I, Br, Cl, H and F
- Odor
- Taste
- Yeasts
- Various fermentation products
- Non-polar substances (substances which are non soluble in water)

Regeneration: Active carbon can be regenerated easily by oxidizing the organic matter. The efficiency of the active carbon decreases by 5-10% [lenntech.com/activecarbon-regeneration.htm]. A small part of the active carbon is destroyed during the regeneration process and must be replaced. Since the activated carbon is an expensive product, the cost of replacing the saturated carbon would be prohibitive in most of the cases. It should therefore be regenerated, and four methods have been developed for this purpose. [www.lenntech.com/activecarbon-regeneration.htm]

- **Steam regeneration**: This method is restricted to regenerating carbon which has only retained a few very volatile products [www.lenntech.com/activecarbon-regeneration.htm].

- **Thermal regeneration:** By pyrolysis and burning off of adsorbed organic substances. In order to avoid igniting the carbon, it is heated to about 800 °C in a controlled atmosphere. It requires considerable investment in either a multiple-hearth furnace and it causes high carbon losses [//www.lenntech.com/activecarbon-regeneration.htm].

- **Chemical regeneration:** Some process based on the action of a solvent used at a temperature of approximately 100 °C and with a high pH [www.lenntech.com/activecarbon-regeneration.htm].

- **Biological regeneration:** This method of regeneration has not yet been applied on an industrial scale [www.lenntech.com/activecarbon-regeneration.htm].

Activated Carbon's high initial cost and the need for a costly regeneration system have necessitated the investigation of other inexpensive adsorbents such as clay mineral. Cost effectiveness and availability are among the main criteria in selecting an adsorbent in addition to its adsorptive properties.

2.4.2 Clay Minerals

Minerologists use the term "clay minerals" for a group of hydrous layered magnesium- or alumino-silicates (phyllosilicates). Each magnesium- or alumino-phyllosilicate is essentially composed of two types of sheets, octahedral and tetrahedral, designed O and T, respectively. Each sheet is composed of planes of atoms, arranged one above the other, a plane of hydroxyls and/or oxygens above a plane of aluminums and/or magnesiums or silicons, the latter above another plane of hydroxyls and/or oxygens, and so on. [Yariv and Cross, 2002]

The tetrahedral sheet is composed of three parallel atomic planes, which are composed of oxygens, silicons and oxygens, respectively. Figure 2.2 shows the structure of tetrahedral sheet.

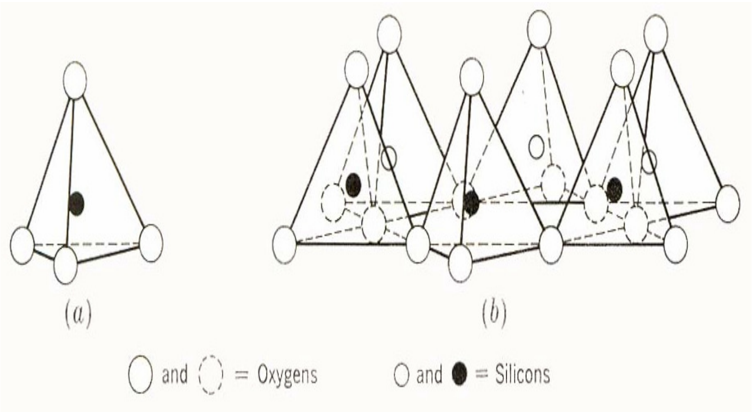


Figure.2.2: Diagrammatic sketch showing (a) single silica tetrahedron and (b) the sheet structure of silica tetrahedrons arranged in a hexagonal network.

The tetrahedra are arranged so that all of their apices point in the same direction with their bases in the same plane. The oxygens form an open hexagonal network in this plane, often referred to as the hexagonal or perforated oxygen plane (or O-plane).

Aluminum atoms can replace silicon atoms in the tetrahedral sheet, thereby contributing a negative charge to the sheet. The substitution of Al for Si changes the surface properties of the perforated oxygen plane, since Si – O – Al groups (known as alumino-siloxane groups) are better donors of electron pairs than are Si – O – Si groups. [Yariv and Cross, 2002]

The octahedral sheets are arranged to form a hexagonal network, which is repeated indefinitely to form an $[Mg_6O_{12}]^{-12}$ or $[Al_4O_{12}]^{-12}$ layer. The structure of tetrahedral sheet is shown by Figure 2.3

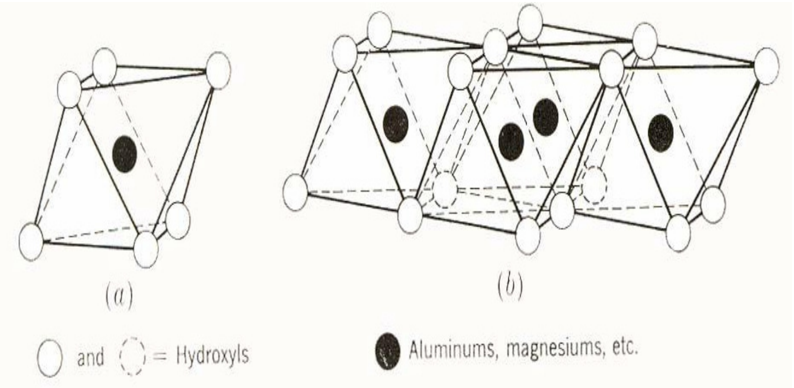


Figure 2.3: Diagrammatic sketch showing (a) single octahedral unit and (b) the sheet structure of the octahedral units.

A side view of the octahedral sheet shows that it is closely packed, being composed of a dence hexagonal plane of Mg or Al atoms sandwiched between two dense hexagonal "hydroxyl planes". The hydroxyl plane is an important contributor to the surface properties of some clay minerals. [Yariv and Cross, 2002]

According to their crystal structure clay minerals are divided into two groups such as TO and TOT minerals.

- **The TO – Type Layer Silicates**

A mineral layer of the serpentine – kaolin group is composed of a single tetrahedral sheet condensed with a single octahedral sheet into one unit layer, designated by 1:1 or "Tetrahedral – Octahedral" (TO).The ideal structural formulas of layers of serpentine and kaolinite are $[Mg_6Si_4O_{10}](OH)_8$ and $[Al_8Si_4O_{10}](OH)_8$, respectively. A side view of the TO layer shows that it is composed of five parallel atomic planes. These are the O, Si, O, OH, Mg, or Al, and OH planes. [Yariv and Cross, 2002]

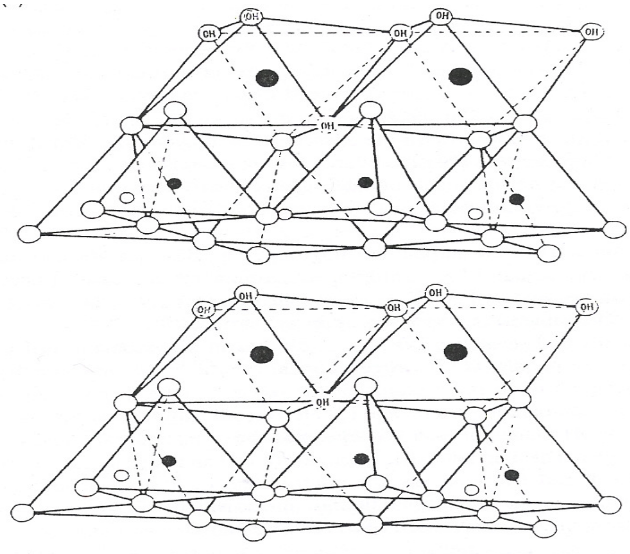


Figure 2.4: A structural scheme of a TO type (1:1) layer silicate. (O) O or OH; (•) Si; (●) Mg or Al

- **The TOT-Type Layer Silicates**

The interlayer space of an expanding TOT clay mineral lies between two parallel silicate layers, bordered by two O planes, and the oxygens belonging to siloxane groups. The wettability and resulting structure of the interlayer structure are the outcome of (1) thermal motion of water molecules in the environment of the mineral, (2) electrostatic attraction forces between water molecules and the exchangeable cationic species, and (3) attraction and dispersion forces between TOT layers. [Yariv and Cross, 2002]

Swelling is the process by which the clay mineral expands beyond its original limit as a result of adsorption of water in to the interlayer space. The uptake of water molecules is dependent on the humidity and water vapor pressure in the environment of the mineral. [Yariv and Cross, 2002]

Talc, Pyrophyllite, Smectites, Vermiculites, Illites, Sepiolite and Palygorskite are composed of TOT sheets.

Smectites: Minerals of the smectite group (sometimes known as the montmorillonite group) consist of TOT layer. A small fraction of the tetrahedral Si atoms is isomorphically substituted by Al and/or a fraction of the octahedral atoms (Al or Mg) is substituted by atoms of lower oxidation number. The resulting charge deficiency is balanced by hydrated cations, mainly K, Na, Ca, and Mg, of which more than 80% is located between the parallel clay layers

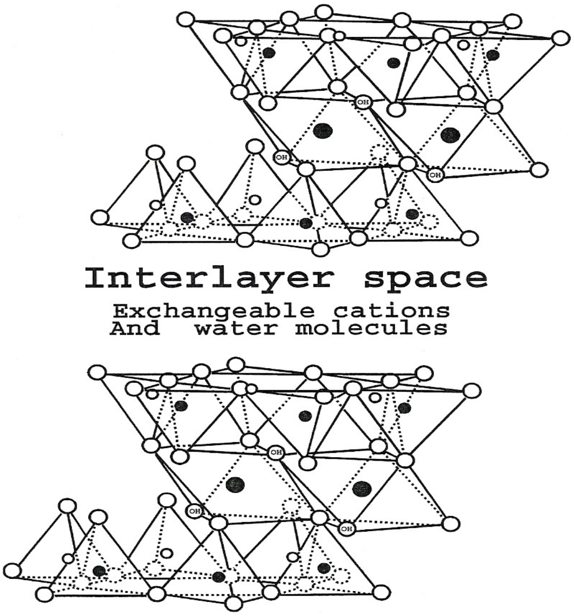


Figure 2.5: A structural scheme of an expanding TOT type (2:1) clay mineral. (O) O or OH; (•) Si; (●) Mg or Al

These ions are hydrated due to the fact that, in nature, smectites are formed in aqueous environments. Because they are hydrated, these cations are only loosely held by the negatively charged clay layers. The original cations are exchangeable by other inorganic and organic cations.

Water and polar organic molecules are attracted by the exchangeable cations and may intercalate between the layers, causing the structure to expand in the direction perpendicular to the layers. The interlayer space between the TOT layers, obtained as a result of the expansion of the clay, has special chemical properties. [Yariv and Cross, 2002]

2.4.3 Modified Clays

Silicon-based adsorbents, hectorite-based activated clays, and organo-cationic clays are the groups of adsorbents most often studied for removing colorants from oils. [Caglayan et al., 2005]

Clay minerals especially smectites are generally modified by applying a known type of activation, i.e., acidic, cationic, anionic, organo-cationic, or thermal, to form new active sites and/or to rainforce existing ones.

In the acid-activation mechanism (e.g., dry or wet process), the free protons formed attack the –OH groups that exist in tetrahedral and octahedral layers to increase the number of Lewis and Brønsted acid sites over the lattice. [Caglayan et al., 2005]

Organoclays are generally clay and alkylammonium complexes. Smectites are widely used in their synthesis because of their high cation exchange capacity, swelling capacity, high surface area, and resulting high adsorption/absorption capacities Due to hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature, which makes natural clays ineffective sorbents for adsorbing organic compounds. Replacement of the exchange ions by organic cations (or surfactants) can create a hydrophobic or organophilic surface. Intercalation of organic surfactants between layers of clays can not only change the surface properties from hydrophilic to hydrophobic, but also greatly increase the basal spacing of the layers. [Carmody et al., 2007] Quaternary ammonium compounds hold apart the aluminosilicate layers permanently. The cations fill the interlayer space and are contemplated as flexible pillars, resulting from the mobility of the alkyl chains. Therefore, the interlayer distance varies depending on the layer charge and on the alkyl chain length. [Meier et al., 2001] Organoclays are widely used as rheological additives in paints, inks, cosmetics and as pollutant absorbing agents in soil remediation programs. [Baldassari et al., 2006]

Pillared interlayered clays (PILCs) represent a new class of microporous solids that have found a wide range of potential applications in catalytic, adsorption and separation processes.

Pillaring clay (bentonite, hectorite, etc.) by altering the basal spacing with polycations of group IVB (Ti, Zr), group VB (V), group VIIB (Fe, Ni, Pd), groups I and IIB (Cu, Zn), or group IIIA (Al) cations have been examined the most. The pillared clays have been shown to have higher surface areas with selective acidity. One of the most intensively studied and interesting materials is the Al-pillared montmorillonite. Montmorillonite is used because of the same reason mentioned in the previous section.

The interest in clay mineral catalysts was renewed by the development of clays expanded by organic compounds (Barrer & MacLeod, 1955), because zeolites are not suitable for the conversion of relatively large organic molecules. However, the disadvantage of organic pillars is the low thermostability and the resulting collapse of the pillared clay structure. The use of inorganic compounds, such as A1 (Brindley & Sempels, 1977; Lahav *et al.,* 1978; Plee *et al.,* 1987; Schutz *et al.,* 1987), and Zr (Vaughan *et al.,* 1979; Yamanaka & Brindley, 1979; Bartley & Burch, 1985; Bartley, 1988) as pillaring agents solved this problem. On calcination, the polyoxocations dehydrate and dehydroxylate and react to metal oxide pillars providing a permanent microporosity and increased thermostability. [Kloprogge et al., 1994]

Using natural Na-montmorillonite, a complete intercalation can be easily achived with both Microwave-Hydrothermal (M-W) and the Conventional-Hydrothermal (C-H) methods under mild temperature conditions (~70°C). Microwave irradiation method aims to decrease time-consuming and energy-intensive in preparation of modified clays. [Baldassari et al., 2006] The modifying process is difficult to extend to an industrial scale by conventional procedure. Time-consuming procedure is most suitable for industrial scale.

2.5 Biodiesel

Biodiesel is the name given to a renewable diesel fuel that is produced from fats and oils. The reaction of a fat or oil with an alcohol, in the presence of a catalyst, yields a mixture of methyl esters which are known as biodiesel, and glycerol. The process shown below is known as transesterification process.

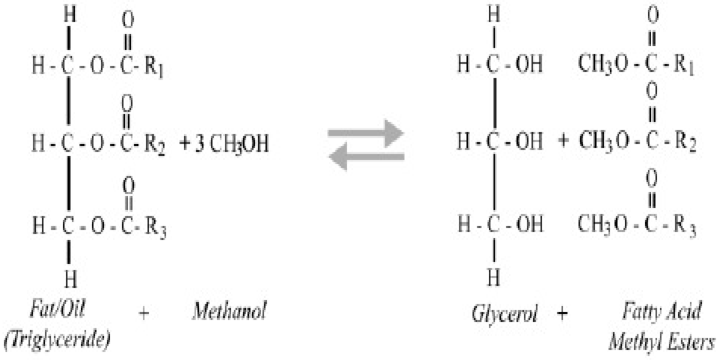
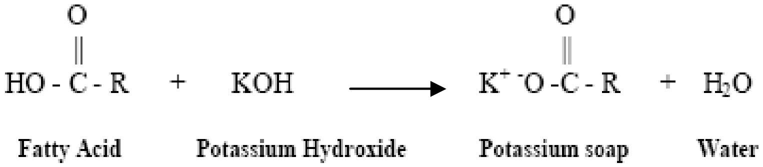


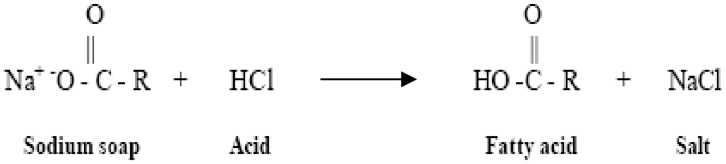
Figure 2.6: Schematic of the Transesterification Process [Anderson et al., 2003]

Glycerol is removed from the methyl esters by gravity. After glycerol seperation, the methyl esters pass through a methanol stripper and then enter a neutralization step, before water washing. When an alkali catalyst such as KOH, NaOH is added to oil, the free fatty acids react with the catalyst to form potassium or sodium soap and water as shown in the following reaction.



$$\mathrm{HO-\overset{\overset{O}{\|}}{C}-R} + \mathrm{KOH} \longrightarrow \mathrm{K^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R} + \mathrm{H_2O}$$

Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids,as shown in the following reaction.



$$\mathrm{Na^{+}\,{}^{-}O-\overset{\overset{O}{\|}}{C}-R} + \mathrm{HCl} \longrightarrow \mathrm{HO-\overset{\overset{O}{\|}}{C}-R} + \mathrm{NaCl}$$

The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process.

After the seperator, the glycerol stream contains only about 50-60% glycerol. It contains some of the excess methanol and most of the catalyst and soap. The methanol content requires the glycerol to be treated as hazardous waste. The first step in refining, the methanol in the glycerol is removed by a vacuum flash process, or another type of evaporator. After methanol recovery, acid is added to glycerine to split the soaps into free fatty acids and salts. The free fatty acids are not soluble in the glycerol and will rise to the top where they can be removed and recycled. The salts remain with the glycerol although

At this point, the glycerol should have a purity of approximately 80-85% and is typically sold to a glycerol refiner. The glycerol refining process takes the purity up to 99.5 to 99.7% using vacuum distillation and bleaching processes. [Gerpen, J. V.,] Biodiesel production and glycerine refining process are shown by Figure 2.7.

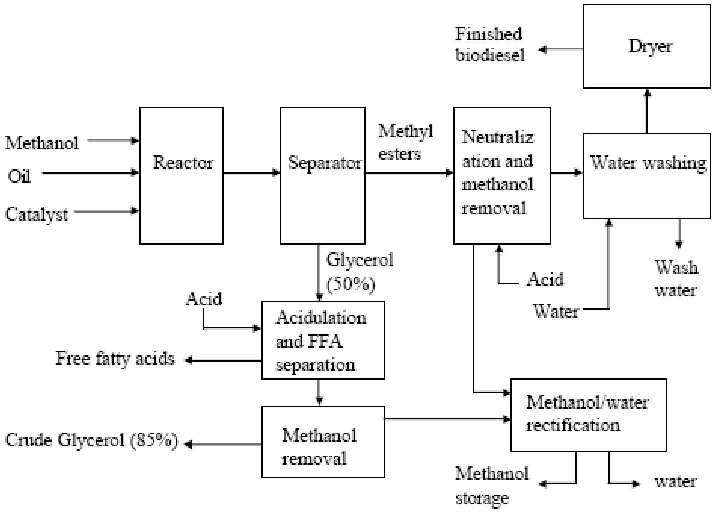


Figure 2.7: Process flow schematic for biodiesel production [Gerpen, J. V.]

2.5.1 Handling of Glycerine

Glycerin actually is a commercial product. It is a sweet-tasting, colorless and thick liquid and it can be dissolved into water or alcohol, but not oils.

After the seperation of unused catalyst and soaps, glycerine is sent to storage as crude glycerine. The crude glycerine is vacuum distilled to produce distilled glycerine and the residue (distilled bottom). The glycerine distilled over at a top temperature of 120°C -126°C and the bottom temperature at 165°C – 190°C and pressure of 5-6 mm Hg. [Yong, 2001] Unwanted reactions such as polymerisation, oxidation etc. can be minimized by vacuum distillation at a lower temperature.

The distilled bottom comprised mainly salt, high boiling MONG (polyglycerol, sugar components, free fatty acids and partial glycerides) and some glycerol. [Yong, 2001]

2.5.2 Characterization of the Distilled Glycerine

- **Glycerol content.** The average glycerol content of the distilled glycerine is about 96.0%. Thus, the crude glycerine with 50-60 % glycerol is successfully refined to a considerably higher purity by the simple vacuum distillation. [Yong, 2001]

- **Ash content.** Salts, such as sodium chloride and sodium sulphate, mainly constituted the ash, and the distillation has effectively removed them. The average ash content of the distilled glycerine is about 0.03-0.07 %, markedly lower than the 17.0% in the crude glycerine. [Yong, 2001]

- **pH.** The distillation is done at pH 4 to 5. [Yong et al., 2001] The free sodium hydroxide reacted with the fatty acids to form short and medium chain soaps which foamed easily at the high temperature. A higher pH obviously indicates more sodium hydroxide and more formation of soap. The sodium hydroxide also accelerated the polymerization of glycerol to polyglycerol as it is a catalyst for polymerization. Thus, the best pH for distilling the crude glycerine was below 5, at which all the soap was converted to free fatty acids, obviating foaming. [Yong et al., 2001]

- **Soap content.** The distilled glycerine is free of soap. This is expected as the distillation is done at pH 4.5 to 5 in which any soap present would have been hydrolysed. [Yong, 2001]

- **Water content.** The average water content in the distilled glycerine is less than in the crude glycerine. The low water content is due to the high vacuum used vaporizing the water. [Yong, 2001]

- **Matter Organic Non-glycerol (MONG):** The average MONG in the distilled glycerine is 2-3%; much reduce from the 20-25% in the crude glycerine. MONG in the crude glycerine comprise mainly partial glycerides, free fatty acids, oxidation products and the polymerized compounds of glycerol. These impurities mostly remained in the residue although some distilled over, especially at >126oC. The MONG content in the distilled glycerine can be further reduced by purification, e.g. ion exchange, deodorization and bleaching. [Yong, 2001]

- **Odour and Colour:** Colouring pigments come from carotenoids, chlorophlly, and related compounds. Colour and odour problems can be mostly avoided by using a high quality raw material, treating and storing crude glycerol properly, and avoiding high temperatures for extend time period. If the MONG content is high (3-5%), odour, taste, and colour reversion problems may exist in the final product. Trimethylene glycol, which is present in MONG, can affect the colour of glycerine and also lead to problems in storage. [Edward, 1996] Removal of these impurities from crude glycerine requires the use of materials with strong adsorption power. [Kaynak et al., 2004]

2.5.3 Use of Glycerine

Glycerine is used in wide range applications because of its key properties. It is a natural product, non-toxic, and generally recognized as safe for human consumption. It is an excellent humectants, emulsifier, and plasticizer. It is compatible with a wide variety of materials and mixes well. It possesses antioxidant properties. Figure 2.8 shows uses of glycerine

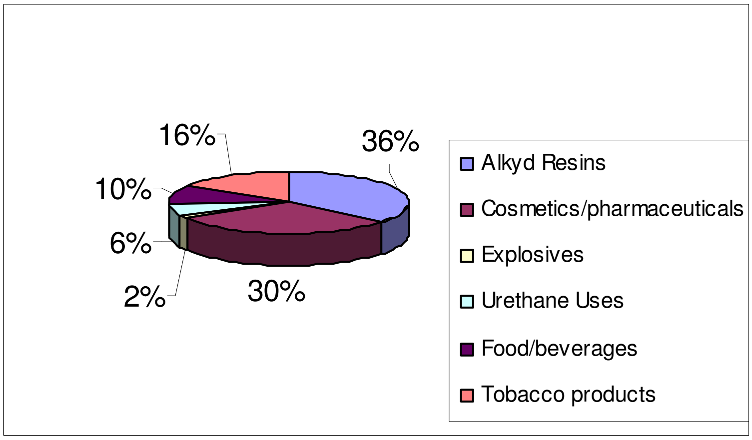


Figure 2.8 Glycerine uses [Edward, 1996]

- Cosmetics: Widely used for cosmetic applications, acting as bodying agent, emollient, humectant, lubricant and solvent; present in skin creams and lotions, shampoos and hair conditioners, soaps and detergents.

- Food and Beverages: Used in a wide variety of applications; serves as a solvent, carrier, emulsifier, conditioner, freeze preventer, and coating; used in wine, liqueurs.

- Pharmaceuticals: Used in salves and dressing, antibiotic preparations, capsules and suppositories.

- Resins: Includes ester gums, phthalic acid and maleic acid resins

- Tobacco: Used as a humectant, softening agent, and flavor retainer

- Explosives: A large amount is consumed in the manufacture of nitroglycerin-based explosives.

2.5.4 Economic Feasibilty

There have been substantial increases in biodiesel production in recent years, a trend that is expected to continue. Biodiesel production in the United States has increased dramatically from 500,000 gallons in 1999 to 70 million gallons in 2005 (National biodiesel Board, 2006).

The cost of biodiesel production depends on production volume, chemical technology, glycerine prices, feedstock and its quality.

The principal by–product of biodiesel production is the crude glycerol, which is about 10 %wt of vegetable oil. This is a very important industrial feedstock.

The market value of glycerine effects net biodiesel production price. There is a linear relationship between glycerine market price and biodisel production cost. Figure 2.9 shows the impact of the market value of 80 % (w/w) glycerine on the unit cost of biodiesel production.

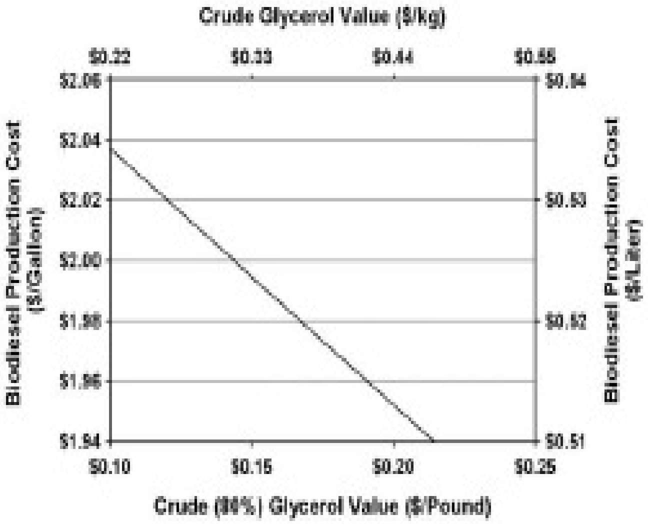


Figure 2.9: Impact of the market value of 80% (w/w) glycerol on the unit cost of biodiesel production [Haas et al., 2005]

Biodiesel production cost is predicted about US$0.52-53/l. [Haas et al., 2005]

The commercial glycerol market as an 80% w/w aqueous solution reduces production costs by ≈6%. [Haas et al., 2005]

Refined glycerine in the US has averaged roughly $0.77-88/kg in 2007, and is forecast to increase into the range of $1.05/kg in 2008 [www.napm-ny.org/resources/commodity.html].

3.0 EXPERIMENTAL STUDY

3.1 Materials Used

The bentonite used in this study was obtained from Karakaya Mine (Tokat). Clay was washed with distilled water and impurities such as iron oxide and silica were removed by differential sedimentation technique. The removal of these impurities was followed by drying the material at 60°C for 96 h. After being dried at 60 °C, it was pulverized to pass through a 530 µm sieve. The chemical analysis and the other characteristic properties of the raw and phase separated clays are given in Tables 3.1 and 3.2, respectively.

Table 3.1 Chemical analysis of raw clay

Constituent	**Value (%)**
SiO_2	56.57
Al_2O_3	16.26
Fe_2O_3	3.72
Na_2O	2.49
MgO	1.86
K_2O	1.17
CaO	2.95

Table 3.2 Chemical analysis of phase separated clay

Constituent	**Value (%)**
SiO_2	58.66
Al_2O_3	18.22
Fe_2O_3	4.5
Na_2O	2.62
MgO	2.16
K_2O	0.53
CaO	0.6

Hexadecyltrimethylammonium bromide (HDTMAB), $AlCl_3$ and NaOH used in the modification, were purchased from MERCK and Riedel de Haën, respectively. Specifications are given in Table 3.3.

Table 3.3 Specifications of the reagents used in the modification

Specifications	HDTMAB	Aluminum Chloride	Sodium Hydroxide
Formula	$C_{19}H_{42}BrN$	$AlCl_3$,	NaOH
Molecular weight (g/mol)	364.46	133.34	40
Purity, %	97	98	99

Distilled glycerine is supplied from DİPER Chemicals Inc. Specifications of glycerine are shown at Table 3.4.

Table 3.4 Specifications of glycerine

Specifications	**Value (%)**
Formula	$C_3H_8O_3$
Molecular weight (g / mol)	92.0542
Glycerine Content (%)	Min. 99
Specific Gravity (g/cm3) @ 25°C	Min. 1.26
Ash Content (%)	Max. 0.01
NaCl (%)	Max. 0.01
Sulphates (%)	Max. 0.1
Arsenic (ppm)	Max. 0.01

3.2 Preparation of Al-pillared Bentonite

The aluminum hydroxy-oligomeric solution was prepared by dropwise addition of 0.2 M NaOH to 0.2M $AlCl_3$ under the vigorous stirring at 80°C. During the reaction; temperature and rate of addition were kept as constant. After addition of NaOH solution was completed, the mixture was allowed to age by using microwave irradiation at 360 W 15 minutes. After the aging, the mixture was cooled to the room temperature.

Intercalation studies of adsorbent were performed by the reaction between clay dispersion and pillaring solution by using Microwave (MW) irradiation. Before the intercalation, the pillaring solution was added to the dispersion containing 10% of clay with a mechanical stirring to obtain a homogenous dispersion at room temperature. The resulting dispersion was subjected to microwave irradiation for 10 minute at 360 W. At the end of irradiation, the solid washed several times with the pure water to remove the unreacted impurities from the adsorbent structure. After each washing cycle, the pH and electrical conductivity values of filtrate was measured to decide the end of washing step. When electrical conductivity value was reached to the value which was less than 20 µS, the washing was stopped. After washing step, samples were dried in an electrical oven at 60°C.

The amounts of Al^{3+} and OH-/Al^{3+} ratios used in the preparation of pillaring solution and Al^{3+}/clay ratio used in the intercalation are shown in Table 3.5.

Table 3.5 OH-/Al^{3+} and Al^{3+}/clay ratios of Al-pillared clays

Samples	**nAl^{3+}, mole**	**Al^{3+}/clay**	**OH^-/Al^{3+}**
1	0.1	1.8	1.4
2	0.15	1.8	1.4
3	0.2	1.8	1.4

3.3 Preparation of Organo-Bentonite Complexes

The organobentonite was prepared by adding HDTMAB with the amounts equivalent to 1.0 times the CEC of the natural bentonite. Dispersion of 10% (w/w) bentonite was prepared for intercalation. Five hundred milliliters of surfactant solution was added into the dispersion. After mixing, the solutions were put into microwave oven for 5 min at 360W. After the ion exchange reaction, solid and liquid phases were separated. The solid was washed with 1000 mL of 1:1 ethanol-water mixture and distilled water until negligible amount of surface active agent was observed by the methyl orange method, involving complexation of cationic surfactant with methyl orange at acidic condition. After the removal of ion pairs, organo-bentonite was dried in Oven, Microwave oven and Freeze Dryer and ground.

3.4 Preparation of Organo-Inorgano Bentonite Complexes

Organo-Inorgano bentonite has prepared in two steps. In the first step, 10 grams of phase separated clay was disturbed in water. Aluminium hydroxy-oligomeric solution was added in clay slurry and stirred at room temperature. After obtaining homogenous dispersion, the mixture was put into microwave oven at 360 W for 5 minutes. At the end of the exposure time, the solid was washed with the pure water until electrical conductivity was reached to a value which is less than 20 µS.

In the second step, an appropriate amount of HDTMAB was added into Al-pillared bentonite sample. After mixing 15 minutes, the dispersion was put into microwave oven for 5 min at 360W. The mixture was cooled and filtered. The solid phase was washed with 1000 mL of 1:1 ethanol-water mixture and distilled water until negligible amount of surface active agent was observed. The amount of surface active agent was determined by using the method mentioned in Section 3.3 After washing step, samples were dried in an electrical oven at 60°C and ground to powder.

3.5 Characterization of Adsorbents

3.5.1 XRD analysis

XRD analyses were carried out in a Siemens-AXS X-Ray diffractometer D5000, Bragg-Brentano-geometry, equipped with graphite primary monochromator and scintillation counter. Two different methods were used in the preparation of the samples. First the powdered samples were prepared to identify the phases of the clay and then the textured samples were prepared trough sedimentation on glass slides to observe the changes in basal space of smectite after pillaring.

3.5.2 SEM Analysis

Morphologies and surface compositions were determined by Environmental Scanning Electron Microscopy (ESEM) Philips 515.

3.5.3 FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopic analysis was done with diffused reflectance infrared fourier transform (DRIFT) in solid phase in the range of 600-4000 cm^{-1} using mercury-cadmium-telluride (MCT) detector in transmittance mode (Brucker IFS66 FTIR spectrometer, Germany). Diffused reflectance sampling cell (Spectratec, USA) was used to determine the spectra of crude and modified clays. For this purpose, ball-milled samples of sorbent were mixed with potassium bromide (ratio 1:300) and kept under dry air overnight prior to running FTIR-DRIFT spectroscopy. The data obtained from FTIR-DRIFT spectra were evaluated by Kubelka Munk transformation with OPUS 5.5 software, using the following expression:

$$F(R\infty) = \frac{(1 - R\infty)^2}{2R\infty} = \frac{K}{S} \qquad \text{Eqn. 1}$$

where:

$F(R)$ = reflectance; Kubelka Muka function for R

K = absorption co-efficient

S = scattering co-efficient; ∞ = thickness of the indefinite layer

3.5.4 Simultaneous Thermal Analysis (STA)

The measurements were performed on a STA 449 C Jupiter from NETZSCH-Gerätebau GmbH equipped with a Thermogravimetry / Differential Scanning Calorimetry (TG/DSC) sample holder. The equipment is connected with a quadruple mass spectrometer 403 C Aëolos from IPI / Inprocess Instruments/NETSCH- Gerätebau GmbH. Before the measurements, all samples were allowed to equilibrate at a relative humidity of 53% in a dessicator above saturated $Mg(NO_3)_2$ solution for at least 48 h.

The differential thermal analysis (DTA) was performed by using 200 mg of samples heated with the heating rate that is, the temperature ramp 10°C/min and calcined alumina was used as an inert reference material under the air atmosphere and the sensibility of 500 μV.

3.5.5 BET surface area

Surface area measurements were performed on Quantachrome Autosorb automated gas sorption system by using nitrogen as an inert gas. Except the crude clay, the samples were out gassed at 60 °C for 16 hours. In the case of crude clay, the outgas temperature was 140°C for the same time.

3.5.6 Color Measurements

Color measurements were made by means of a Lovibond PFX880 Tintometer with a 5.25-inch column. Color was read in red and yellow scales.

Color measurements is based on matching the color of the light transmitted through a specific depth of sample to the color of light originating from the same source, transmitted through glass color standards. Measurements are initiated by just a single key press and take less than 25 seconds to complete.

3.6 Bleaching Experiment

For bleaching experiments the change in color of glycerin with time, amount and temperature was studied by batch technique. A certain amount of adsorbent was added to 100 gram distilled glycerin under the vigorous stirring. At the end of the mixing period, glycerin and clay mixer was filtered. Color of filtrate was measured by Lovibond PFX880 Tintometer. Finally, Bleaching Efficiency (BE) is calculated from the following equation.

$$BE\,(\%) = \frac{(First\,Color - Final\,Color)}{First\,Color} * 100 \qquad \text{Eqn.2}$$

Soap amount in glycerin is analyzed by titration method with 0.1 N HCl. Removal of soap (RS) is calculated from Eqn.3.

$$RS,\% = \frac{(Initial\ Soap\ Content - Final\ Soap\ Content)}{Initial\ Soap\ Content} * 100 \quad \text{Eqn.3}$$

4.0 RESULTS AND DISCUSSION

4.1 Characterization of Adsorbents

4.1.1 X-Ray Analysis

The effect of modification on basal spacing of crude clay was studied using the X-ray diffraction analysis technique. Intercalation of cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of layers. This expansion is readily determined by Xray Diffraction analysis. Results of XRD analysis is given in Figure 4.1 for untreated and size fractionated samples. As shown in the Figure, some of the phases are removed during the size fractionation. The peak representing Na-smectite phase has d001 value equal 12.60 A° indicating the mineral is Na-montmorillonite

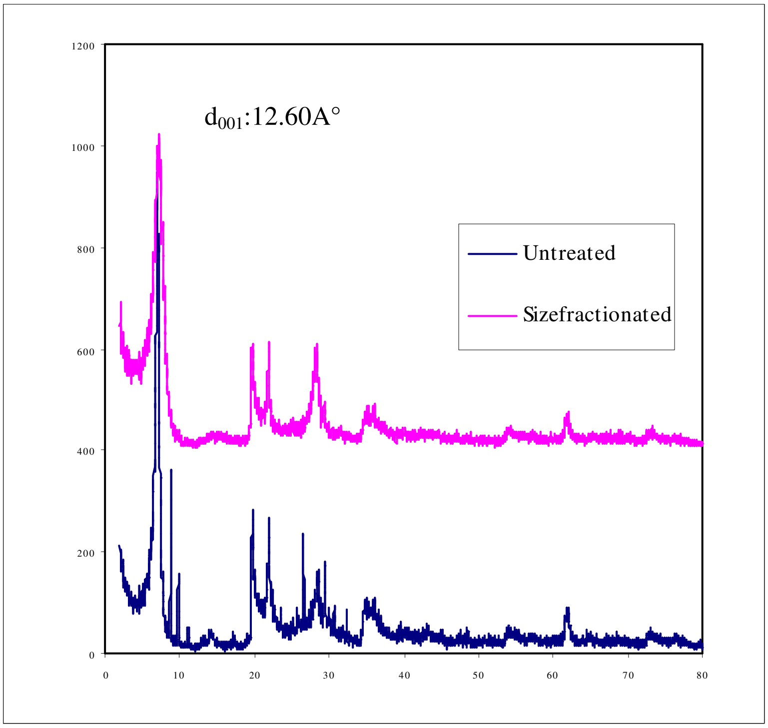


Figure 4.1: XRD patterns of raw clay and crude clay

The XRD pattern of FD, OD, MW Dried and Commercial organoclays are given in Figure 2, Figure 3, Figure 4 and Figure 5, respectively. After modification by HDTMAB, for organoclay the reflection peak of the basal plane dramatically shifts to smaller diffraction angle showing that the interlayer of the mineral expanded due to the intercalation of alkyl ammonium cation.

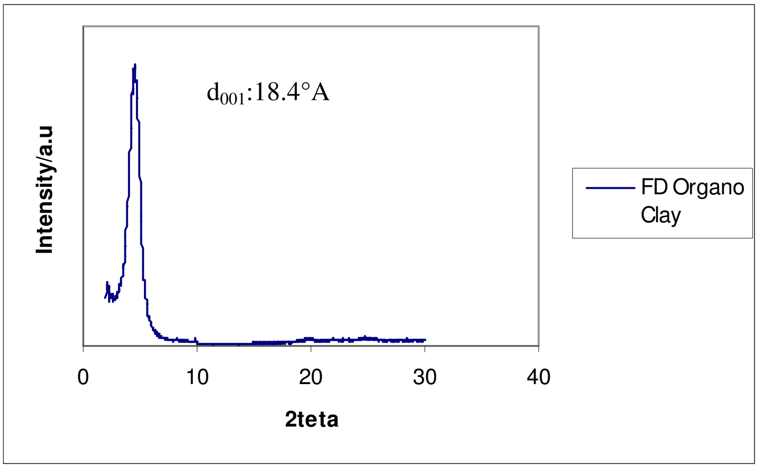


Figure 4.2: XRD Pattern of Freeze Dried Organo Clay

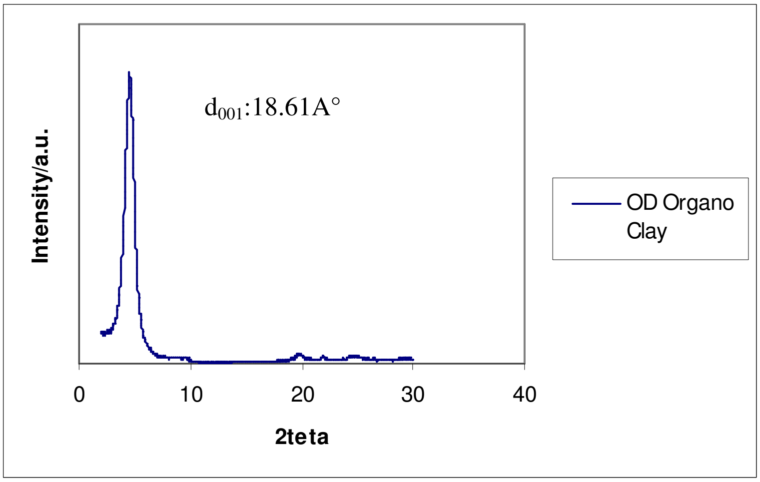


Figure 4.3: XRD Pattern of Oven Dried Organo Clay

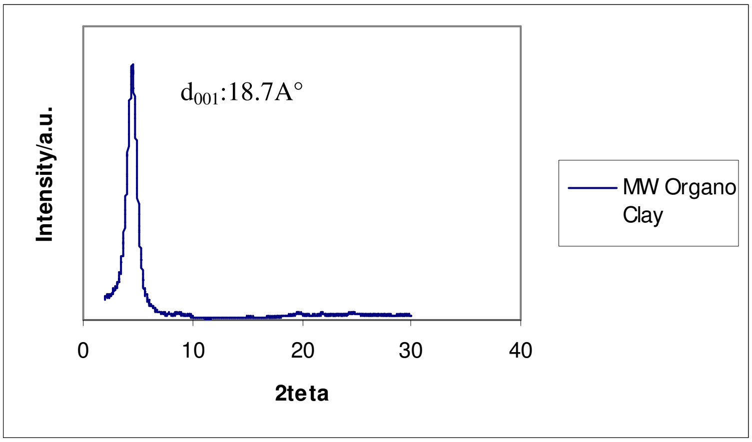


Figure 4.4: XRD Pattern of Microwave Dried Organo Clay

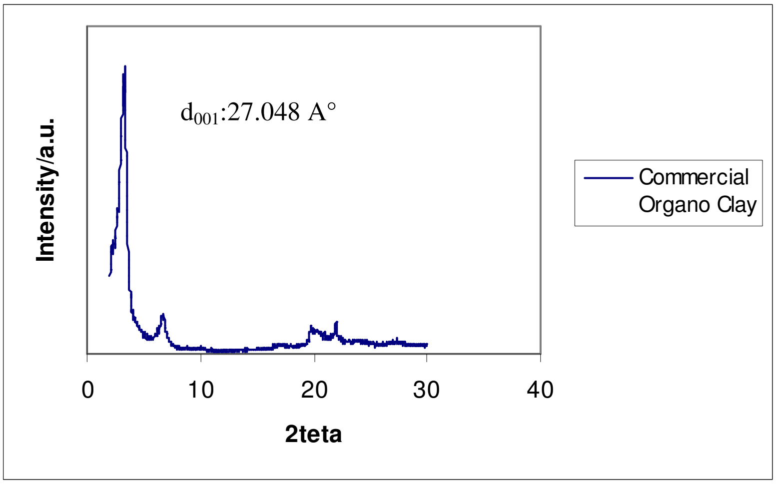


Figure 4.5: XRD Pattern of Commercial Organo Clay

Corresponding d001 values of the FD, OD, MW and Commercial Organo Clays are given in Table 4.1.

Table 4.1: Basal spacings (d001) (Å) and expansion in interlayer distance of organo clays

Sample Name	**d_{001}, °A**		**Increase in Basal Spacing, °A d_{001} – 12.60**	
	Room dried	P_2O_5	Room dried	P_2O_5
FD Organo Clay	19.3	18.4	6.7	5.80
OD Organo Clay	19.4	18.61	6.8	6.01
MWD Organo Clay	19.7	18.7	7.1	6.10
Commercial Organo Clay	27.0		14.4	

A number of previous studies have demonstrated that the d-spacing of the organoclays depend on the length of the alkyl chains and the packing density of the surfactants within the galleries of clay minerals [Frost et al., 2005]. XRD measurements of organo clays were made at 2 different drying conditions. Clays were kept over the P_2O_5 to obtain bone dried samples. The increase in basal spacing shows that the alkyl ammonium cations form a monolayer on the surface according to the model proposed by Lagaly and Weiss [1970]

Beside crude and organo clays, Al- pillared clays and Organo-Inorgano clays were subjected to XRD analysis. The change in interlamellar spacings is given in the Table 4.2.

Table 4.2: Basal spacings (d001) (Å) and expansion in interlayer distance of Al-Pillared Clay and Organo-Inorgano Clay

Sample Name	**d_{001}**	**Increase in Basal Spacing (d_{001} – 12.60)**
Al-Pillared Clay (n_{Al}=0.1)	17.05	4.45516
Al-Pillared Clay (nAl:0.15)	15.83900	3.239
Al-Pillared Clay (nAl:0.2)	15.97870	3.3787
Organo-Inorgano (nAl:0.1)	16.00331	3.40331

A close exami,nation of the table reveals that there are no significant changes in the increase of basal spacings with the increasing amount of aluminum and the increase in basal spacing is highest in the case of 0.1 M Al-Pillared clay.

4.1.2 SEM Analysis

SEM images show surface morphology of crude clay and organo clays.

As shown in Figure 4.6, the crude clay has a typical montmorillonite structure. From the view of the mineral, it is seen that the crude clay has leaf-like structure with curly margins. This view is typical for smectites.

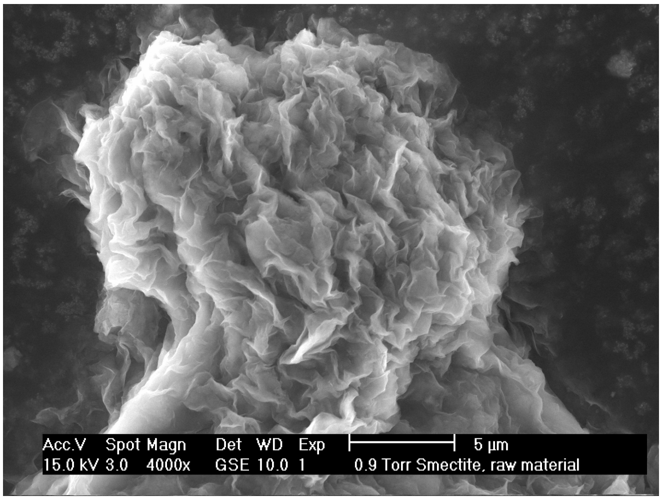


Figure 4.6: Scanning Electron Micrograph of raw clay X4000

SEM images of organo clay with three drying conditions are given in the Figure 4.7. Organo clays show significant changes in the morphology. Compared with the morphology of the raw–montmorillonite, organo clays have cloudy structure and the margins become relatively flat in organo clays as shown in Figure 4.7. On the other hand, expansion is observed in organo clays micrographs. The transformation of the curved plates to flat ones might be mainly controlled by the interactions between the hydrocarbon chain–silicate surface and the hydrocarbon chain–hydrocarbon chain of alkylammonium cations. [He et al., 2005]

As shown in Figure 4.7, surface morphology was affected significantly from drying conditions. Oven dried and Microwave dried organo clays have relatively more flat margins.

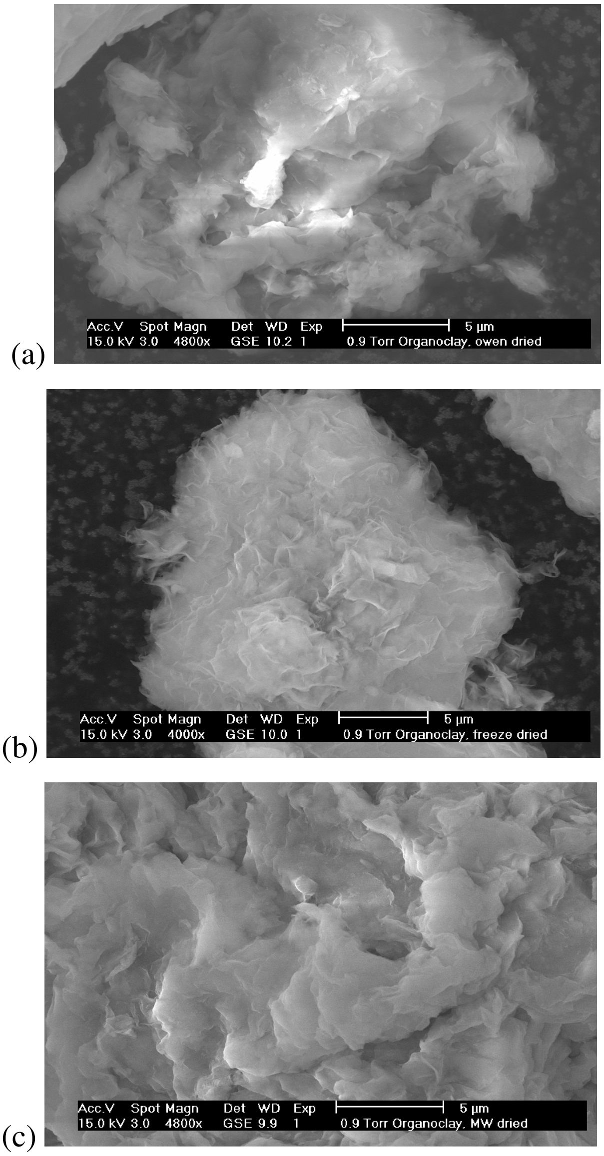


Figure 4.7.: Scanning Electron Micrograph of Organo Clay (a) Oven Dried X4800 (b) Freeze Dried X4000 (c) Microwave Dried X4800

Figure 4.8 shows SEM image of commercial organo clay. As shown in this figure, commercial organo clay has curly margins. Compared with the morphology of OD, FD and MW dried organo clays; commercial organo clay has more cloudy structure.

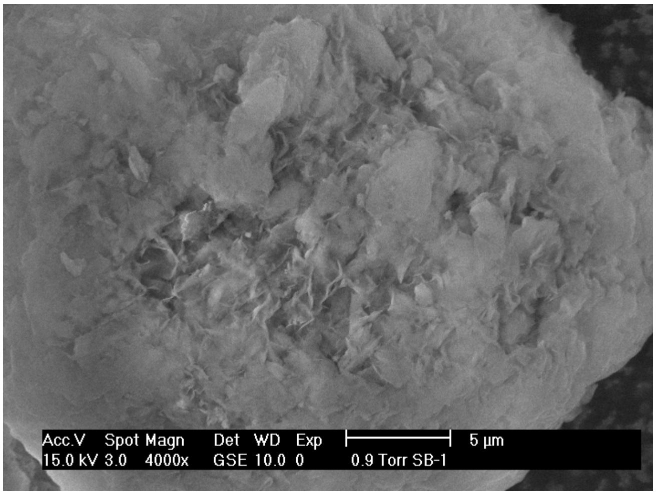


Figure 4.8: Scanning Electron Micrograph of Commercial Organo Clay X4000

4.1.3 BET Surface Area

Since the adsorption is a surface phenomenon, the total surface area is of importance in the determination of adsorption efficiency. In this study BET surface area by N2 adsorption was determined for crude clay. The N_2 adsorption is given in Figure 4.9

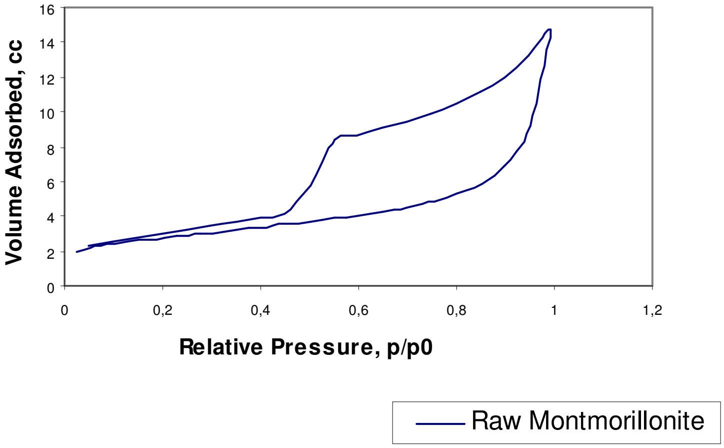


Figure 4.9: Nitrogen adsorption of raw montmorillonite

The data obtained from the analysis of adsorption isotherm is given in Table 4.3, Table 4.4 and Table 4.5.

Table 4.3: Surface area of raw motmorillonite

Method	Surface Area, (m2/g)
Multipoint BET	54.24
t Method External Surface Area	42.2
t Method Micropore Surface Area	12.03

Table 4.4: Pore volume of raw motmorillonite

Method	Pore Volume (cm^3/g)
Total Pore Volume	0.121
t Method Micropore Volume	$6.25*10^{-3}$

Table 4.5: Pore size of raw motmorillonite

Method	Pore Size (A°)
HK Method Pore Width	3.625
SF Method Pore Diameter	4.477

According to the results of isotherm analysis, raw clay has mainly mesoporous structure. Since the alkylchains intercalated on the surface prevent the entrance of N_2 probe molecules, the surface area of organo clays can not be measured.

4.1.4 FTIR Analysis

The whole DRIFT spectra of crude and organo-clays are given in Figures 4.10 and 4.11. Later the spectra were divided by two different figures, Figures 4.11 a and b, involving O-H stretching and Si-O stretching regions.

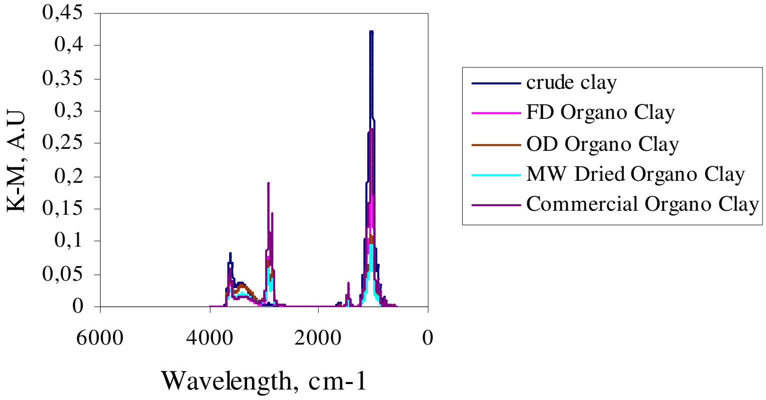


Figure 4.10: DRIFT spectrum of crude clay and Organo Clays

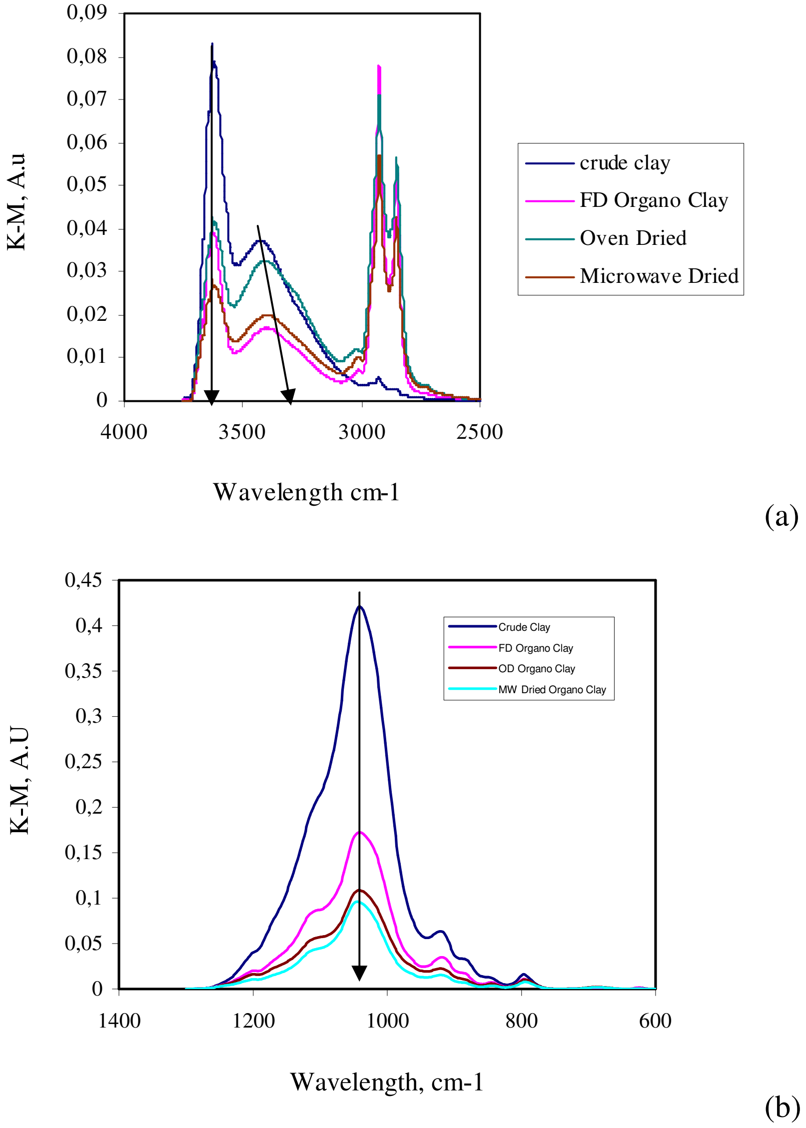


Figure 4.11: FTIR Spectrums of Crude Clay and Organo Clays, (a) OH reagion (b) Si-Region

As shown in Figure 4.11.a. there is no change in the maximum of peaks corresponding O-H stretching of structural hydroxyl groups. However a slight shift is observed the maximum of the peaks representing O-H stretching of water. This can be attributed to the change in the magnitude of stretching and proves that hydropobicity of clay increases with modifying organic surfactant. Freeze dried, Oven dried and Microwave Dried Organo clays show nearly same characteristic feature. Figure 4.11.a. also shows a peak in a range between 3100-2700 cm^{-1}. this peak correspond to C-H stretching vibration in the alkyl chains.C-H streching comes from organic substances in the structure. As the bulkiness of hydrocarbon chains on clay surface increases, peaks of these molecules become more observable in the spectra of complexes.

Structural differences in the clay samples after the pillaring processes were determined by FTIR analysis. The FTIR spectra of crude -, 0.2 M Al-pillared -, organo-inorgano and organo clays are displayed in Fig. 4.12, 4.13, 4.14 and 4.15.

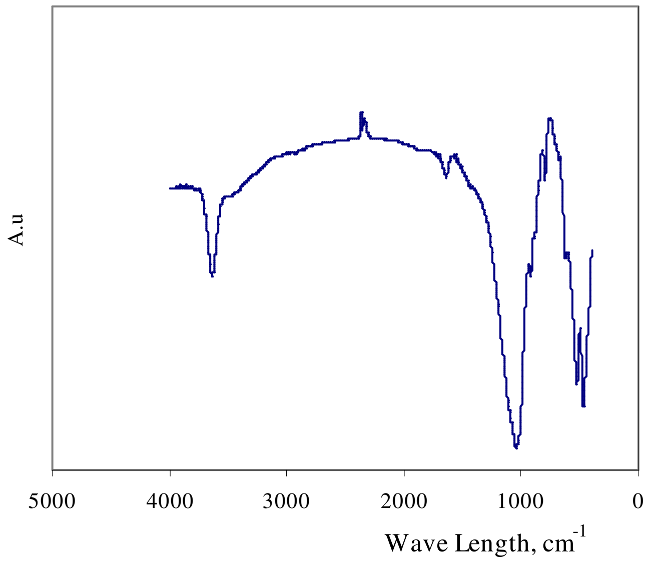


Figure 4.12: FTIR spectrum of crude clay

When the spectra of crude and pillared clays are compared, it is seen that the crude clay has a shoulder at the region 3622-3626 indicating OH stretching of water whereas Al-pillared clay has an expanded shoulder at the region 3442-2636. The enlargement of the shoulder is attributed to the increase in OH stretching of water due to the existence of Al_{13} ions and their relatively big hydration shells. This result is in convenience with the results reported by Kloprogge et al., [1999].

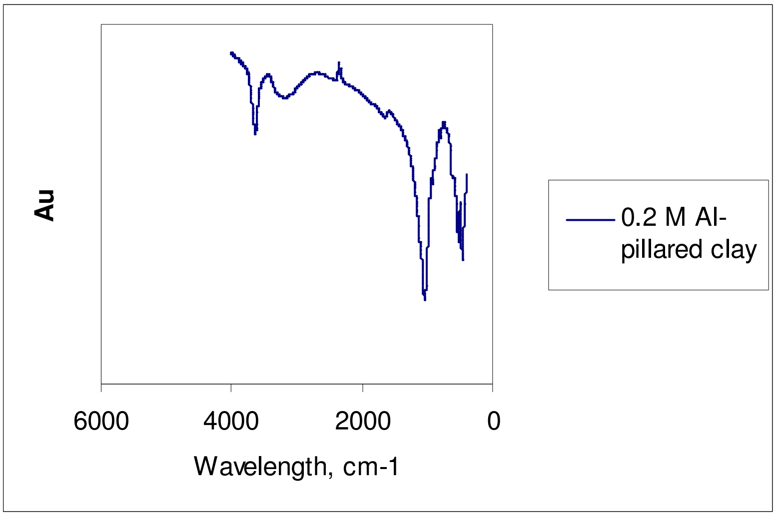


Figure 4.13: FTIR spectrum of 0.2 M Al-pillared clay

The FTIR spectrum of organo-inorgano clay is given in Figure 4.14. A close examination of the figure reveals that the spectrum has all features of the Al- pillared and organo clays. This result points that both Al_{13} and surfactant molecules were intercalated successfully.

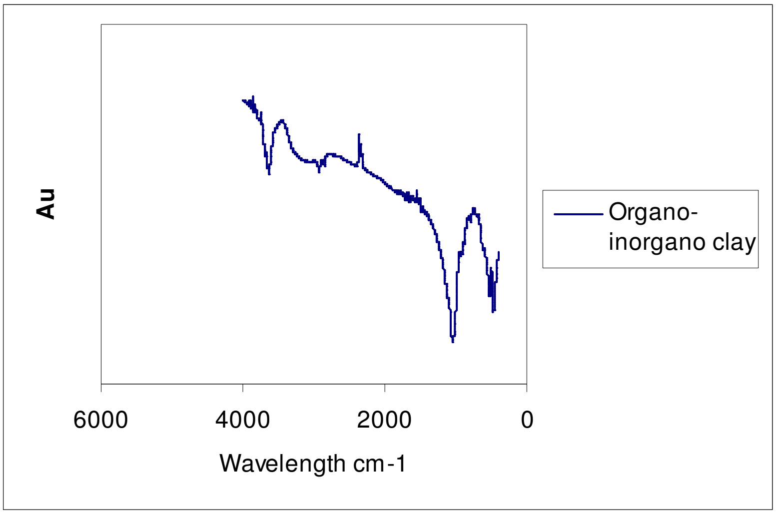


Figure 4.14: FTIR spectrum of organo-inorgano clay

The FTIR spectra of Freeze dried organo-clay is given in Figure 4.15. As shown from this figure organo clay has peaks at the wavelengths 2730, 2985 and 1471cm^{-1}. The existence of the peak at 1471cm^{-1} proves that organic surfactants were intercalated in the interlayer surface of clay.

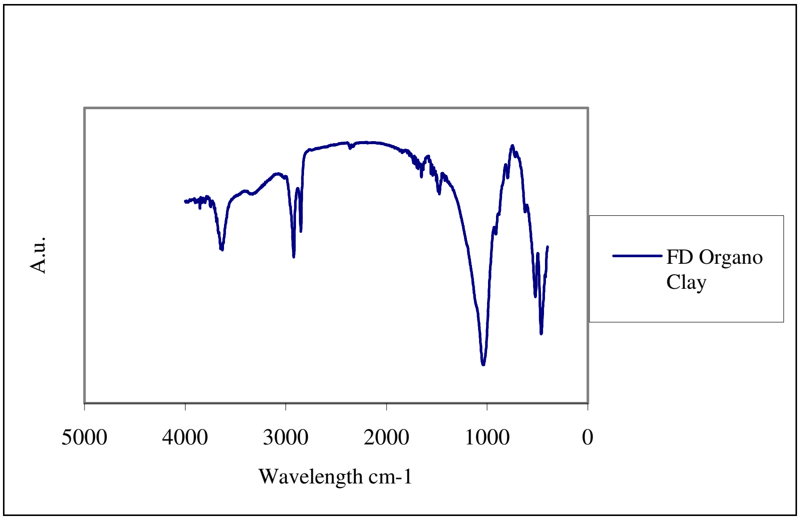


Figure 4.15: FTIR spectrum of FD organo clay

4.1.5 STA Analysis

STA analyses are used to improve the interpretation of thermal events by providing both DSC and TGA data simultaneously on the same sample. The DSC analysis identifies exothermic/endothermic transitions while the TG analysis evaluates weight changes.

Smectites lose water when heated. Water losses are endothermic reactions. Two endothermic and an exothermic peak are obtained from raw clay DSC curve. These are the characteristic peaks of Na-bentonite.

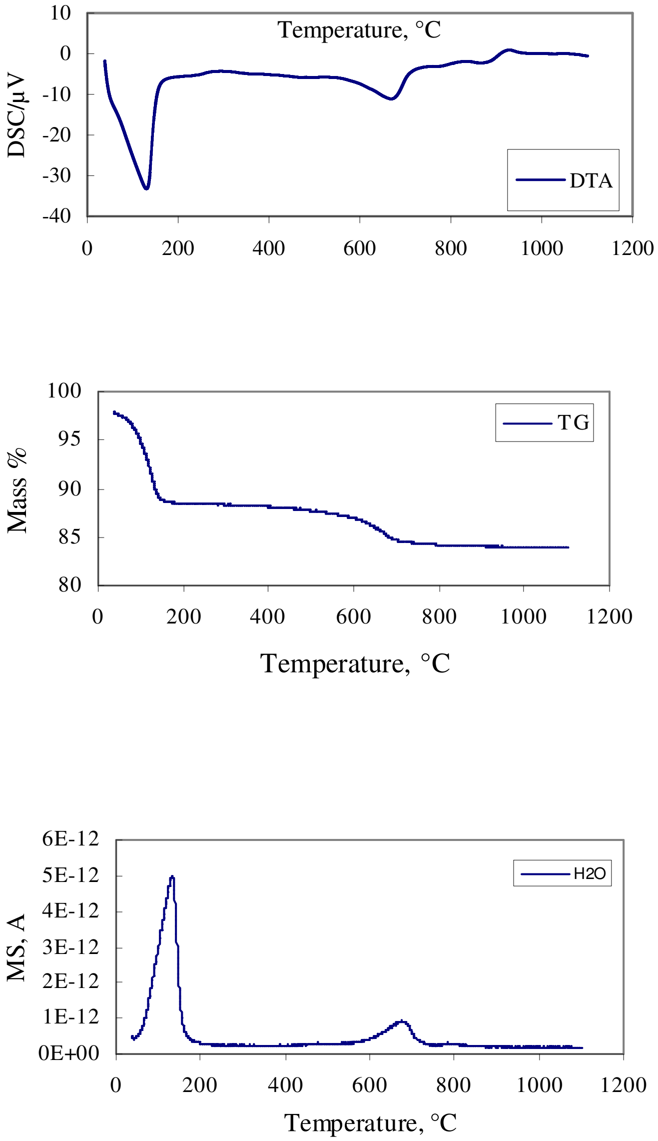


Figure 4.16: Thermogram of crude clay

First endothermic peak with maximum intense is observed about 131°C. In this region, heat is adsorbed by raw clay which is consumed for dehydration of interlayer and surface water. During dehydration, a mass loss about 9.2 %is observed as shown in Figure 4.16.

A second endothermic peak occurs about 600-700°C. This peak indicates the loss of hydroxyl groups from the lattice in the form of water (dehydroxylation). As shown in Figure 4.16, there is a 3.2 % mass loss at about 600-700°C because of dehydroxylation.

There is a small exothermic peak around 900°C. This peak associated with the recrystallization of the clay layers.

Differential scanning calorimetry (DSC) is also used in this study to characterize the thermal stability of hexadecyltrimethylammonium bromide-modified montmorillonites dried at different conditions.

Dehydration of interlayer and surface water region is observed in the 0-200°C temperature range for all of organo clays. The mass losses are about 2-3 % as shown in Figure 4.17. The decrease in the mass loss in this region is attributed to the hydrophobic structure of the surface.

The most distinguished difference between the raw montmorillonite and organo montmorillonite is in the temperature range 200 - 500°C. The organic constituent in the organo-clay starts to decompose somewhere above 200°C. It can be concluded, therefore, that the main weight losses over the temperature range 200 - 500°C are due to the decomposition of organic compounds as shown in CO_2 figures. HDTMAB decomposes or is combusted at about 200°C. First exothermic peak is observed about 240-260°C. This exothermic peak comes from oxidation of total adsorbed organic matter on the external surface. Loss of HDTMAB molecules from between the clay sheets starts above 350°C. Oven Dried and Microwave Dried Organo Clays have two endothermic peaks above 350°C. The reason for the two peaks is due to different structural arrangements of the HDTMAB molecules in the interlayer gallery.

Dehydration, dehydroxylation and oxidation of organic compounds are continuous reactions. Because of this reason, endothermic and exothermic peaks are also shown between 500-800 °C.

Because of the oxidation of organo clay, “Petroleum Coke” forms in the interlayer space with a high degree of cross linking. [Edward, 1996] This coke can be oxidized only at higher temperatures. Between 925-935°C, third exothermic peak shows oxidation of “Petroleum Coke”. The main gaseous products of the oxidation of organic compounds are evolved CO2, NO2 and water.

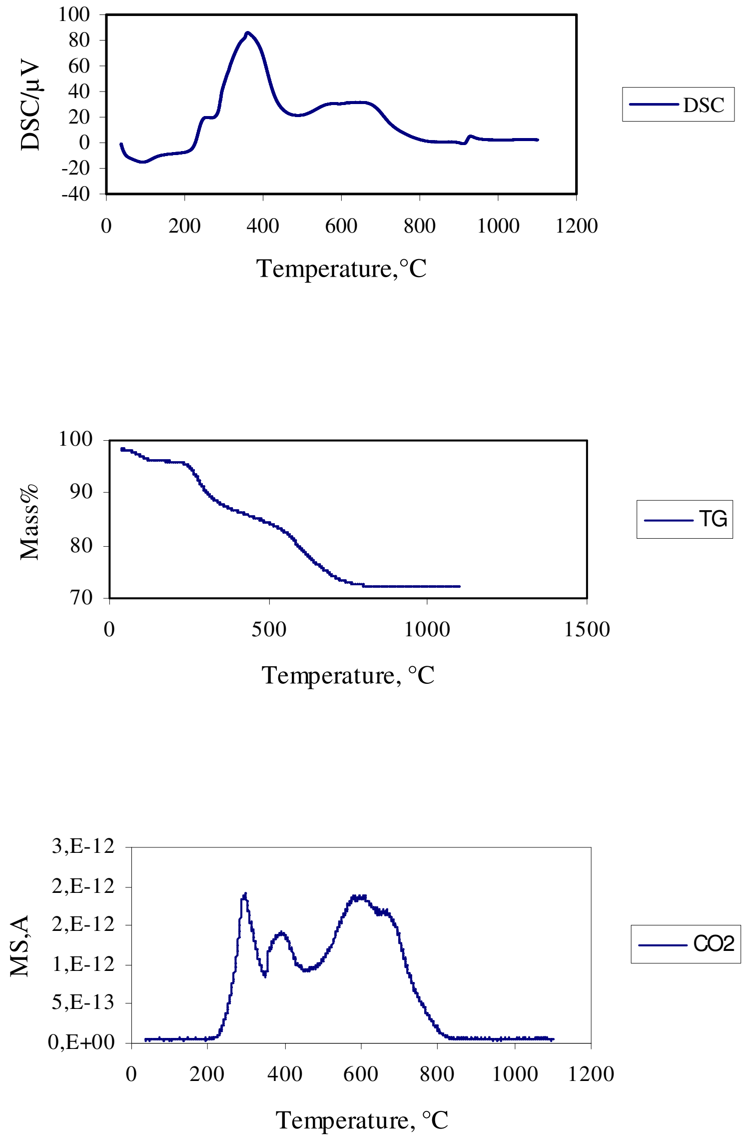


Figure 4.17: Thermogram of Freeze Dried Organo Clay

Evaluation of The data obtained from STA analysis

The amount of CO_2 released was used to estimate the amount of HDTMA intercalated. It is assumed that all the CO_2 is released as a result of the decomposition of organic compound. The reaction stoichiometry,

$$C_{19}H_{42}BrN + 59/2O_2 \Longrightarrow 19CO_2 + 21H_2O$$

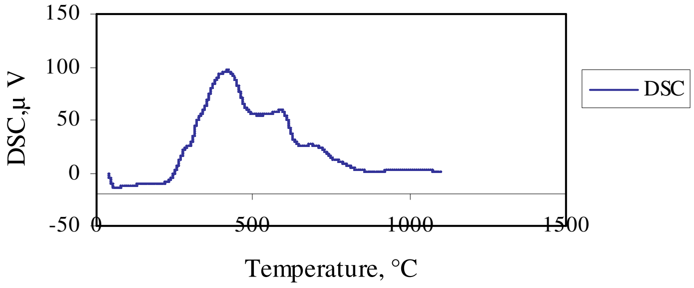
The amount of CO_2 for 102.446 mg of organoclay was found to be 57 mg by the thermogravimetric analysis. According to the reaction stoichiometry given above, the amount of HDTMA corresponding to this amount is 24.84 mg and 2427 mg for 10 gram of organoclay. Since the amount of HDTMA used in the modification is 3165 mg, approximately 73% of the alkylammonium cations were intercalated. Therefore, only 73% of the active sites on the clay surface are occupied instead of 100%. This result indicates that the surface was partially hydrophobized.

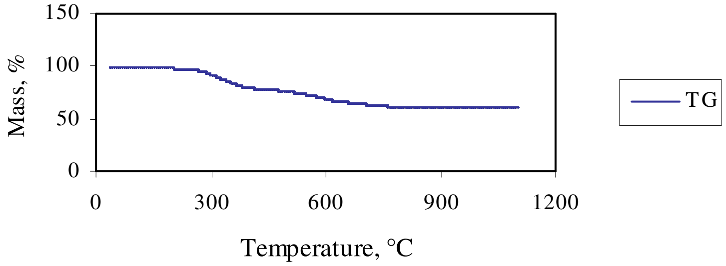
As shown in Figure 4.18 thermogram of commercial organo clays shows nearly same characteristics with freeze dried organo clays.

Dehydration of interlayer and surface water region is observed between 0-200°C ranges. As shown in Figure 4.18, decomposition of organic compounds starts at 200 °C. The main weight losses come from decomposition of organic compound between 200 - 500°C. During this temperature range, CO2 is obtained as a gaseous product.

First exothermic peak is observed about 280-290°C.This exothermic peak comes from oxidation of total adsorbed organic matter on the external surface. Oxidation of internal surfactant molecules start above 400°C.

There is an exothermic peak at about 900°C. This peak comes from oxidation of “Petroleum Coke”.





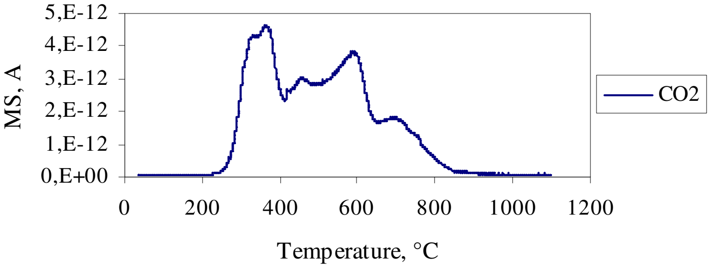


Figure 4.18 Thermogram of Commercial Organo Clay

4.2 BLEACHING OF GLYCERINE

Distilled glycerin was subjected to bleaching by using crude, organo, commercial organo, Al-pillared and organo-inorgano clays. The effect of time, temperature and adsorbent amount on bleaching efficiencies of the above mentioned adsorbents were determined. The maximum values of the parameter studied were determined by considering the operational conditions in the biodiesel production plant. The efficiency was determined by measuring the reduction in color of the glycerin. This was carried out by color measurements in the Lovibond PFX880 Tintometer.

4.2.1 Effect of Time

The experiments were carried out at atmospheric condition with the glycerin at 50ºC and %1 adsorbent amount. Coloring materials shows different characteristic features and they are adsorbed in different times. Due to their high adsorption kinetics, smaller molecules are adsorbed first. Although they show more affinity to the surface, the adsorption of bigger molecules will take time due to their low adsorption kinetics. Therefore, bleaching efficiency will change depending on time. The results of the experiments done by using Crude and Al-pillared clays are given in Figures 4.19a and 4.19b those of the experiments with organo clays in Figures 4.20a and 4.20b The maximum bleaching efficiency is obtained at about 10 minutes for Crude and Al-Pillared Clays as shown in Figures. The decrease in bleaching efficiencies after 5 and 15 minutes contact time is attributed to oxidation in the glycerin.

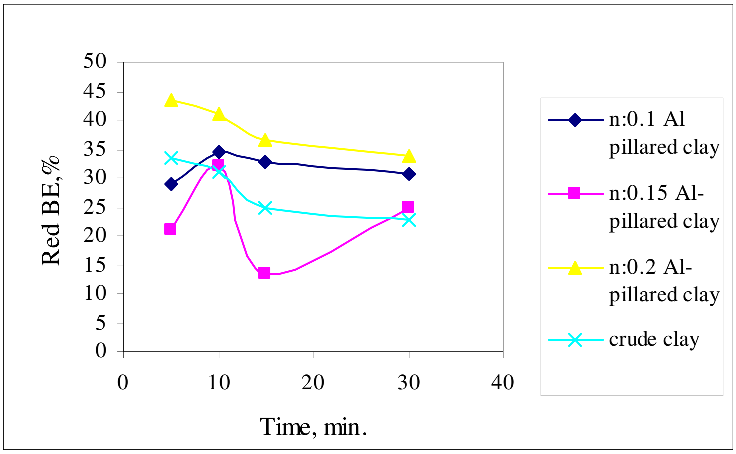


Figure 4.19.a: Effect of time in Red scale @ 50°C, for 1% of crude and pillared clays

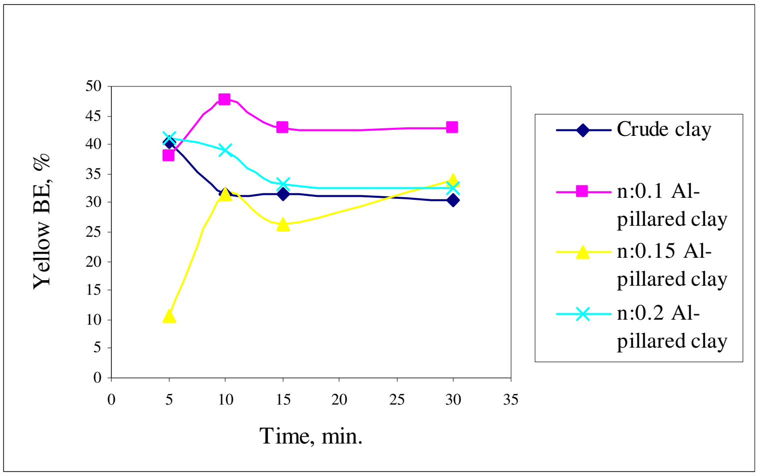


Figure 4.19.b: Effect of time in Yellow scale @ 50°C, for 1% of crude and pillared clays

For organo clays, the time required to reach maximum bleaching efficiency is about 45 minutes for three types dried organo clays. At this time, it is observed that Oven Dried Organo Clay shows the greater bleaching efficiency than the others. From the graph, bleaching efficiency increases with time for commercial organo clay.

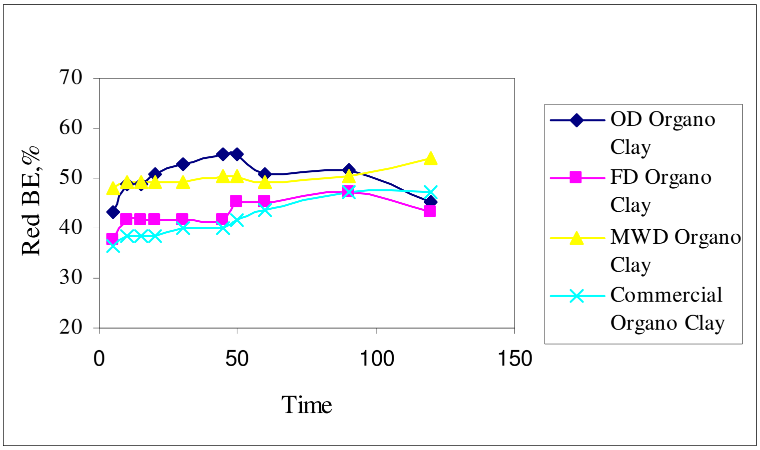


Figure 4.20a: Effect Time in Red scale @ 50°, for 1% of MW, OD, FD and Commercial Organo clays

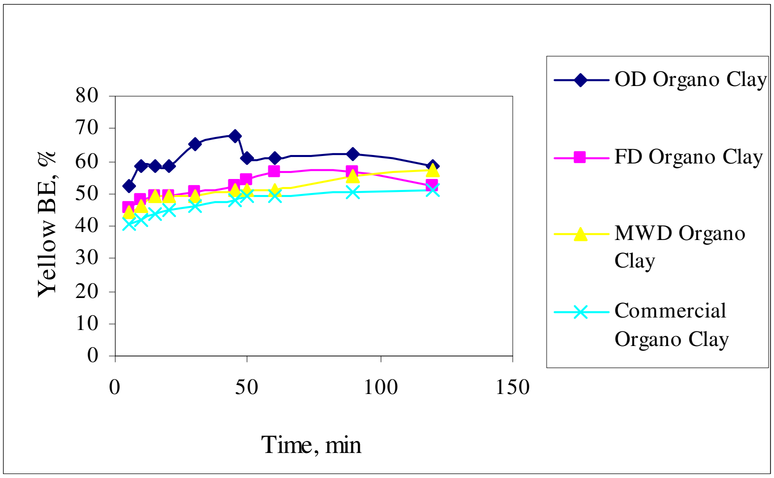


Figure 4.20b: Effect Time in Yellow scale@ 50°, for 1% of MW, OD, FD and Commercial Organo clays

The effect of time on bleaching efficiency of Inorgano-organo clay is given in Figures 4.21 and b. As shown in the Figures there is no considerable change in B.E. after 30 minutes and maximum B.E. is observed at about 15 minutes.

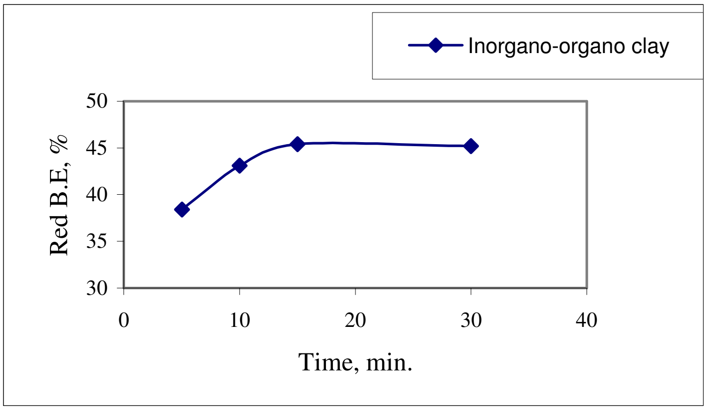


Figure 4.21.a: Effect of time in Red scale @ 50°, for 1% of Organo-Inorgano clay

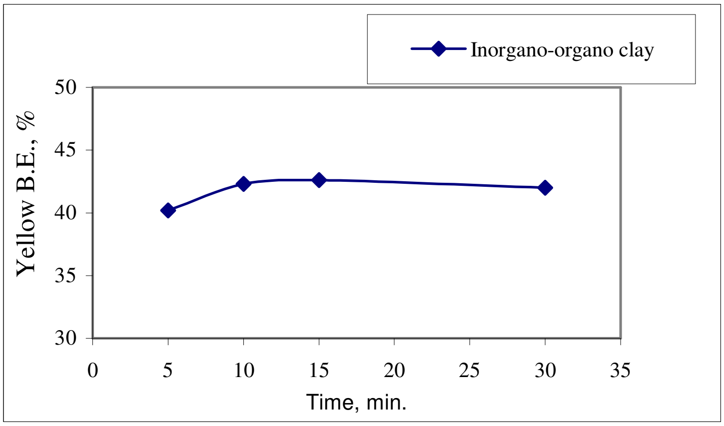


Figure 4.21.b: Effect of time in Yellow scale @ 50°, for 1% of Organo-Inorgano clay

4.2.2 Effect of Amount

Crude and Al-Pillared clays were added to the glycerin at 50°C–60°C in amounts 0.5%–3% and stirred for 30 min at constant temperature. The results obtained are shown in Figures 4.22.a and 4.22.b. A close examination of the figures reveals that an increase in the amount of adsorbent causes an increase in the bleaching efficiency regardless of type of the adsorbent. As shown from these figures, there are no linear relation between BE and adsorbent amount and Al-pillared clays exhibit different characters in red and yellow scales. However, the amounts of adsorbents are limited at 3% since this is the maximum amount of activated carbon used in the production plant.

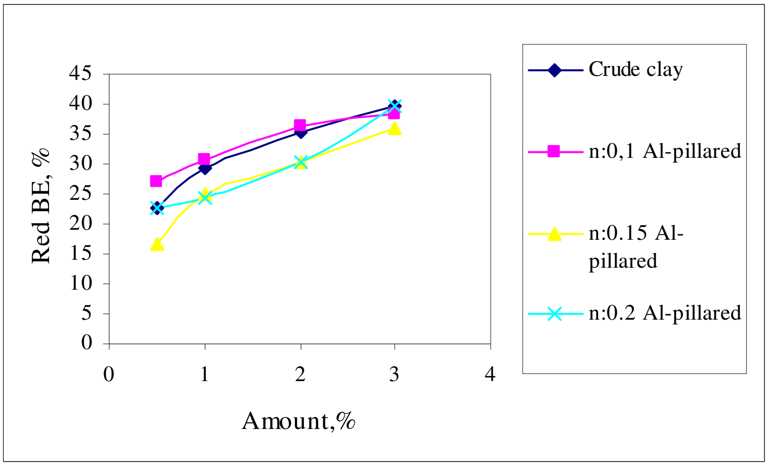


Figure 4.22.a: Effect of amount of crude and pillared clays in Red scale

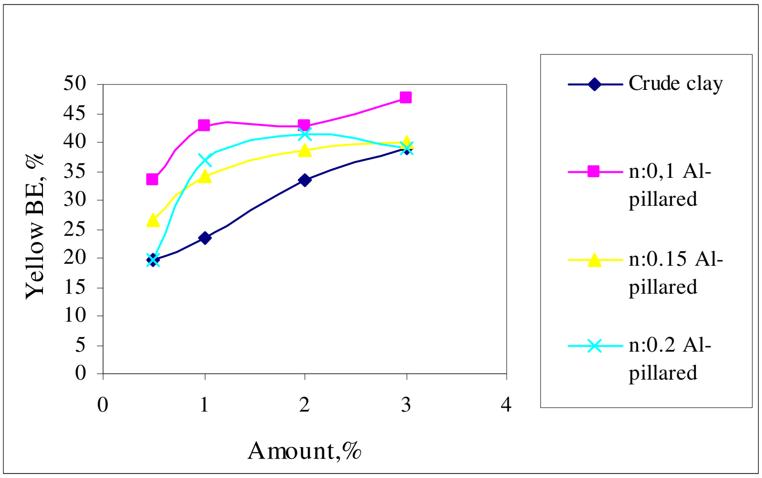


Figure 4.22.b: Effect Amount of crude and pillared clays in Yellow scale

Organo clays exhibit the same behavior and a continuous increase is observed for all organo clays. However, the curves have two different regions distinguished by the change in slope. In the first region placed between 0,5-1% adsorbent amount, bleaching efficiency increases very rapid. Although, the increase in bleaching efficiency is very slow at the second region. Ultimately, the rate of increase is approximately same for four type organo clays.

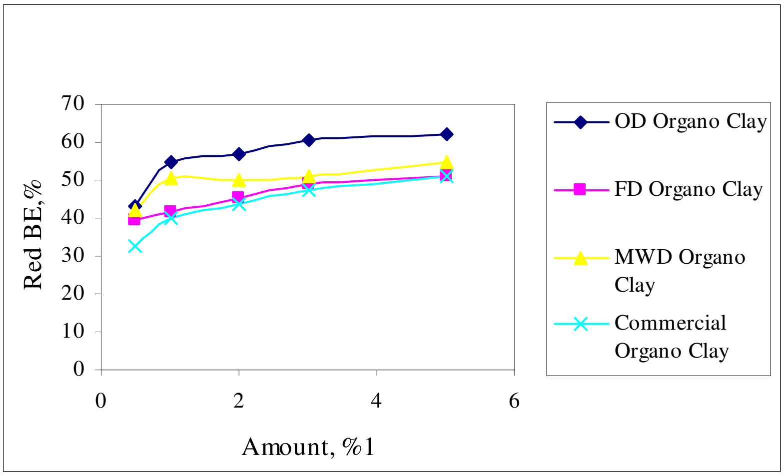


Figure 4.23.a: Effect of amount of organo clays in Red scale @50°and 45min

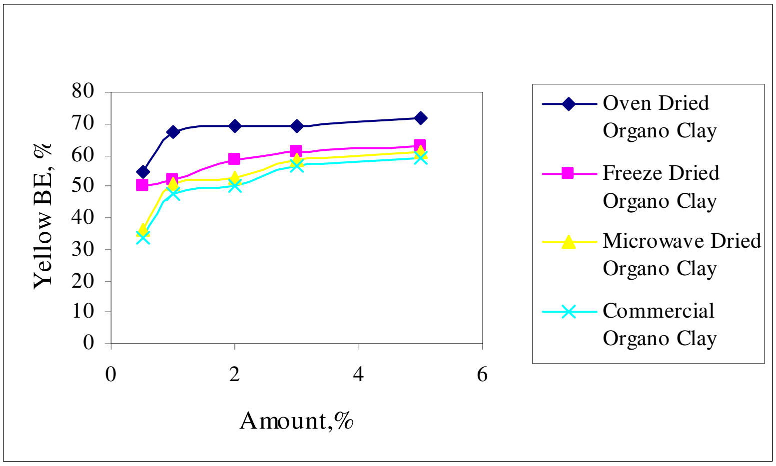


Figure 4.23.b: Effect of amount of organo clays in Yellow scale @50°and 45min

As seen from Figures 4.24.a and b, BE increases with increasing amount of adsorbent. This is an expected result.

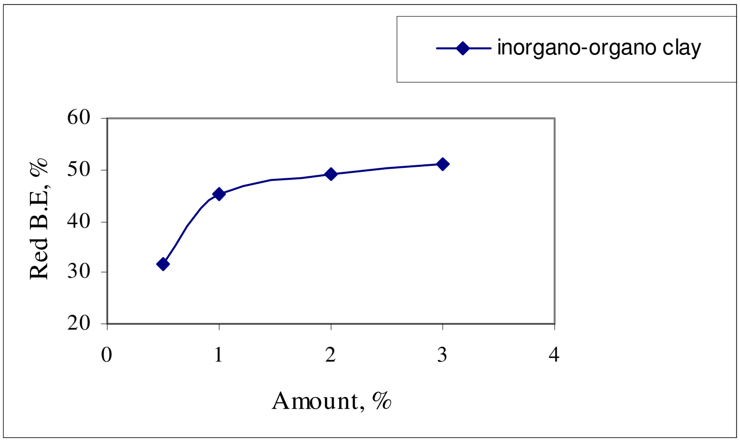


Figure 4.24.a: Effect of amount of organo-inorgano clay on B.E in Red scale @ 50°C and 30 min

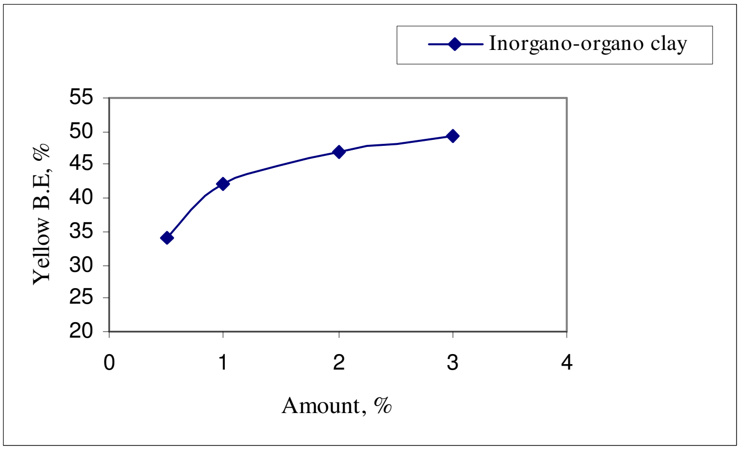


Figure 4.24.b: Effect of amount of organo-inorgano clay in Yellow scale @ 50°C and 30 min

4.2.3 Effect of Temperature

Although the high operation temperatures are also another factor affecting the process economics, high viscosity of glycerin requires working at relatively high temperatures to obtain an effective mixing. Therefore a temperature range between 30°C and 70 °C was chosen.

As shown in the following figures, Al-Pillared Clays exhibit different bleaching behaviors. Except the pillared clay with n_{Al}=0.2, the BE increases with increasing temperature whereas the BE decreases for crude clay and has a maximum value in the case of organo clays.

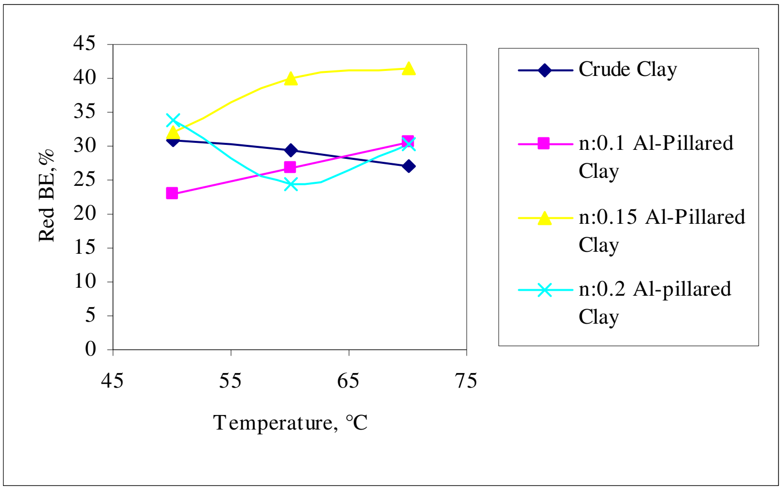


Figure 4.25.a: Temperature effect of crude clay and pillared clays in Red scale

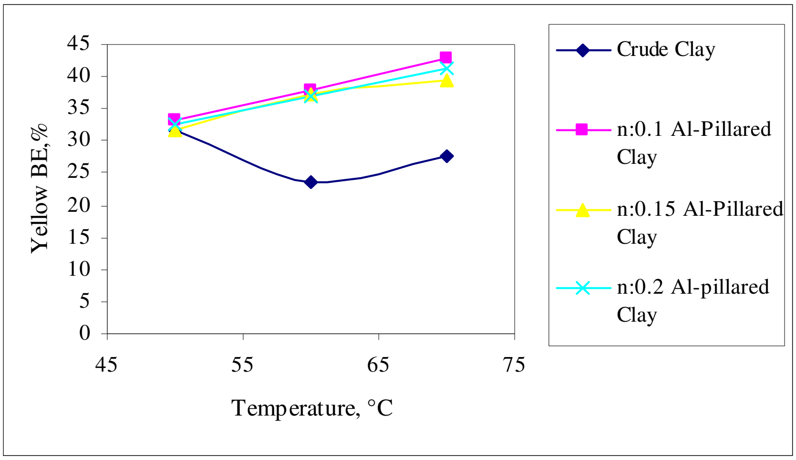


Figure 4.25.b: Temperature effect of crude clay and pillared clays in Yellow scale

As seen from the Figure 4.26.a and 4.26.b, maximum bleaching efficieny of organo clays is observed at about 50°C and bleaching efficiency of oven dried organo clay is much higher than the other organo clays.

On the other hand, higher temperature may increase the rate of oxidation and polymerization reactions. As shown in Figure 4.26.a and Figure 4.26.b, there is a decrease in bleaching efficiency after 50°C. At 70°C, bleaching efficiency turns to its initial value.

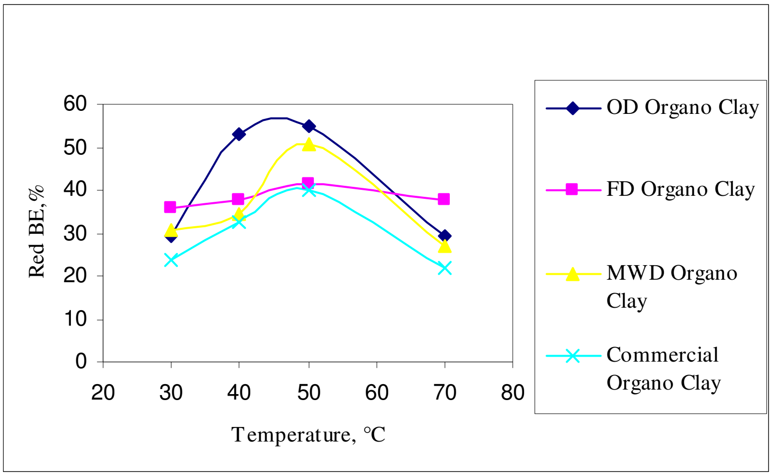


Figure 4.26.a: Temperature effect of MW, OD, FD and Commercial organo clay in Red scale @45min, 1%

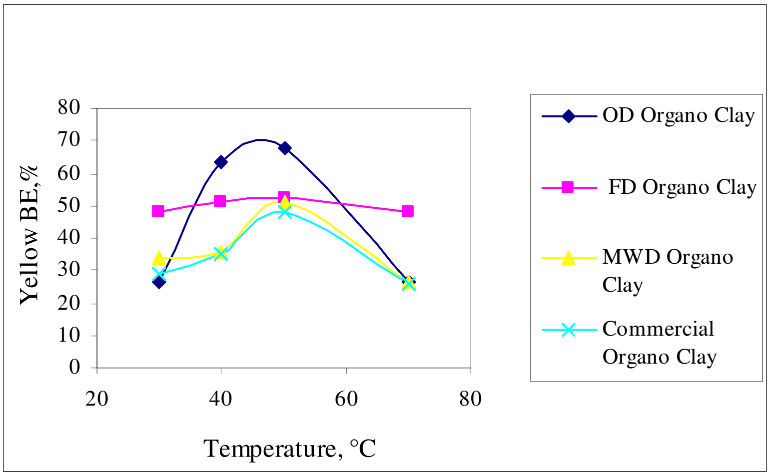


Figure 4.26.b: Temperature effect of MW, OD, FD and Commercial organo clay in Yellow scale @ 45min, 1%

As shown in Figures 4.27.a and b, maximum bleaching efficieny of inorgano-organo bentonite is observed at about 50°C. After this temperature, B.E decreases a lower point.

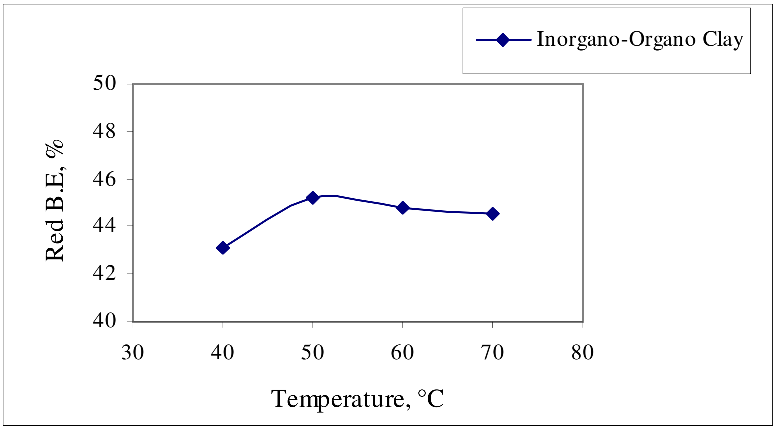


Figure 4.27.a: Effect of Temperature to the BEs of organo-inorgano clay in Red scale@ 30 min.

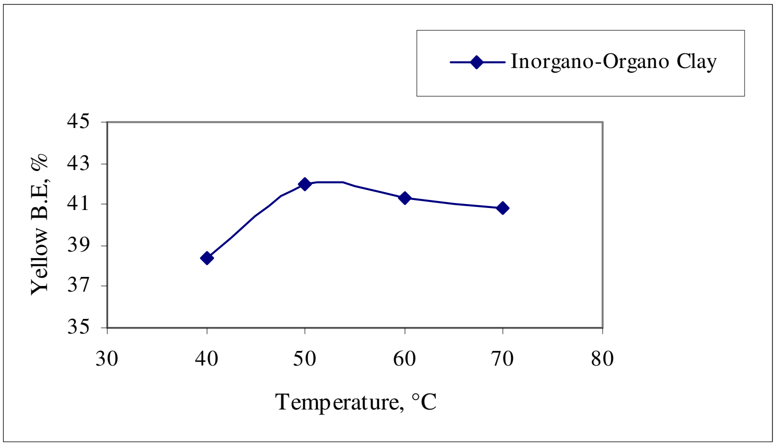


Figure 4.27.b: Effect of Temperature to the BEs of organo-inorgano clay in Yellow scale@ 30 min.

A comparison of the maximum BEs of the clay samples is given by Table 4.6. As seen from Table 4.6, Oven Dried Organo Clay has maximum bleaching efficiency with 54.7 % red and 67.4 % yellow values.

Table 4.6: Comparison of adsorbents

Adsorbents	Maximum BE, %	
	Red	Yellow
Crude Clay	33.3	40.3
0.1 M Al-Pillared Clay	34.6	47.6
0.15 M Al-Pillared Clay	41.6	39.3
0.2 M Al-Pillared Clay	43.5	41.2
OD Organo Clay	54.7	67.4
FD Organo Clay	47.2	56.5
MWD Organo Clay	54.0	57.0
Commercial Organo Clay	47.3	51.2
Inorgano-Organo Clay	45.4	42.6

4.3 THE CHANGE IN SOAP CONTENT

Since the bleaching by adsorption is also used to remove impurities such as soaps and catalysts and metallic compounds and prooxidants in addition to improve the color of the oil, the change in the soap content was also determined.

The effect of time on the removal of soap is given in figure 4.28. A close examination of the figure reveals that the amount of soap removed increases with increasing time and ultimately reaches a certain value after 50 minutes. After this time, there is no change in the amount of soap removed.

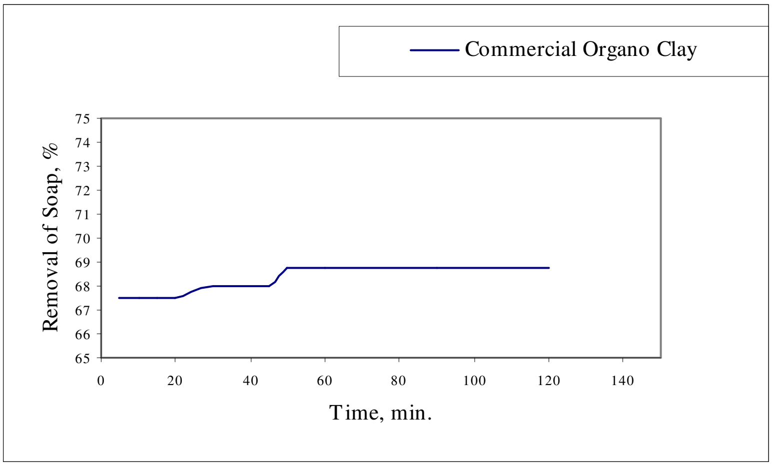


Figure 4.28: Removal of soap depending on time @ 50°C

As shown in the Figure 4.29, removal of soap continuously increases with increasing amount of organo clay.

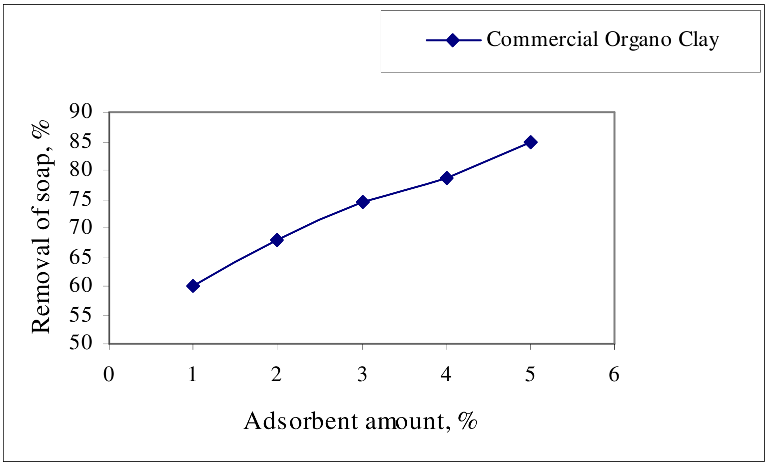


Figure 4.29: Removal of soap depending on adsorbent amount

Effect of temperature on the removal of soap is shown in the Figure 4.30. At temperatures exceeding 50 °C, removal of soap starts to decrease in parallel with bleaching efficiency.

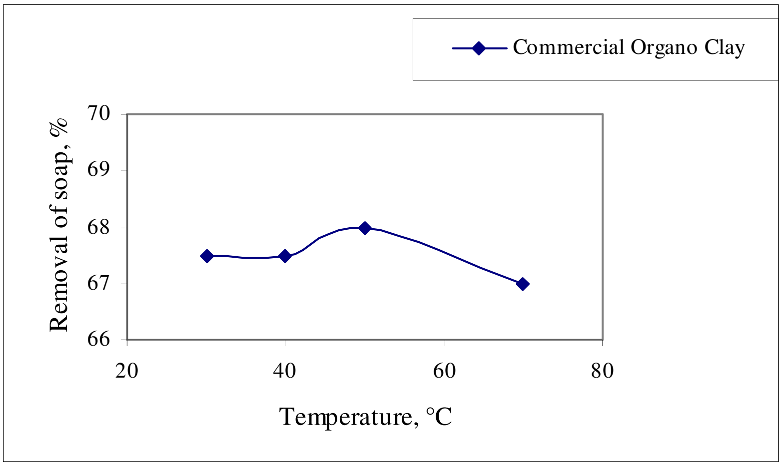


Figure 4.30: Removal of soap depending on temperature

All of the soap removal experiments were made for commercial organo clay. However, glycerine bleached with other adsorbents was subjected to UV measurements and no considerable difference between the absorbances measured for succeeding contact times was observed

Table 4.7 gives the % removal of soap. As seen from the table, the highest % removals are obtained by using OD and FD organo clays.

Table 4.7: Comparison of the adsorbents in terms of removal of soap

Adsorbents	Condition	Removal of Soap, %
Crude Clay	t:10 min., T:50°C m:1% adsorbent	51.9
n:0.1 Al-Pillared Clay	t:30 min., T:50°C m: 1% adsorbent	52.1
n:0.15 Al-Pillared Clay	t:10 min. T: 70°C m:1% adsorbent	50.9
n:0.2 Al-Pillared Clay	t:30 min., T: 70°C m: 1% adsorbent	71.6
OD Organo Clay	t: 45 min., T:50°C m:1% Adsorbent	74.2
FD Organo Clay	t:45 min., T: 50°C m:1% adsorbent	74.2
MW Organo Clay	t.45 min., T:50°C m:1% adsorbent	69.8
Commercial Organo Clay	t:45 min., T:50°C m:1% adsorbent	68.0
Inorgano-Organo Clay	t:45 min., T:50°C m:1% adsorbent	60.3

4.4 The Use of Adsorbent Mixture

Modified clays are cheaper than activated carbon but they are not as effective as activated carbon. Activated carbon and modified clay mixtures give the best economic and quality way in bleaching process.

Distilled glycerine with 8.1 R 63Y first colors is bleached to 0.1 R and 0.6 Y color by 3% activated carbon. This efficiency was not obtained with modified clay.

As shown from Table 4.8, the best result is obtained by %1 Microwave Dried Organo Clay and %1 Activated carbon mixture. The mixture is effective as 3% activated carbon to obtain technical glycerine.

Table 4.8:Adsorbent mixtures @ 50°C, 45 min.

Adsorbent	Final Color
%3 Activated carbon	0.1R 0.6Y
%1 Microwave Dried Organo Clay +%1 Activated carbon	0.4R 0.8Y
%1 Microwave Dried Organo Clay +%0.5 Activated carbon	1.3R 1.8Y
%2 Microwave Dried Organo Clay +%0.5 Activated carbon	1.0 R 1.3Y

5.0 CONCLUSION

It was concluded that the microwave irradiation method is successful to obtain modified clay. The 73% of the active sites is occupied when the amount of HDTMA is 100% of CEC under the microwave irradiation in very short times.

The longer contact times are not suitable for bleaching in the case of the crude and pillared clays. And also the higher bleaching temperatures are not suitable for crude clay.

Organoclays are most efficient in the removal of colorful components and inorgano organoclays have the BE values between inorgano- and organo clays.

It was also concluded that the organoclays have limited efficiencies in the removal of colorful components of crude glycerine and therefore it is able to use them only as coadsorbents.

The mixture containing 1% of activated carbon and %1 of microwave dried organoclay is effective as 3% of activated carbon for 50°C and 1 hour contact time and the reduction obtained in the amount of activated carbon points that the organoclays has synergistic effect.

The use of the mixture has the potentialities to evaluate a more feasible process economics.

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