Use of Domestic Minerals for Vegetable Oil Bleaching

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ABSTRACT

In this thesis, acid activation and characterization studies were conducted for different clay samples and bleaching capacity of the selected acid activated clay samples for sunflower oil were determined. The samples selected for this study were naturally occuring clays from Ankara and Eskişehir regions. The acid activated zeolite was also used for the purpose to compare its bleaching performance with commercial bleaching clay, Tonsil and the acid activated clays.

The clay minerals were activated with hydrochloric acid (HCl) at three acid concentrations (1 N, 3 N, 5 N), activation times (1h, 2h, 3h) and different dry clay/acid ratios. The clay samples from the Ankara and Eskişehir regions were defined as montmorillonite according to X- ray diffraction (XRD). XRD results proved that acid activation caused structural changes in the treated montmorillonites, montmorillonite peaks gradually disappearing and yielding to an amorphous montmorillonite structure. The TGA results showed a significant weight loss between 30° - 200°C (≈15%) for the Ankara clay and between 20° - 200°C (≈12%) for the Eskişehir clay. This was most probably due to the removal of free and hydrogen-bonded water molecules. Maximum surface area was obtained for the acid activated Ankara clay treated with 1 N HCl for 3 hours. It was determined to be 849.1 m^2/g. Also, maximum surface area was 269.7 m^2/g for the acid activated Eskişehir clay treated with 5 N HCl for 1hour. Then the surface area of the acid activated clays decreased sharply with the acid activation. The chemical compositions of the solutions and clays after acid activation were determined using ICP and EDX analysis, respectively. According to the results, the dissolution amount of CaO, Na_2O, MgO, K_2O, Fe_2O_3 and Al_2O_3 increased along with increasing acid concentration and treatment time. The SiO_2 content and the SiO_2/Al_2O_3 ratio increased as a result of dissolving of aluminium ions. This ratio increased from 6.0 to 7.5 for the acid activated Eskişehir clay and from 2.7 to 3.9 for acid activated Ankara clay.

Acid activated clays were tested for the assessment of their bleaching efficiency for sunflower oil in the laboratory. Bleaching tests were carried out with earths prepared at different acid activation conditions such as acid concentration and activation times. The absorbance value was measured at 455 nm and found to be 0.429 for the neutralized sunflower oil. Peroxide value and free-fatty acid content of the neutralized oil were found to be 16.8 meq/kg and 0.07 %, respectively. The oil bleached with the

acid activated Ankara clay had a peroxide value of 46.2 meq/kg first, which decreased to 22.4 meq/kg and the free-fatty acid content was observed to be around 0.08 %. For acid activated Eskişehir clay, peroxide value of the bleached oil initially increased up to 31.2 meq/kg, then decreased under the peroxide value of neutralized oil (16.8 meq/kg) and free-fatty acid content of bleached oil approximately was around 0.09 %.

The bleaching parameters which were used for testing were 1 % earth concentration and 30 minutes contact time at 100°C bleaching temperature. At these selected parameters, acid activated Eskişehir clay (5 N 1h HCl treatment), Ankara clay (1 N 3h HCl treatment) and zeolite (2 N 6h HNO_3 treatment) were compared with the commercial bleaching clay, Tonsil. The smallest value of absorbance and bleaching efficiency were found to be 0.084 and 80 %, respectively with the Eskişehir clay and these values were determined to be 0.083 and 81 % with the Tonsil under the same conditions. The absorbance value and bleaching efficiency of the bleached oil with acid activated Ankara clay were determined to be 0.114 and 73 %, respectively using the selected bleaching parameters. Bleaching performance of Ankara clay was found to be lower when compared with the result of Eskişehir clay.

At the selected bleaching point, results of lovibond red and yellow color of bleached oil indicated that the Eskişehir clay and Tonsil were close to each other in bleaching efficiency (Red color: 0.8 and 1.1; yellow color: 20 and 20 for Tonsil and Eskişehir clay, respectively). Zeolite did not reach the required bleaching performance. The bleaching efficiency was 25 % with raw zeolite and it hardly increased to 46 % with the acid activated zeolite. In addition, red and yellow color values were higher than the other clays (red color:2.6; yellow color: 30).

As a result, Eskişehir clay gave a better bleaching performance compared to Ankara clay and Zeolite. Maximum bleaching efficiency was achieved after 30 minutes of contact time with 1 % earth concentration at 100 °C bleaching temperature following 5 N 1h HCl treatment for Eskişehir clay.

ÖZ

Bu çalışmada farklı kil çeşitlerinin asit aktivasyonu ve karakterizasyonu gerçekleştirilmiş ve seçilen aktive edilmiş kil çeşitlerinin ayçiçek yağındaki renk açma kapasiteleri belirlenmiştir. Çalışma için seçilen kil örnekleri Ankara ve Eskişehir bölgelerinden temin edilmiştir. Ayrıca aktive edilmiş zeolit örneği de ayçiçek yağının renk açma işleminde kullanılmış, renk açma performansı ticari ağartma toprağı olan Tonsil ve asitle aktive edilen kil örnekleri ile karşılaştırılmıştır.

Kil örnekleri hidroklorik asit ile farklı asit konsantrasyonlarında (1 N, 3 N, 5 N), aktivasyon zamanlarında (1 saat, 2 saat, 3 saat) ve farklı asit kil oranlarında aktive edilmiştir. X-ışınları kırınımı (XRD) sonuçlarına göre Ankara ve Eskişehir killerinin montmorillonit mineraline sahip oldukları görülmüştür. Asit aktivasyon ile killerin yapısında değişikliklerin meydana geldiği, montmorillonit piklerinin yavaş yavaş kaybolmaya başladığı ve amorf bir yapının oluştuğu X-ışınları kırınım sonuçları ile gözlemlenmiştir. Termal analiz (TGA) sonuçlarına göre, Ankara kili için 30°C ile 200°C arasında (≈15%), Eskişehir kili için ise 20 °C ile 200 °C arasında (≈12%) muhtemelen serbest ve hidrojen bağlı su moleküllerinden kaynaklanan ağırlık kaybı olduğu gözlenmiştir. Ankara kili için maksimum yüzey alanı 1 N HCl konsantrasyonu ve 3 saat asit aktivasyon işlemi sonucunda elde edilmiş ve 849.1 m^2/g olarak bulunmuştur. Bu değer Eskişehir kili için 5 N HCl konsantrasyonu ve 1 saatlik işlem sonucunda 269.7 m^2/g olarak bulunmuştur. Asit aktivasyonuna devam edilmesi durumunda yüzey alanında düşme gözlenmiştir. Asit aktivasyon sonrası elde edilen çözeltinin ve killerin kimyasal kompozisyonları sırasıyla ICP ve EDX analizleri kullanılarak tespit edilmiştir. Sonuçlar ışığında CaO, Na_2O, MgO, K_2O, Fe_2O_3 ve Al_2O_3 çözünme oranları artan asit konsantrayonu ve zamanla artmıştır. SiO_2 içeriği ve SiO_2/Al_2O_3 oranı ise Aluminyum iyonunun çözünmesine bağlı olarak artmıştır. Bu oran aktive edilen Eskişehir kili için 6.0'den 7.5'ye, aktive edilen Ankara kili için 2.7'den 3.9'a yükselmiştir.

Aktive edilen killer laboratuvarda ayçiçek yağının renk açma işlemi için test edilmiştir. Renk açma işlemi, farklı aktivasyon koşullarında örneğin farklı asit konsantrasyon ve aktivasyon zamanlarında yapılmıştır. Nötralize ayçiçek yağının absorbans değeri (455 nm) 0.429, peroksit değeri 16.8 meq/kg, serbest yağ asit içeriği %0.07 olarak bulunmuştur. Asit ile aktive edilmiş Ankara kili ile yapılan renk açma

işlemi sonucunda yağın peroksit değeri başlangıçta 46.2 meq/kg iken daha sonra 22.4 meq/kg'a düşmüştür. Serbest yağ asit değeri % 0.08 civarında bulunmuştur. Asit ile aktive edilmiş Eskişehir kili ile yapılan renk açma işleminde ise peroksit değeri 31.2'e yükselmiş fakat bu değer 16.8 meq/kg değerinin altına düşmüştür. Serbest yağ asit içeriği ise % 0.09 civarında gözlenmiştir.

Renk açma işlemi için uygulanan parametrelerden 100°C de %1 toprak konsantrasyonu ve 30 dakika işlem zamanı seçilmiş ve bu noktalarda aktive edilmiş Eskişehir (5 N, 1 saat HCl), Ankara (1 N, 3 saat HCl), ve Zeolit (2 N, 6 saat HNO_3) topraklarıyla elde edilen sonuçlar ticari olarak aktive edilen kil (Tonsil) ile karşılaştırılmıştır. Eskişehir kili ile yapılan renk açma işleminden elde edilen en küçük absorbans değeri ve renk açma verimi 0.084 ve % 80 olarak bulunmuş ve bu değerler aynı koşullarda yapılan Tonsil ile 0.083 ve % 81 olarak bulunmuştur. Aktive edilen Ankara kili ile yapılan renk açma işlemi sonucunda ise absorbans değeri ve renk açma verimi 0.114 ve %73 olarak tespit edilmiş, renk açma performansı Eskişehir kiline göre düşük bulunmuştur.

Renk açma işlemi için seçilen parametrelerde, aktive edilen Eskişehir kili ile Tonsilin lovibond kırmızı ve sarı değerleri yakın bulunmuştur (Kırmızı renk : 0.8 ve 1.1 sırasıyla Tonsil ve Eskişehir kili için, sarı renk: 20 her iki kil için). Aktive edilmiş zeolit ise istenen renk açma performansını gösterememiştir. Ham zeolit ile yapılan renk açma işleminden elde edilen verim % 25 iken bu değer ancak aktive edilmiş Zeolit ile % 46 ya yükselebilmiştir. Ayrıca lovibond kırmızı ve sarı değerleri (2.6 ;30) diğer örnekler ile yapılan renk açma işlemi sonuçlarına göre yüksek bulunmuştur.

Sonuç olarak Eskişehir kili ile yapılan renk açma işlemi en iyi sonucu vermiştir. Maksimum renk açma işlemi 5 N, 1 saat asit aktivasyon sonucunda elde edilen Eskişehir kili ile %1 toprak konsantrasyonu ve 30 dakika renk açma parametreleriyle elde edilmiştir.

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CHAPTER 1

INTRODUCTION

In edible oil refining, either by chemical or physical process, the bleaching treatment is a critical step and the conditions for bleaching step depend on the type of crude oil and its quality. The main task of bleaching is the removal of color pigments and the decomposition of hydroperoxides. This increases the shelf life and aesthetic value of the product (Baranowsky et al. 2001).

For bleaching process, bleaching clays are used. Neutral clays, activated earths, synthetic silicates and carbon black are the basic kinds of materials used in edible oil bleaching (Wiedermann 1981). Bleaching earths mainly consist of bentonites or montmorillonites, and these are finelly crystalline silicate of aluminium with various amounts of alkali metals and transition metals (Tsai et al. 2002).

Compared to naturally active clays, activated bleaching earths indicate higher activity. So acid treatment is applied to neutral clays to enhance sorptive properties. The activation of montmorillonite is usually done with mineral acid (hydrochloric acid or sulphuric acid) and the specific surface area (BET) is increased by this treatment. The amount of acid and conditions depend on the raw clays used and the maximum activity depends also on the type of oil (Baranowsky et al. 2001).

The principal goal of the use of bleaching clays is the elimination of a series of contaminants that can be divided into three groups. That are primary, secondary and tertiary. The primary contaminants are oil soluble components; proteins, sterols, tocopherols, hydrocarbons and natural pigments. The secondary contaminants are organic compounds; free fatty acids, peroxides, ketones, aldehydes. The tertiary contaminants are chemical compounds; solvents, biocides, soaps, heavy metals (as Fe^{+3} and Cu^{+2}), phosphoric and citric acid and others (Valenzuela Diaz and Souza Santos 2001).

Processing crude oils to finished edible food products is obtained by several factors;

➢ Consumer preferences

➢ Sensory quality and stability characteristic of oils

➤ Preparation of hardened products from vegetable oils, such as margarines (Mounts 1981).

In Turkey, Tonsil has been used as commercially activated bleaching earth. Tonsil is produced from natural bentonites by activation. Turkey exports raw bentonite especially to Germany and then imports activated bleaching earth from the other countries. Bentonitic earths do not evaluated enough for using in vegetable oil refining in the domestic market. The scope of this study is the evaluation and activation of domestic earths from Ankara and Eskişehir regions with different process parameters for activation and bleaching process and to compare their bleaching efficiency with Tonsil. Also, acid activated zeolite was used in the bleaching of sunflower oil to see its bleaching efficiency and compared with activated clay samples.

CHAPTER 2

THE MINERAL SOURCES

2.1. Definition

The term bentonite was first used to describe clay material hosted by the Benton Shale of Wyoming, U.S.A. Subsequently a number of definitions have been used for bentonite based on mineralogy and/or origin and/or end usage. With respect to industrial minerals the following definition is useful: Clay consisting essentially of minerals of the smectite clay mineral group and physical properties are dictated by the dominant mineral, regardless of mode of origin and occurrence. Clay material with a capacity to decolorize and purify oil to commercial grade is also composed of smectite clay minerals, but the dominant mineral is calcium montmorillonite (Vancouver 1994).

Another mineral source is the alumino-silicate crystal structure known as "zeolite" which has uniformly sized pores throughout its crystal structure. The crystal structure for the types of zeolite is determined by the ratio of silicon to aluminum in the crystal when the crystal is formed. All naturally occurring zeolite is hydrophilic and contains aluminium. Dealuminizing natural zeolite makes it hydrophobic.

2.2. The Origin of Earths

Bentonites have formed for several million years through alteration such as weathering of volcano ash which settles in valleys and shallow areas of ground and multiple layers form and thus small bentonite deposits develop. Bentonite is a clay–rich material mainly consisting of smectite. Smectite is including montmorillonite, beidellite, nontronite, saponite, hectorite, sauconite, and stevensite (Mounts 1981). The smectite is primarily montmorillonite. Bentonite contains also feldspar, chalcedony, quarts, plagioclase, calcite, dolomite, analcite, pyrite, etc.

Natural zeolites are found in various settings such as solids and land surfaces, marine deposit, alkaline lakebeds and geothermal deposits. There are about 40 known naturally occuring zeolites species in addition to about 150 synthetic species.The most common natural zeolites are clinoptilolite, mordenite, chabazite,

phillipsite, erionite, analcime and ferrierite. One of them, clinoptilolite is the most abundant (Christie et.al 2002).

2.3. Montmorillonite

2.3.1. Structure

The clays are one of the more important industrial minerals defined as a natural, earthy, fine-grained material and are composed mainly of silicon, aluminum, oxygen or hydroxyl group but they may also contain appreciable quantities of iron, alkalies, and alkaline earths. As seen from the Figure 2.1, the silicon atom is equidistant from four oxygens or hydroxyls arranged in a tetrahedron and the tetrahedrons are combined to form a hexagonal network and the aluminium is embedded at the centre of an octahedron of six oxygens or hydroxyls. The network of octahedrons between the silica layers share the oxygen-hydroxyl atoms.
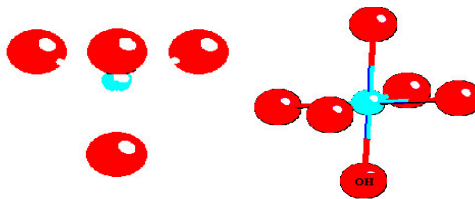
Figure 2.1. Figure of SiO_4 tetrahedron and $Al(OH)_6$ octahedra.

Chemical composition of the clay mineral is based on a hydroxyl-aluminosilicate framework and mainly composed of plate-like particles and layer structure divided into three types, 1:1, 1:2 and 2:1:1 layers and also having slit-shaped pores (Mounts 1981, Tsai et al. 2002). The individual layers are held together (i.e. Van der Waals attractive forces, hydrogen bonding or weak electrostatic attraction) (Rouquerol 1999). The structure of 2:1 type montmorillonite is represented in Figure 2.2.

The smectite group of clay mineral consists of several clay minerals and the most important industrially minerals are sodium montmorillonite and calcium montmorillonite (Murray 2000). If the dominant exchangeable cation is calcium, then the mineral in the smectite group is calcium montmorillonite and if it is predominantly sodium, it is sodium montmorillonite (Murray 2000). Sodium ions are monovalent and lead to a higher swelling capacity compared to calcium ions which is bivalent and used

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for the decolorization of vegetable, animal and mineral oils due to lower swelling capacity. The acid activation of clays are made on non-swelling smectites (Ca-bentonite). Because the swelling bentonites may show processing difficulties as high viscosity dispersions and difficult mass transport on the acid activation process (Valenzuela Diaz and Souza Santos 2001).
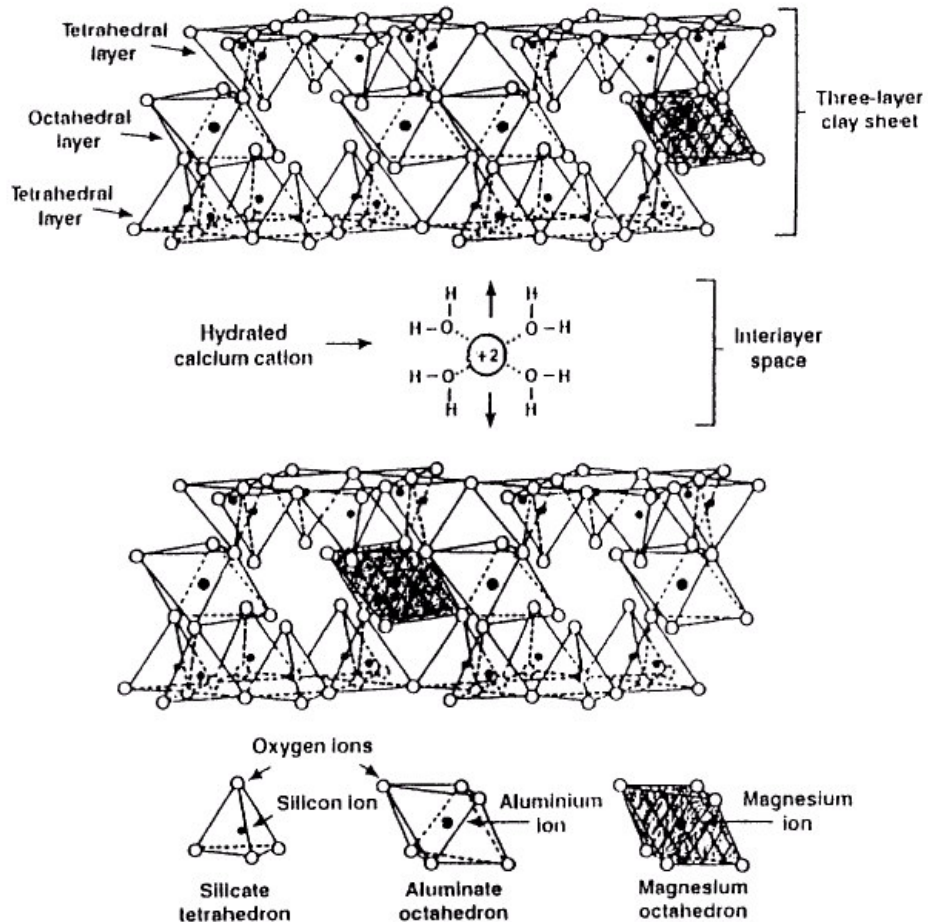
Figure 2.2. The structure of 2:1 type montmorillonite (Chitnis and Sharma 1997).

The properties of natural montmorillonite can be enhanced generally by alkaline activation, organic modification and acid activation, due to the substitution of exchangeable cations in the interlayered area or partially dissolving of the cations in the octahedral area. The properties of the modified montmorillonite are related to structural parameters and its modified chemical composition (Lu et al. 2003).

Isomorphic substitution is the substitution of one cation for another in the mineral structure and major source of negative, permanent charge in soils. Substitution in the octahedral sheet (Fe^{+2} and / or Mg^{+2} for Al^{+3}) and in the tetrahedral sheet (Al^{+3} for

Si^{+4}) causes negative charge on the outer basal oxygens (Bray and Redfern 1999). The replacements leave a negative charge on the crystalline surface, which is neutralized by positive ions such as Ca^{+2}, Na$^+$, Mg^{+2}, K$^+$, and H$^+$. These ions are known as exchangeable cations (Morgan et al. 1985). Due to the substitutions, the 2:1 layers are not electrically neutral so they have a negative charge balanced by interlayer exchangeable cations and their amount indicates the cation-exchange capacity (CEC) of the clay (Valenzuela Diaz and Souza Santos 2001, Chitnis and Sharma 1997).

By the acid activation the aluminium ions are replaced with hydrogen ions, so bleaching power of montmorillonite increased and montmorillonite readily taking up water and organic molecules between the aluminosilicate sheets (Bray and Redfern 1999).

2.3.2. Applications

Some important properties of clay minerals that relate to their applications:

- 2:1 layer,
- Tan, olive green, gray or white colors,
- Octahedral and tetrahedral substitutions which creates a charge imbalance in the 2:1 layer,
- High layer charge,
- High base exchange capacity,
- Thin flakes and laths,
- Very high surface area,
- High adsorption capacity,
- High viscosity (Murray 2000).

Clays are important in process industries, engineering, construction, agriculture, geology and environmental applications. Some of them are used for decolorization, chemical carriers, ceramics, paper, paint, drilling fluids, plastics, liquid barriers and catalysis. Improvement of mining and processing techniques will lead to growth of traditional clay applications (Murray 2000). In most these applications, uses of montmorillonite are the consequence of its properties such as ion exchange, plasticity, swelling, density, compaction, etc (Bala et al. 2000).

2.4. Zeolite

2.4.1. Structure

Zeolites are crystalline, porous 3-dimensional aluminosilicates of the alkaline-earth (mainly Ca) and alkali (mainly Na and K) metals (Christie 2002). They belong to the class of minerals known as "tectosilicates" with uniform nanometersized pores and shape of the rings of oxygen contrasts with the wide range of pore sizes in activated alumina, silica gel and activated carbon (Mumpton 1999). Their three dimensional framework is composed of tetrahedral AlO_4^{-5} and SiO_4^{-4} units that are combined by oxygen atoms (Christie 2002). Collective polyhedra from frameworks are generally open and contain channels and cavities thus zeolites are able to gain and lose water reversibly and to exchange extraframework cations without change of crystal structure. Small molecules can pass through entrychannels, but larger molecules are excluded (Mumpton 1999). All zeolites are molecular sieves that can selectively adsorb molecules on the basis of their size, shape or electrical charge (Christie 2002). Because of the strong local electrical dipole moment in the lattice framework, zeolites adsorb all polar and non-polar molecules into their specific framework. The schematic drawing of the zeolite pore structure is given in Figure 2.3.
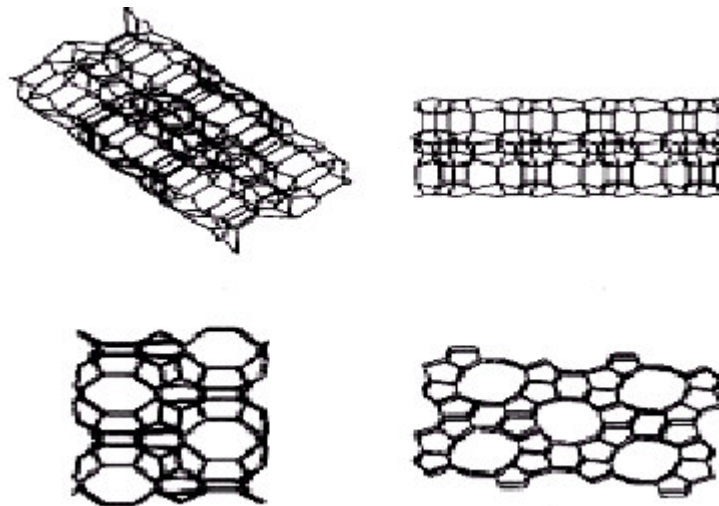
Figure 2.3. Schematic drawing of the zeolite pore structure (Chau et al. 2002).

The extraframework cations weakly bonded can be exchanged by washing with a strong solution of another cation. The CEC (cation exchange capacity) of a zeolite is a function of the amount of Al. Al substitutes for Si in the framework tetrahedra so if the Al content is greater, extraframework cations is needed to balance the charge (Mumpton 1999).

High-silica zeolites are important in refining and petrochemical applications. The crystallization involves complete filling of the void regions by an organo-cation guest molecule. Afterthat, the guest molecule is thermally decomposed (Wu et al. 2002).

Clinoptilolite is a zeolite of the heulandite group being the most abundant in nature. This zeolite contains three channels, limited by a system of tetrahedral rings. These channels are occupied by water molecules and compensating cations, which neutralize the anionic charge of the framework. It is well established that the multiple uses of these materials are based on their physicochemical properties, which explain their wide range of applications in numerous agricultural and industrial areas (Rivera 2000).

Many of the naturally occuring zeolites can be created synthetically. One major advantage of zeolites is that they are naturally occuring and they are often very cheap. Natural zeolites do not compete with their synthetic counterparts (zeolites) in catalytic and adsorption applications. Because they have lower adsorption capacities and most natural materials have smaller pore openings than the others (Mumpton 1999).

2.4.2. Applications

Zeolites are used for a variety of applications ranging from catalytic cracking of hydrocarbons in petroleum refining to separations.

Like talc, diatomite, vermiculite and bentonite, zeolite minerals possess;

➢ Cation exchange,
➢ Attractive adsorption,
➢ Dehydration-rehydration,
➢ Catalysis properties (Mumpton 1999).

2.5. Characterization of Mineral Sources

Characterization studies are necessary to characterize the clays obtained from different regions to see whether they have desired properties or not.

In this section, five of characterization techniques used in this study are summarized. These are;

➢ X-ray diffraction (XRD),

➢ Scanning electron microscopy and energy dispersive X-ray analysis,

➢ Termal analysis (TGA),

➢ Inductively coupled plasma atomic emission spectroscopy ; ICP-AES

➢ Physical adsorption measurement.

2.5.1. X-Ray Diffraction Technique

X-rays are photons produced easily by bombarding a material surface with a wavelength of the order of a fraction of a nanometre compared with the hundreds of nanometres of light waves. X-ray beam incident on a material penetrates many micrometres into the bulk and the direction of the diffracted beam intensity is determined by the periodicity of the atom planes in the crystalline solid (Flewitt and Wild 2003).

Beam of characteristic X-rays of wavelength λ is incident on a single crystal surface at an angle θ which produces a diffracted beam. The diffracted beam intensity provides a measure of the distribution and position of atoms within the crystal. The position of intensity peaks in the diffracted beam is characteristic of the material examined and unknown phases can be identified by comparision with standards, JCPDS Powder Diffraction File (Flewitt and Wild 2003).

2.5.2 Scanning Electron Microscopy and Energy Dispersive X-ray Analysis

The electron gun operates typically over a voltage range 0-30 keV sometimes extending up to 60 keV depending upon the type of instrument. The specimen is scanned by the incident electron beam and electrons emitted from the surface are

collected and amplified to form a video signal (Flewitt and Wild 2003). For examining the microstructure of materials, SEM is one of the techniques.

2.5.3. Thermal Analysis (TGA)

Thermogravimetric analysis a complementary analytical technique that quantify the details of thermally induced reactions in clays. It gives information about the water content and types of water in the structure. Therefore, by thermogravimetric analysis weight loss of samples can be determined as it is heated to elevated temperatures in a certain atmosphere. Thermogravimetric analysis of the clay samples indicated the removal of free water molecules around 100° C and hydrogen bonded and coordinated water molecules around 200°C. Dehydroxylation of the samples takes place through a wide range of temperature, but maximum dehydroxylation takes place at 600-750°C (Bala et al. 2000).

2.5.4. Inductively Coupled Plasma Atomic Emission Spectroscopy ; ICPAES

Atmospheric-pressure inductively coupled plasmas (ICPs) are flamelike electrical discharges and the practice of elemental and isotopic ratio analysis have been revolutionized. In all major ICP-based methods (ICP-AES, ICP-AFS, ICP-MS), the test sample is typically converted to an aerosol and transported into the plasma where the desolvation, vaporization, atomization, excitation, ionization processes occur. ICP-MS and ICP-AES are the two most powerful means for rapid, multielement determinations among the cited methods (Montaser et al. 1998). Determining elemental concentrations are translated to oxide formula to indicate the final composition of materials.

2.5.5. Physical Adsorption Method

Adsorption is a surface phenomenon which depends on the specific affinity between solute and adsorbent (Rossi et al. 2003). Whenever a solid surface is exposed to gas or liquid, adsorption occurs. Adsorption techniques also are used for the characterization of the surface properties and texture of fine powders. In addition to these, in many academic and industrial laboratories on porous materials such as clays, ceramics and membranes undertake adsorption measurements. Especially, gas

adsorption procedures are used for determining the surface area of a diverse range of powders and porous materials (Rouquerol et al. 1999).

In adsorption two kinds of forces are involved; physical adsorption (physisorption) or chemisorption (Rouquerol et al. 1999). Weak forces are referred to Van der Waals forces and promote a physical adsorption. Physical adsorption is reversible at the same temperature by lowering the pressure (Patterson 1992). A second type of the adsorption depends upon forces of chemical attraction between the surface and solute molecules in a liquid. This is called chemisorption. Chemisorption of β-carotene occurs on aluminosilicate surfaces with some of the exchangeable cations acting as active sites (Kheok and Lim 1982). In the bleaching of oils with adsorbents Van der Waals (physical) adsorption and chemical forces (chemisorption) can play a part. This depends upon the adsorbent, the nature of the minor component (adsorbate) and the conditions of their contact (Patterson 1992).

Bulk of the adsorption occurs in mesopores and micropores of the clay (Hajjaji et al. 2001). These pores of minerals are classified by their sizes ;

➢ Pore < 2 nm called micropores

➢ 2 nm< pore <50nm called mesopores

➢ Pore > 50 nm called macropores (Valenzulela Diaz and Souza Santos 2001)

Adsorption Isotherms

The adsorption isotherm is the relation between the amount adsorbed and the equilibrium pressure or concentration at constant temperature. The overall shape of an isotherm is managed by the nature of the gas-solid system, the operational temperature and the pore structure of the adsorbent (Rouquerol et al.1999).

At very low surface coverage, linearity of the isotherm is usually observed. The deviation from linearity may be toward the pressure depends on the scale of surface heterogeneity and the magnitude of the adsorbate-adsorbate interactions. The various physisorption mechanisms are discussed by using the six major types of isotherms in the IUPAC classification as shown in Figure 2.4. (Rouquerol et al.1999).
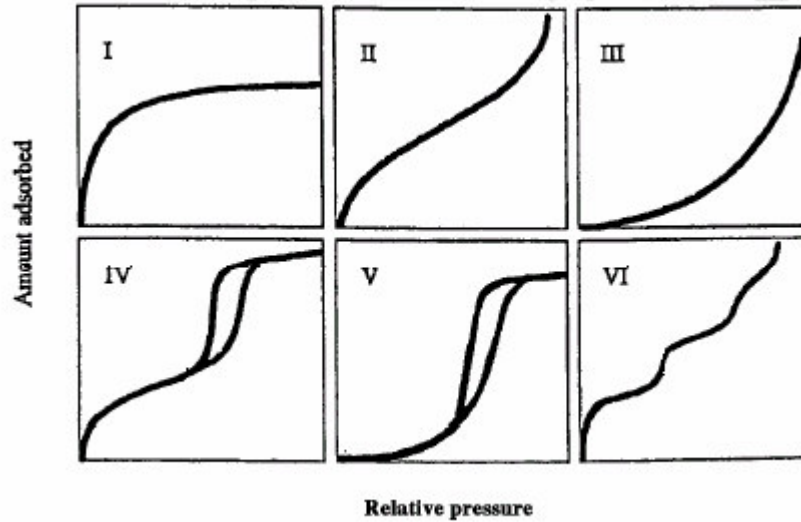
Figure 2.4. The IUPAC classification for adsorption isotherm.

Clay minerals (which are aggregated powders) appear to give normal Type II isotherms. Type II isotherms are obtained with aggregates of plate-like particles (Rouquerol et al.1999).

BET (Brunauer-Emmett-Teller) Model

Gas adsorption technique is applied for the determination of surface area. The BET method is still used as a standart procedure for surface area determination. The original BET treatment obtained an extension of the Langmuir kinetic theory of monomolecular adsorption to an infinite number of adsorbed layers. The adsorbed molecules in one layer can act as adsorption sites for molecules in the next layer at any pressure below the saturation vapour pressure $p°$ fractions of the surface (θ_o, θ_1, θ_2,............θ_i,....) are covered by 0,1,2,....i,...layers of adsorbed molecules (θ_o represents the fraction of bare surface) in the BET model. Nitrogen (at 77K) is the most suitable adsorptive for standard surface area determination (Rouquerol et al. 1999).

At equilibrium, characterized by the pressure p and θ_o (bare surface) and θ_i (covered surface) remain constant. The rate of condensation on the bare surface can be equated the rate of evaporation from the first layer:

$$a_1 p \theta_o = b_1 \theta_1 \exp(-E_1/RT) \tag{2.1}$$

where a_1, b_1 : adsorption and desorption constant for the first layer,

E_1 : the positive value of the so-called energy of adsorption in the first layer.

Assume that; a_1, b_1 and E_1 are independent of the quantity of adsorbed molecules.

In the same way, at the equilibrium pressure p, the fractions of the surface θ_2, θ_3,.... θ_I,..must remain constant, so;

$$a_2 p \theta_1 = b_2 \theta_2 \exp(-E_2/RT)$$
$$a_3 p \theta_2 = b_3 \theta_3 \exp(-E_3/RT)$$

$$\begin{matrix} . & & . \\ & & \\ . & & . \end{matrix}$$

$$a_i p \theta_{i-1} = b_i \theta_i \exp(-E_i/RT) \tag{2.2}$$

where θ_{i-1} : surface covered by i-1 layer

θ_I : surface covered by i layer,

a_i and b_i : adsorption and desorption constant respectively,

E_i : energy of adsorption in the ith layer.

The sum of the fractions of surface equals unity:

$$\theta_0 + \theta_1 +.......+\theta_i +.....= 1 \tag{2.3}$$

$$n = n_m[1\theta_1 + 2\,\theta_2 +.......+i\theta_i +.....] \tag{2.4}$$

a_i, b_i and E_i are different for each adsorbed layer in pirinciple but two main assumption are used for the derivation of the BET isotherm equation.

i) The energy of the adsorption E_i has the same value for the second and all higher layers as   the liquefaction anergy, E_L, of the adsorptive (i.e. $E_2=E_i=E_L$).

ii) The multilayer has infinite thickness at $p/p^0=1$ ($i=\infty$).

BET model can be described as:

$$\frac{n}{nm} = \frac{CX}{(1-X)(1-X+CX)} \tag{2.5}$$

where $X= p/p^0$

$C \approx \exp(E_1-E_L)/RT$

E_1-E_L : net molar energy of adsorption

Equation (2.5) can be written in the linear form:

$$\frac{p}{n(p^o-p)} = \frac{1}{n_mC} + \frac{C-1}{n_mC} * \frac{p}{p^o} \qquad (2.6)$$

The BET plot $(p / n(p^0-p)$ versus p/p^o) should be straight line with slope = $(C-1)/n_mC$ and intercept = $1/(n_mC)$ over the apprioximate range p/p^o = 0.05-0.3.

The specific surface area a (BET) is obtained from the BET monolayer capacity, n_m.

$$a(BET) = n_mL\sigma \qquad (2.7)$$

where L: Avogadro constant,

σ: average area occupied by each molecule in the completed monolayer (σ = 16.2 $\AA^2$ for N_2 molecule).

2.6. Acid Activation of Mineral Sources

2.6.1. Introduction

Natural active clays possess some bleaching activity and show a high adsorption capacity due to their high surface area. However, compared to naturally active clays, activated bleaching clays show a much higher activity (Baranowsky et al. 2001). Activated bleaching earth was first produced by Pfirschinger Mineralwerke in 1907 and by Erdwerke Kronwinkl Franz Schmidt & Co. GmbH in 1909 (Baranowsky et al. 2001).

Acid treatment is carried out with concentrated mineral acids such as sulfuric, hydrochloric and phosphoric acids (Chitnis and Sharma 1997). Chemical composition and physical structure of montmorillonite changes during acid activation to maximize specific properties (Morgan et al. 1985). In addition, by exchanging the inorganic cations (Ca^{+2}, Na^+, K^+) with organocations, the hydrophilic aluminosilicate surface of montmorillonite can be rendered hydrophobic (Lu et al. 2003, Madejova 2002).

2.6.2. The Process of Acid Activation and Effects of the Acid Treatment

Adsorbents are activated by a mineral acid treatment resulting in the de-lamination of the structure, a number of metal ions in the octahedral layer and impurities such as calcite are also removed by leaching with an inorganic acid at

elevated temperatures (Sarıer and Güler 1987, Valenzulela Diaz and Souza Santos 2001). In addition to these, the edges of the platelets are opened and as a result of all these changes, the pore diameters and the surface area increase. The pores with the diameters and the surface area with acid treatment range from 2.0-6.0 nm and 200-400 m^2 / g respectively (Valenzulela Diaz and Souza Santos 2001). The higher the degree of activation, the higher the degree of cation substitution by the H^+ ions of the acid in the clay structure such as Ca-Bentonite + $2H^+$ $\leftrightarrow$ H-bentonite + Ca^{+2}. Such treatment leads to leaching of aluminium, magnesium and iron cations from the octahedral layer to partial removal of aluminium ions from the tetrahedral layer that relocated in the interlayer space (Flessner 2001). The processing of acid activation is represented in Figure 2.5.

```
Mining ⟹ Crushing ⟹ Acid treatment ⟹ Washing

Sizing ⟸ Grinding ⟸ Drying ⟸ Filtering
```
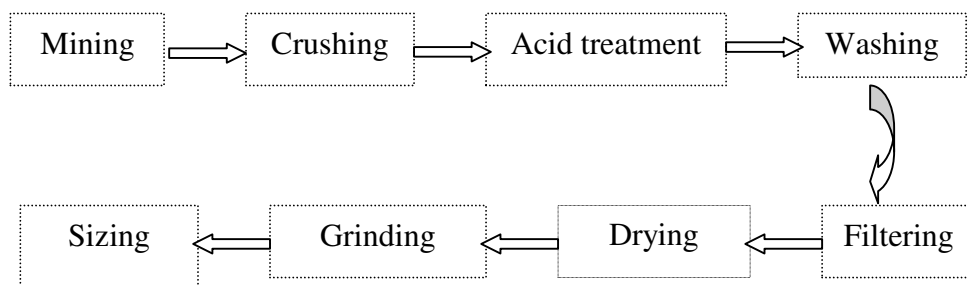
Figure 2.5. Processing of acid activation (Richardson 1978).

Acid and catalytic properties of acid activated clays must be taken into account. The change in surface area, porosity and the type and concentration of the ions in the exchangeable site are observed due to the acid treatment of the clay. Al^{+3} and Mg^{+2} ions are removed from the octahedral sites in the clay during acid activation and relocated in the interlayer space and they act as acid centers. Thus acid activation promotes catalytic activity by increasing the number of Brönsted and potential Lewis acid sites. The Brönsted acidity of clay is either due to free acid or due to the dissociation of water molecules (Chitnis and Sharma 1997). The acid properties of them increase free fatty acids by splitting triglyceride molecules and the catalytic properties are responsible for the decomposition of peroxides (Valenzulela Diaz and Souza Santos 2001).

The most bentonites are not suitable for activation because of high natural bleaching power, however, most clays are poor in natural bleaching activity used for activated clay products (Richardson 1978). Therefore, acid treated clays will be

preferred over the natural clays due to large specific surface area and high adsorption ability for most commercial applications (Lu and Cui 2001).

The nature and type of clay, concentration of the acid, temperature and the time of treatment are the important parameters for acid activation process (Chitnis and Sharma 1997).

Activated bleaching earth is a;

➢ Solid acid

➢ Acidic catalyst

➢ Adsorptive agent

➢ Cation exchanger

➢ Filter aid (Baranowsky et al. 2001)

CHAPTER 3

OIL PROCESSING

3.1. Introduction

About 70 % of all oils and fats produced in the world are vegetable origin. Oils are provided from soya bean, olive, sunflower, cottonseed, palm, coconut, rapeseed, nuts and seeds of plants such as corn (maize) and groundnut. Sunflower oil is obtained from the seed of the plant Helianthus annuus and oil content of it is 22-36%. Color of crude sunflower oil is light amber. When bleaching process is applied, color of it is a pale yellow (Sontag 1979).

The principal impurities of oil are water, free-fatty acids (FFA), pigments, phosphatides, partial glycerides, oxidation products and trace elements such as sulfur, iron, copper, and halogens (Subramanian 1998). These impurities are removed at various steps in the conventional chemical refining, which includes degumming, neutralization, washing, drying, bleaching, filtration, and deodorization (Subramanian 1998). Degumming is done to remove phosphatides. Hydratable phosphatides can be precipitated by adding water to the oil, nonhydratable phosphatides must be destroyed by adding acids. Free-fatty acids are removed by neutralization with alkali hydroxides leading to soaps which can be removed. Undesirable coloured impurities are removed by bleaching with an adsorptive reagent. The undesirable compounds are adsorbed and can be removed together with the adsorbent by filtration. The last step is deodorization and by this step undesirable volatile and odoriferous materials are removed (Haas and Mittelbach 2000). Common process for crude vegetable oil refining is given in Figure 3.1.

```
                          Seeds
                            │
                            ▼
                    ┌───────────────┐
                    │   Crushing    │
                    └───────────────┘
                            │
                            ▼
                    ┌───────────────┐
                    │ Extraction or ├──────▶ Miscella
                    │   pressing    │
                    └───────────────┘             │
                            │                      │
                            ▼                      ▼
                        Crude oil            Evaporation
                            │
                            ▼
                    ┌───────────────┐
         water ────▶│   Degumming   ├──────▶ lecithin
                    └───────────────┘
                      Degummed oil
                            │
                            ▼
                    ┌───────────────┐
sodium hydroxyde ──▶│ Neutralization├──────▶ soapstocks
                    └───────────────┘
                            │
                            ▼
                    ┌───────────────┐
         water ────▶│    Washing    ├──────▶ wastewater
                    └───────────────┘
                      Neutralized oil
                            │
                            ▼
                    ┌───────────────┐
                    │    Drying     │
                    └───────────────┘
                            │
                            ▼
                    ┌───────────────┐
         earth ────▶│   Bleaching   ├──────▶ spent earth
                    └───────────────┘
                            │
                            ▼
                    ┌───────────────┐
         steam ────▶│ Deodorization ├──────▶ condensate
                    └───────────────┘
```

Refined, Bleached and Deodorized Oil
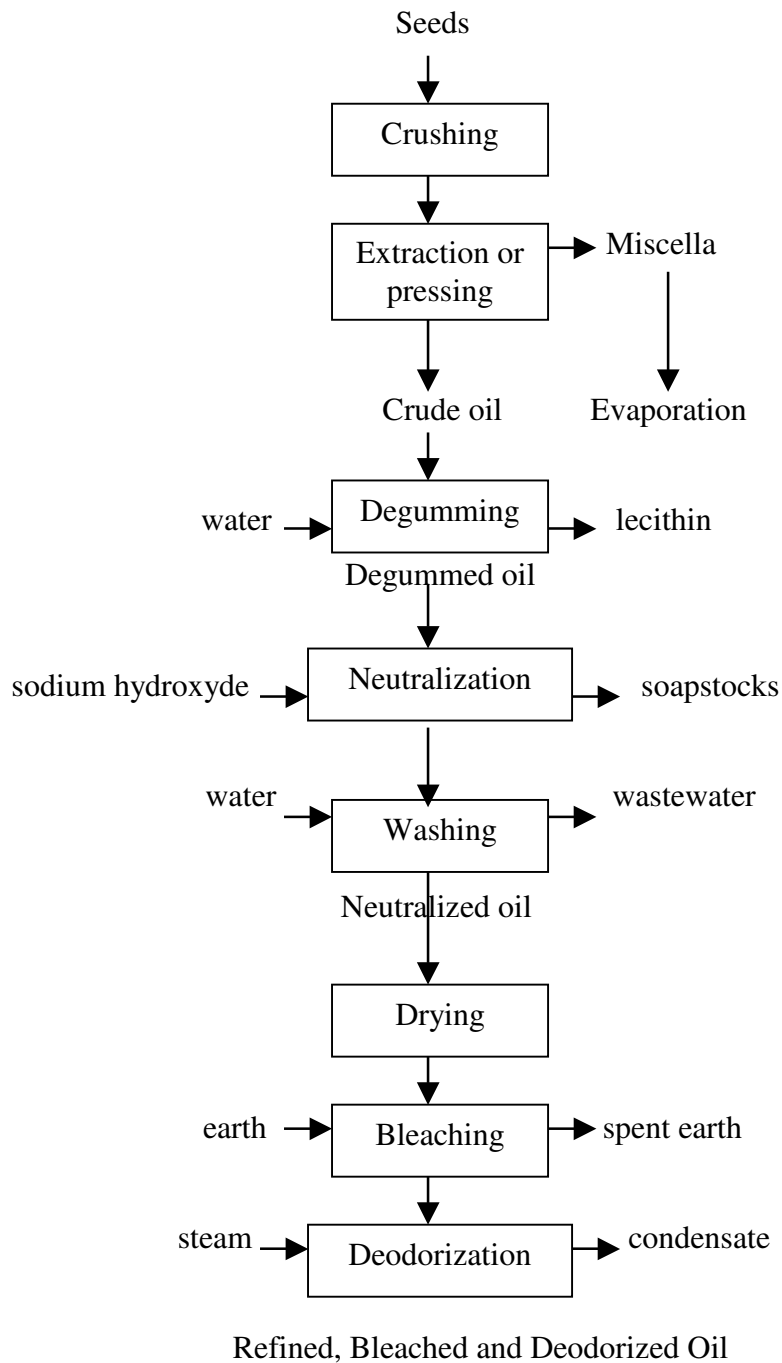
Figure 3.1. Common process for crude vegetable oil refining (Pioch et al. 1998).

3.2. Bleaching of Edible Oils

The bleaching process is applied after degumming and neutralization in the chemical refining and it is more appropriately referred to as adsorption treatment. Crude edible oil still contain undesirable substances such as free-fatty acids, gummy materials and colouring matters. Colouring matters are due to the presence of pigments in the

crude edible oil. These pigments consist of carotenoids, chlorophyll, gossypol and related compounds (Reddy et al. 2001). In addition to these, crude edible oil contains soap residues, phosphatides and metals at trace concentrations (Boukerroui and Ovalı 2002). These substances affect the quality of the end-product by alteration of its taste and colour, the process efficieny and also affect its market value. These impurities from crude oils are removed by using the materials with a strong adsorption power. These materials are called bleaching earths which are usually bentonites activated by heating with strong acids (Boukerroui and Ovalı 2002).

The oil must be dry before bleaching process. Because if the oil contains some moisture, free-fatty acid content of it will increase. Soap should be removed by washing after the neutralization process. Because soap content of oil effects the adsorbent capacity (Mounts 1981).

Bleaching of oils is a process whereby the clay adsorbents is mixed with the oil under specified conditions to remove unwanted color bodies and other contaminants (Richardson 1978). The primary function of the bleaching process is to remove peroxides and secondary oxidation products. In addition, pigments and any traces of gums and soaps from refining are removed (Wiedermann 1981). The process affect significant color reduction. Bleaching process is a combination of catalytic action such as peroxide destruction and equilibrium adsorption for instance pigment removal from oil (Reddy et al. 2001). The peroxides are decomposed into volatile aldehydes and ketones due to further oxidation. Decomposition and dehydration of peroxides and secondary products are represented in Figure 3.2. These products are also adsorbed by bleaching earths (Subramanian et al. 2001).

-CH=CH-CH=CH-CH-CH$_2$-

$\quad\quad\quad\quad\quad$ | $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (Peroxide)

$\quad\quad\quad\quad\quad$ OOH

Activated Clay $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ O

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ ||

$\longrightarrow$ -CH=CH-CH=CH-C-CH$_2$- + H$_2$O

-CH=CH-CH=CH-CH=CH- + H$_2$O

-CH=CH-CH$_2$-CH-CH$_2$- $\quad\quad\quad\quad\quad$ (Secondary Oxidation Product)

$\quad\quad\quad$ OH

Activated Clay

-CH=CH-CH=CH-CH$_2$- + H$_2$O
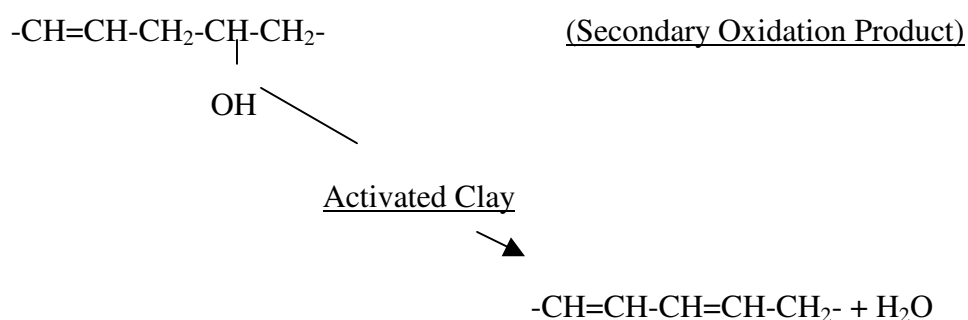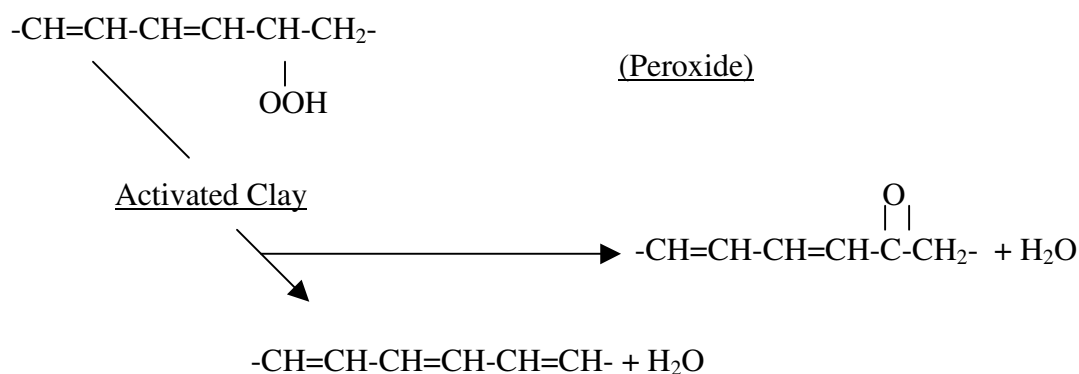
Figure 3.2. Decomposition and dehydration of peroxides and secondary products (Wiedermann 1981).

Bleaching process needs to be carried out under steam / nitrogen blanket or vacuum. Because the activated clay may act as a catalyst for oxidation in the presence of oxygen at the elevated temperatures. Then, oxidation products lead to degeneration and short shelf life of the final product (Reddy et al. 2001).

The general bleaching process is carried out contact temperature in the range of 80-120 °C and contact time ranging from 20-40 minutes under vacuum. The dosage of bleaching earth can vary depending on oil type. Chemical refining usually uses 0.5-2% on a weight basis. However, 2-4 % bleaching earth can be used to meet final color requirements (Valenzulela Diaz and Souza Santos 2001). Flow sheet of bleaching edible oil is shown in Figure 3.3.

Bleaching Clay

Degummed and/or
neutralized oil → | Water removal | → | Oil/clay Suspension formed | → | Impurities adsorbed by the clay | → | Filter | → **Bleached oil**

clay and adsorbed impurities
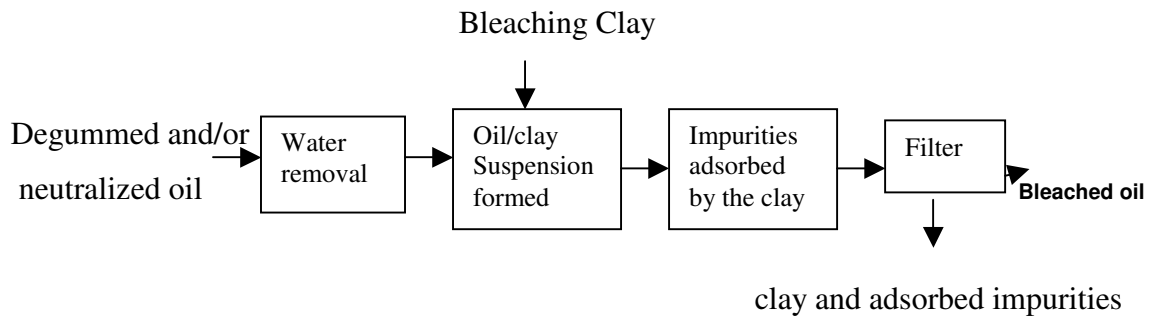
Figure 3.3. Flow sheet of bleaching edible oil.

Oil retention is the characteristic of activated bleaching clays. Acid activation lowers the natural clay's density and increases its oil retention. Because the lower the density and the more void space, the more oil is retained in the used earth. Thus, less amounts of the more activated clays are required to decrease the net oil loss (Wiedermann 1981). Generally oil loss results from oil lost to filter cake (Bera et al. 2004).

For oil retention a typical value is approximately 40%. This value can be reduced to 20-30% by suitable procedures such as steam or nitrogen at the end of the filtration. That is for each 100kg of fresh bleaching earth 25-45 kg of oil are lost (Baranowsky et al. 2001).

3.2.1. The Mechanism of Pigment Adsorption

The coloration in sunflower oil is mainly due to carotenoids (predominant red / yellow color) and small amounts of chlorophyl pigments. The reduction in carotenoids present in the oil results in mainly decolorization and maximum reduction in color are observed during bleaching or decolorization step (Subramanian et al. 1998, Reddy et al. 2001).

Carotene is nutritionally valuable substances, as precursors of vitamin A and for their antioxidant properties in the body. β-carotene is known for the rapid degradation induced by the exposure to light or oxygen. Also the decomposition of β-carotene are catalysed by metallic ions such as Fe^{+3} or Cu^{+2}. These metallic ions highly probable are present on the surface of the adsorbent. They catalyse the reaction or serve as active sites for the chemisorption of β-carotene (Khoo et al. 1978).

Pigments are either disolved in the oil or present in the form of colloidally dispersed particles. They has olefinic groups which can be protonated by the acidic groups (Hui 1996, Srasra and Trabelsi-Ayedi 2000). Adsorption of carotenoid can be catalysed by the Brönsted and the Lewis acidity as shown in Figure 3.4 (Srasra and Trabelsi-Ayedi 2000). β-carotene attaches to the clay surface in the form of carbonium ions either by forming coordination bonds with Lewis sites or by forming hydrogen bonds with Brönsted sites of the activated clay mineral (Sarıer and Güler 1989).
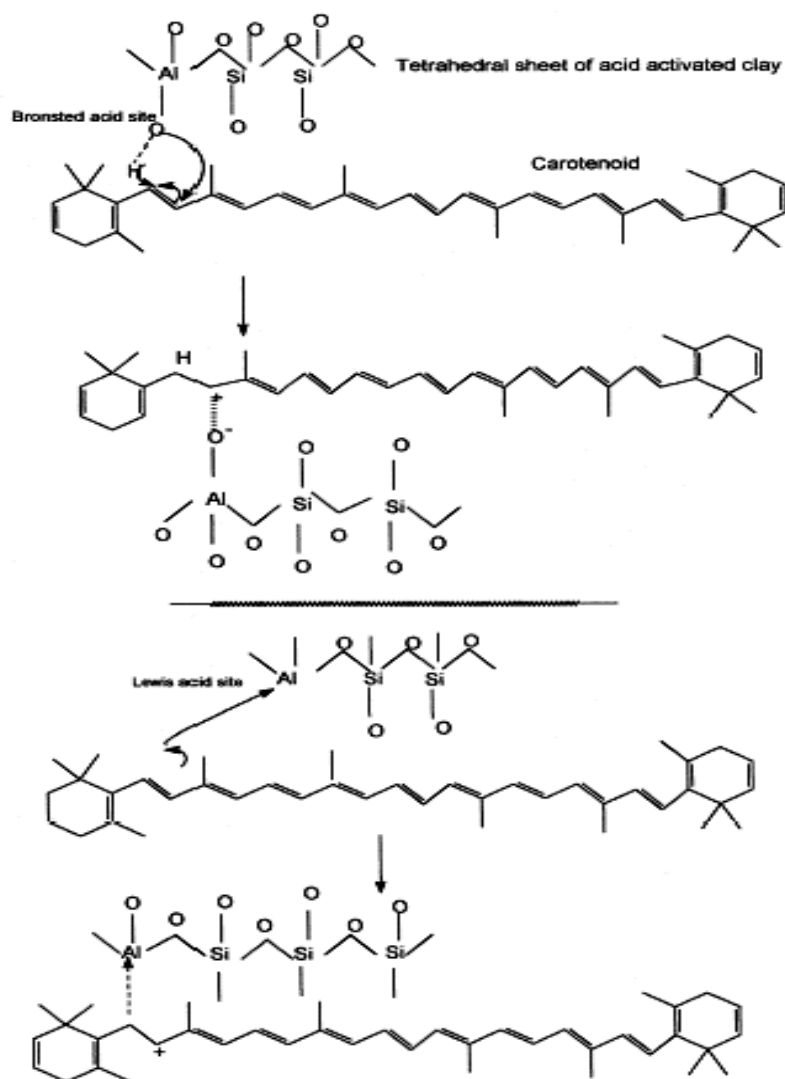
Figure 3.4. The mechanism of carotenoid adsorption on Brönsted and Lewis acid sites (Srasra and Trabelsi-Ayedi 2000).

β-carotene is both electron donor and acceptor and reacts with acid centers of the activated clay surface by means of its seventh carbon atom (Richardson 1978). The cations at the strongly acidic sites are ready to donate a proton to the pigment molecules. Pigment molecules are ready to accept it because of containing electrophilic bonds. As a result, the pigment molecules are held to the clay surface by electrostatic attraction (Patterson 1992). Acid activation of clay and adsorption of pigment molecules are represented in Figure3.5.
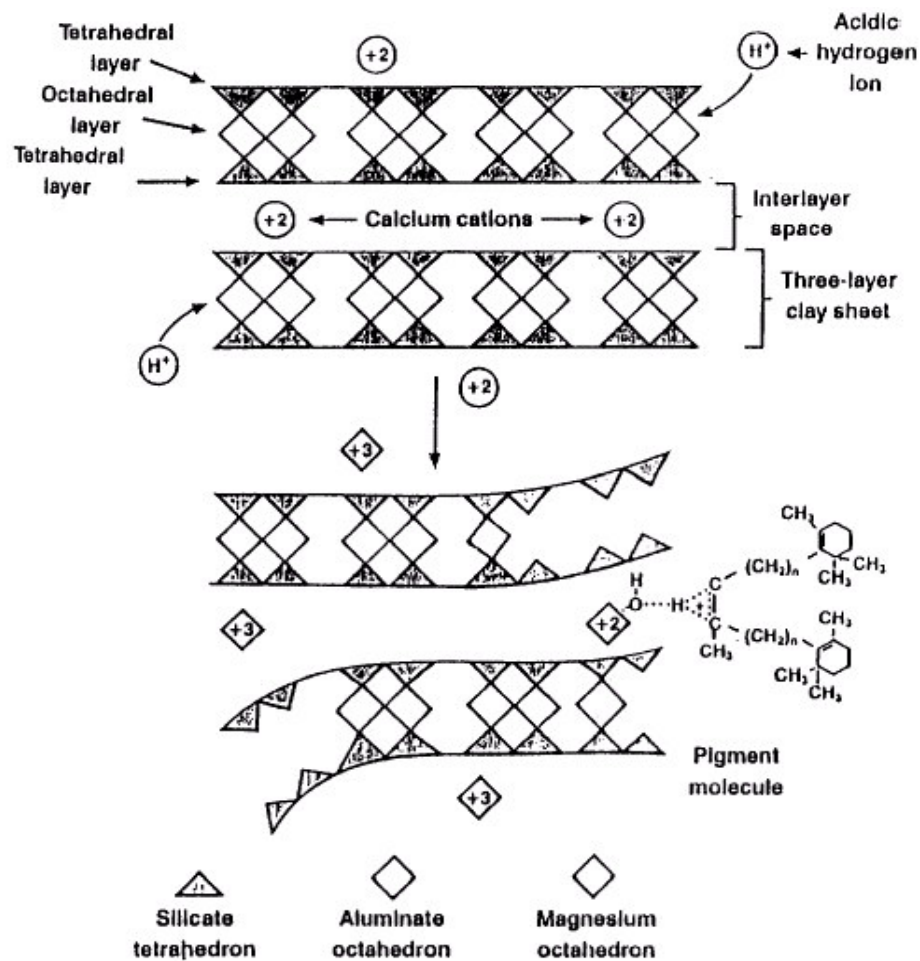
Figure 3.5. Acid activation of clay and adsorption of pigment molecules (Chitnis and Sharma 1997).

Removal of color pigments is necessary from the viewpoint of shelf life as well as aesthetic value (Reddy et al 2001). In the subsequent deodorization step, almost all the thermally degradable pigments are removed (Subramanian et al. 1998).

3.2.2. Important Bleaching Criteria

Important bleaching criteria are activated earth, dosage, time, mixing, temperature and atmospheric pressure vs. vacuum (Wiedermann 1981).

The dosage of activated clay should be the minimum amount to affect removal of impurities as measured by peroxide reduction (Wiedermann 1981).

Finer particle sizes of clays produce better bleaching results. However, filtration rate and oil retention can be affected reversely (Valenzulela Diaz and Souza Santos 2001). Therefore, efficient filtration, short filtration times and minimization of oil retention of filter cake is necessary (Morgan et al. 1985).

Bleaching clays normally contain 10-18 % moisture. If the clay is completely dried prior to use, the structure of it collapses, so bleaching power is reduced because of decreased surface area. In addition to these, adsorptive capacity of acid activated clay is reduced if clay is added to hot oil. Because the moisture in the clay is driven off too rapidly causing collapse of the clay's structure. The acid activated earth should be added to dry, refined oil at 80°C under vacuum conditions and then rapidly brought up to working temperature and held at that temperature for enough time to provide maximal bleach (Wiedermann 1981).

Temperature for vacuum bleaching are lower than for atmospheric to reach optimum color removal. Activity of clay increases while temperature increases. However, decolorization starts to decline after an optimum temperature has been reached. Temperature also affects other properties of the oil. One important is free-fatty acid content. So, temperature should be kept as low as possible to minimize free-fatty acid increase but the temperature should be enough to obtain the desired color (Richardson 1978).

Agitation should be sufficient to achieve good contact of clay with the oil (Wiedermann 1981).

CHAPTER 4

EXPERIMENTAL

4.1. Materials

Neutralized oil provided from Altınyağ Kombinaları A.Ş. (İzmir, Turkey) was used for bleaching process. The clay samples selected for study from Eskişehir and Ankara region were provided from Esan Eczacıbaşı A.Ş. (İstanbul, Turkey) and Sud Chemie (Balıkkesir, Turkey) respectively. Commercially activated clay Tonsil FF was obtained from Ekiz Yağ Fabrikası (İzmir, Turkey).

Acetic acid (100 %), chloroform (extra pure), ethanol, sodium hydroxyde, sodium thiosulfate, and hydrochloric acid fuming (37 %, extra pure) were purchased from Merck (Darmstadt). Potassium iodide was bought from Sigma Chem. Co. (St. Louis, MO). Double distilled water was used in the whole experiment.

4.2. Methods

4.2.1. Characterization Studies

Thermal properties of the clays were analyzed by thermobalance (Shimadzu TGA-51). ~10 mg clays were scanned up to 850°C at heating rate of 10°C/min. Nitrogen atmosphere (40 ml/min) were used for all analyses.

Mineralogy of the natural clays and the crystallinities of the acid treated clays were determined by X-ray diffraction (X-Pert Pro Diffractometer) using $CuK_\propto$ radiation at 45 kV and 40 mA with a step size of 0.02^o, 2θ between 2 and 70, 2θ range.

The microphotographs of the clay crystals were taken by using scanning electron microscopy (SEM, Philips XL 30S) with SE detector at 7.00 kV under vacuum conditions. And also element distributions of clay samples were taken with EDAX instrument.

Chemical composition of the natural clays were determined by fusion dissolution technique using $Li_2B_4O_7$. 0.1 gram of the clay samples were combined with 1 gram of lithiumtetraborate. The dry-powder mixture was placed in a platinum crucible

and fused in an oven at 1000°C for 1 hour. Afterthat, samples were dissolved in hot aqueous 110 ml of 5 % HNO_3 concentration. By adding deionized water, solutions were completed to 250 ml and presented to Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, 96,Varian). The resulting elemental concentrations (i.e. Ca, Mg, Na etc.) were then translated to their oxide forms (i.e. CaO, MgO, Na_2O etc.) to represent the final composition. The acidic solutions of the acid treated clays were also analysed using the ICP analysis.

Physical adsorption methods are widely used to obtain textural properties of materials such as surface area. Specific surface area of samples were determined by using ASAP 2010 (Micromeritics) Adsorption System. Prior to adsorption, the samples were degassed for 24 h under vacuum better than 10^{-5} mbar at 350°C.

Surface area was determined from nitrogen adsorption (at 77K) data by using the Brunauer-Emmett-Teller (BET) equation. In the surface area calculation the adsorption data in the relative pressure (p/p°) ranges from 0.05 to 0.20 were used.

4.2.2. Acid Activation Studies

The following procedure was used, based on the study of Valenzuela Diaz and Souza Santos. 70 grams of the ground clay (dry basis, 105°C) were placed in a 0.5 litre round bottom flask heated by an electrical mantle; 300ml (1N, 3N, 5N) hydrochloric acid (d: 1.19g/ml; 37g HCl/100ml) solutions were added. The dry acid/clay ratio (w/w) were 0.16 (300ml of 1N HCl include 3.7g/100ml so, dry acid/clay ratio =11.1g / 70g ≈ 0.16) 0.48, and 0.8 respectively.

Thermometer, stirrer and reflux condenser were attached to the flask. The temperature was maintained at boiling point (107°C) for variable length of times (1h, 2h, and 3h) with constant stirring. While hot, the clay suspension was transferred to a beaker and washed by decantation with deionized water until it is Cl^- free (tested with $AgNO_3^-$ solution). pH was determined by pH meter (744 Metrohmn) and adjusted between 3.5-4.0. The acid activated clay was filtered in a Büchner funnel, dried at 100°C at 3 hours and reground 100% below 200 mesh using porcelain mortar and pestle to avoid contamination of samples and stored in a dessicator for the decolorization test. Flowchart of acid activation of clay is given in Figure 4.1.

The acid activated clay was used for tests of characterization and evaluated of decolorizing power.

Raw and acid activated Eskişehir and Ankara clay were coded and tabulated in Table 4.1.

Table 4.1. Codes of raw and acid activated Eskişehir and Ankara clays.

Eskişehir clay	Ankara Clay
E : Raw Eskişehir clay	A : Raw Ankara clay
E1-1 : 1 N 1h HCl	A1-1 : 1 N 1h HCl
E1-2 : 1 N 2h HCl	A1-2 : 1 N 2h HCl
E1-3 : 1 N 3h HCl	A1-3 : 1 N 3h HCl
E3-1 : 3 N 1h HCl	A3-1 : 3 N 1h HCl
E3-2 : 3 N 2h HCl	A3-2 : 3 N 2h HCl
E3-3 : 3N 3h HCl	A3-3 : 3N 3h HCl
E5-1 : 5 N 1h HCl	A5-1 : 5 N 1h HCl
E5-2 : 5 N 2h HCl	A5-2 : 5 N 2h HCl
E5-3 : 5 N 3h HCl	A5-3 : 5 N 3h HCl

Raw Clay

↓

Grinding to below 200 mesh

70 gr ground raw clay

(dry basis)

↓

1 N, 3 N, and 5 N HCL →

Mixing of HCl acid with raw clay

↓

Keeping the flask at boiling point (107°C) for selected acid activation times (1, 2 and 3 hours)

↓

Deionized water →

Washing by decantation

→ HCl acid and Cl⁻ ions

↓

Filtrating by Büchner funnel

Filtrate

↓

Drying at 100°C for 3 hours

↓

Grinding to 100 % below 200mesh using porcelain mortar and pestle

Figure 4.1. Flowchart of acid activation of clay.

4.2.3. Bleaching Studies

As shown from the Figure 4.2, the neutralized oil was stirred at 150 rpm under vacuum by using vacuum pump and heated to 80°C in a rotary evaporator (Kika-Werke, Germany). Vacuum was disconnected and the required amount of clay as 0, 0.5, 1, 1.5 per cent (w/w) was added to the hot oil. Then, vacuum was applied and temperature was rised to a top bleaching temperature 100°C (±1). At these conditions, the mixture was held at selected bleaching times. 2 different times; 15 and 30 minutes were

performed for bleaching experiments. At the end, the bleached oil was cooled to 70°C and filtered through the spent earth by vacuum filtration. The mechanism of bleaching of sunflower oil is shown in Figure 4.3.

```
┌─────────────────────────────────────────┐
│   Heating neutralized oil to 80°C with   │
│          agitation at 150rpm             │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│   Adding acid activated clay to a hot    │
│           oil without vacuum             │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│     Heating the mixture to a top         │
│   bleaching temperature (100°C ±1)       │
│            under vacuum                   │
└─────────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────────┐
│  Allowing the mixture to hold at 15 and  │
│   30 min. contact times while agitated   │
│   at the top bleaching tempereture       │
└─────────────────────────────────────────┘
                    │
                    │    Bleached oil-clay
                    │        mixture
                    ▼
┌─────────────────────────────────────────┐
│   Filtrating bleached oil through spent  │
│        clay by vacuum filtration         │
└─────────────────────────────────────────┘
                    │
                    ▼
              Bleached Oil
```
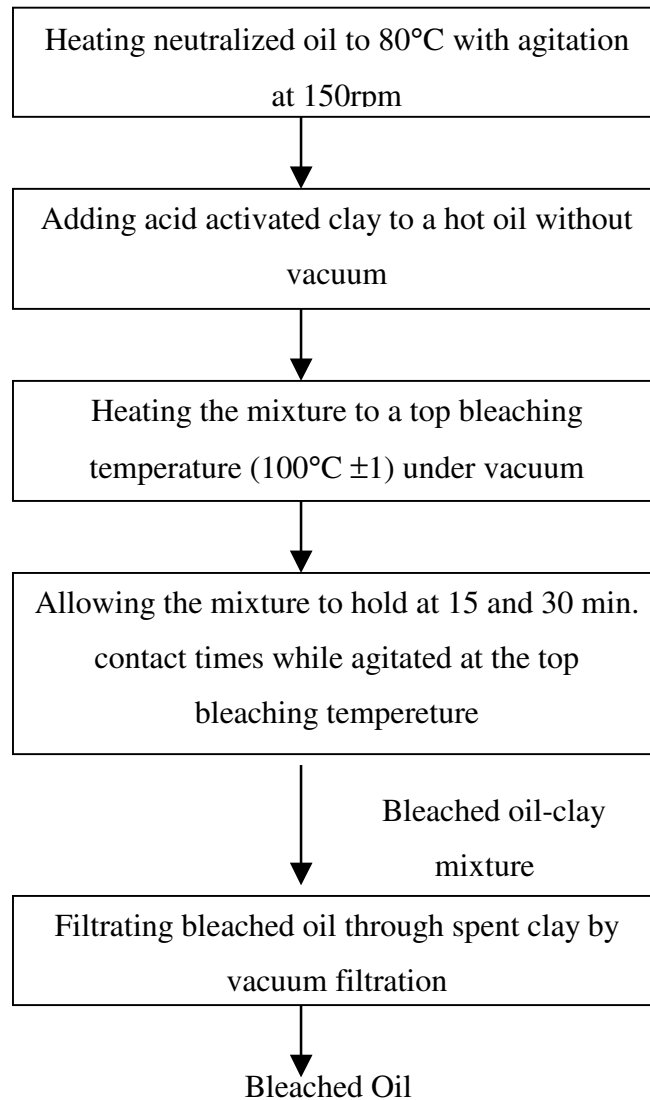
Figure 4.2. Experimental flowchart of bleaching.

Figure 4.3. Mechanism of bleaching of sunflower oil

4.2.4. Analysis of Oil and Montmorillonite

4.2.4.1. Moisture Determination of Bentonite

Moisture of clays were determined by using Sartorious Moisture Analyzer. Results were given as % H_2O.

4.2.4.2. Moisture Determination of Edible Oil

5 ± 0.2g prepared sample was weighed into Al moisture dish and dried to constant weight in vacuum oven at uniform temperature 20-25°C at working pressure which should be ≤ 100 mmHg. Finally, sample was cooled in desiccator for 30 min. and weighed.

Result was given % loss in weight as moisture and volatile matter (AOAC 1995).

4.2.4.3. Free-fatty Acid Content

The amount of free fatty acids were determined by simple titration using AOAC 940.28 method (1995). Few drops of the sunflower oil and 2 ml phenolphthalein were added to 50ml alcohol in clean, dry flask. Then flask was placed in H_2O at 60-65°C until warm and titrated with enough 0.1N NaOH to produce faint permanent pink. 56.4g oil was weighed into the neutralized alcohol and titrated with 0.1N NaOH. Mixture was shaked until same faint permanent pink appears in supernate alcohol. Reported as;

Free-fatty acid (as oleic acid) % = mL 0.1 N NaOH*0.05

4.2.4.4. Peroxide Value Determination

Oil oxidation is determined by measuring the amount of peroxides. Peroxide value is most often expressed as milliequivalent of oxygen per kilogram of fat. Iodine is produced from potassium iodide solution by the peroxides present in oil and titrated against 0.01N sodiumthiosulfate (Patterson 1992).

Peroxide value was measured according to AOAC 965.33 method (1995). 5.00±0.05g sample was weighted into erlenmeyer. 30 ml CH_3COOH-$CHCl_3$ was added

and swirled to dissolve. 0.5 ml saturated KI solution was added and shaked for 1min. 30ml H_2O was added then slowly titrated with 0.01 N Na_2SO_3. Calculated as;

Peoxide Value = (S*N*1000) / g sample

S= mL $Na_2S_2O_3$
N= Normality $Na_2S_2O_3$ solution

4.2.4.5. Color Determination

Two methods were used for measuring colors of neutralized and bleached sunflower oil.

The instrumental color measurement was performed with UV-VIS Spectrometer (Varian Cary Bio 100) to measure light absorbance in the visible region at 455 nm.

The manual color measurement was performed with Lovibond Tintometer. Vegetable oil colour is usually measured using the Lovibond® Tintometer and reported as Lovibond units of red and yellow plus blue or neutral if used. This technique involves matching the colour of light transmitted through a specified depth of oil with the colour of light transmitted from the same source through a set of coloured glass slides. Colour reading is thus subjective and depends on the analyst's judgement as well as on the type and model of colorimeter used.

4.2.4.6. Oil Retention by Adsorbent

In the bleaching process oil retention is required to ascertain the loss of oil due to its retention in the bleaching earth. Oil retention is calculated according to equation;

$$\text{Oil retention } [\%] = \frac{W_{\text{filter cake}} - (W_{BE} - W_{H20})}{W_{\text{filter cake}}} * 100$$

W = Weight in g.
BE = Bleaching earth   (Baranowsky et al. 2001)

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Characterization Studies

5.1.1. Thermal Gravimetric Analysis (TGA)

Results of thermogravimetric analysis were given plot of sample weight (%) as a function of temperature (°C). Total amount of water lost below 850°C for each clay are given in Figure 5.1.
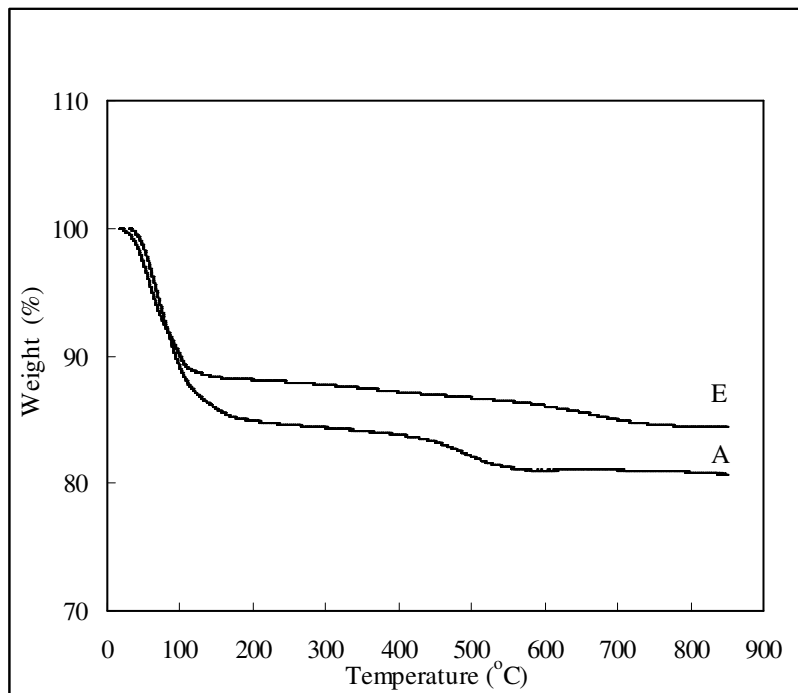

Figure 5.1. Thermogravimetry curves of natural Ankara and Eskişehir clays.

Figure 5.1 shows that weight loss in the temperature range 30° - 200°C (≈15%) was observed for Ankara clay. Higher weight loss was found as ≈11% between 30° and 100°C. Subsequently, a gradual weight loss from 200°C up to 550°C (≈ 4%) was seen. After that almost no further weight loss was observed.

For Eskişehir clay, the significant weight loss was seen as ≈10% between 20° and 100°C. Weight loss was observed to be ≈12% up to 200°C. Subsequently, a gradual

weight loss from 200°C up to 750°C (≈ 3°C) was seen. Then, it showed almost no further weight loss.

Bala et al. (2000), studied the types of water in untreated clay. According to their study, the weight losses of clays are observed with three types of water molecules; free water molecules, hydrogen-bonded water molecules and water molecules strongly coordinated to interlayer cations. Free water molecules should be removed first, and followed by hydrogen bonded/coordinated water molecules in the process of dehydration. So, the higher weight loss between 20°-100°C due to the removal of the free water molecules from the interlayer spaces and the weight loss between 100°-200°C may be due to the hydrogen-bonded and coordinated water molecules. Beyond 200°C the weight loss is due to dehydroxylation which increases with increasing temperature up to 750°C. After 750°C dehydration and dehydroxylation is completed, so weight loss is not observed. Similar tendencies were obtained in the current study.

5.1.2. X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) was applied to confirm the presence of the montmorillonite and to observe the changes in crystallinity between original samples and acid activated samples.
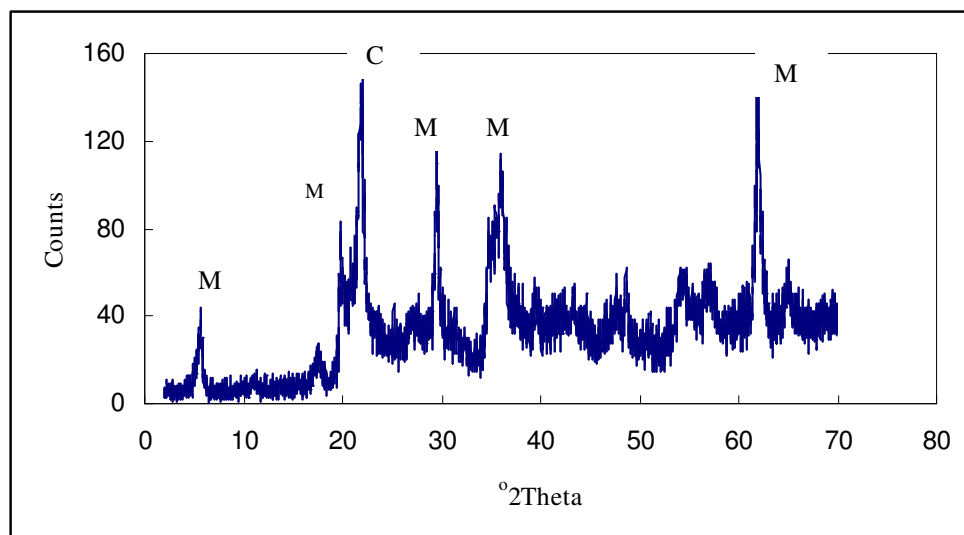

Figure 5.2. X-ray diffractogram of natural Eskişehir clay (M: Montmorillonite, C: Cristobalite low).

X-ray diffractogram of the natural form of the Eskişehir clay as shown in Figure 5.2. indicates presence of montmorillonite as the dominating mineral and also cristobalite low as contaminant. For the natural form of the Ankara clay, X-ray diffractogram as given in Figure 5.3 shows presence of montmorillonite.
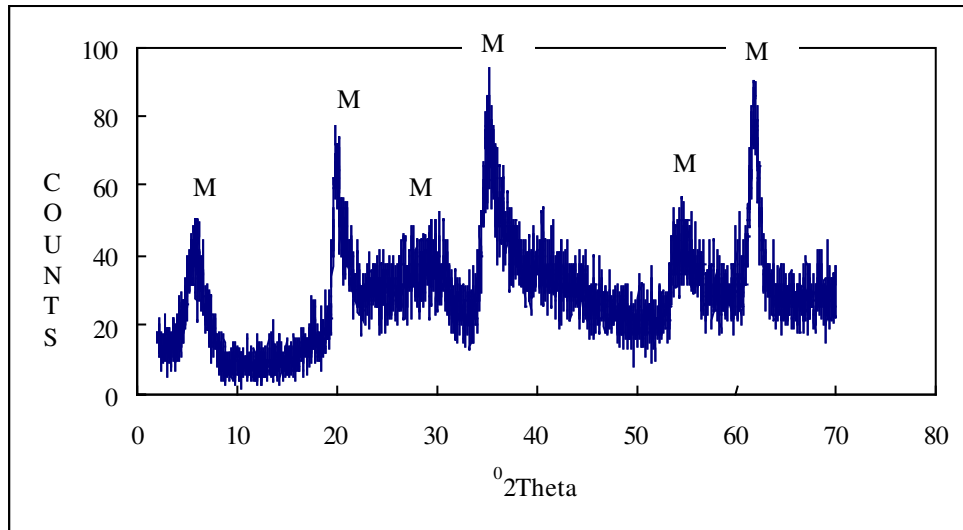

Figure 5.3. X-ray diffractogram of natural Ankara clay (M:Montmorillonite).

X-ray diffractogram of the acid activated Eskişehir and Ankara clay are represented in Figure 5.4. and 5.5, respectively. X-ray diffractogram shows that acid activation causes to change in cristallinity of montmorillonites. This was also observed by Christidis et al. (1997). As seen from the diffractogram, montmorillonite peaks started to disappear and resulted in amorphous structure of smectite. Because over-dissolving of the octahedral cations will result in decrease metal ions in the montmorillonite structure so the layered structure of the original montmorillonite will be destroyed. As a result, the activated product will be converted to an amorphous Si-rich phase or amorphous SiO_2 (Lu and Cui 2001). Also this amorphous phase will effect bleaching efficiency of montmorillonite negatively. As a result, suitable acid activation conditions should be selected to obtain effective performance.
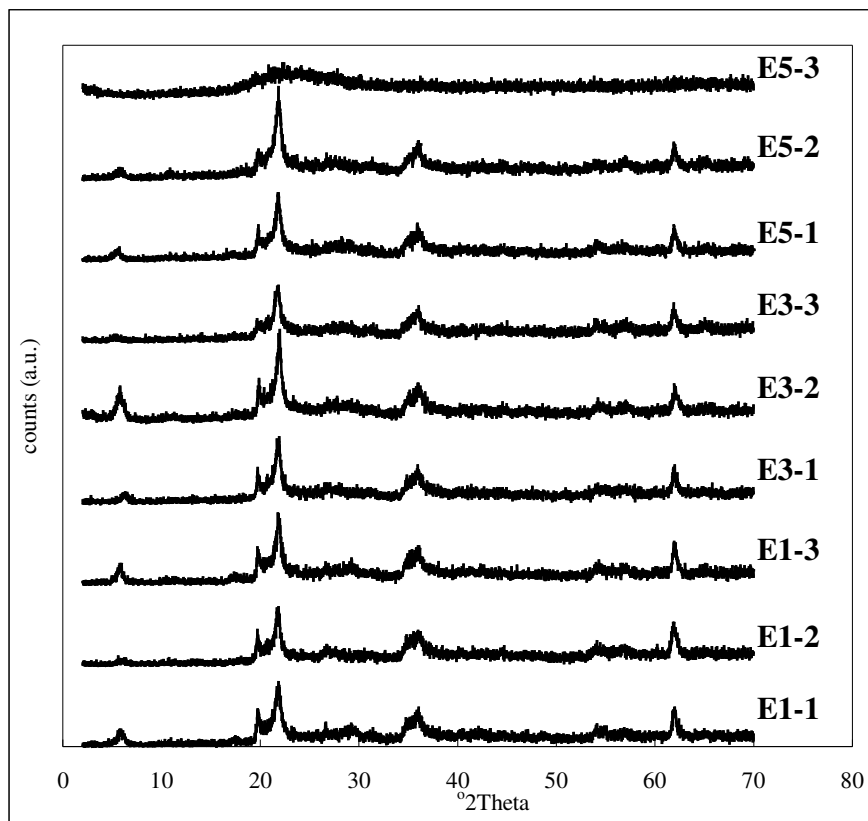
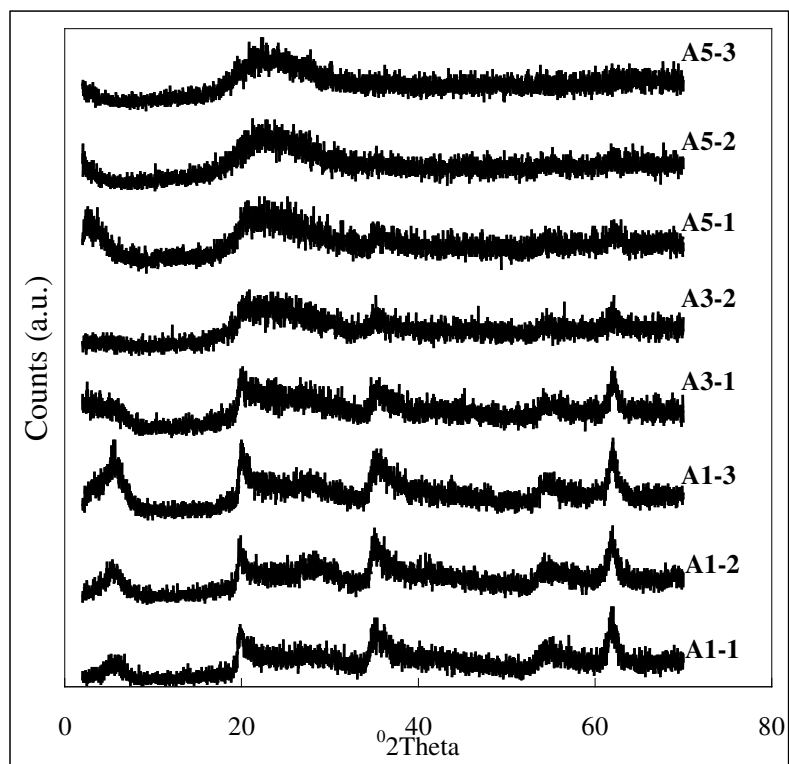Figure 5.4. X-ray diffractogram of the acid activated Eskişehir clays.

Figure 5.5. X-ray diffractogram of the acid activated Ankara clays.

5.1.3. Physical Adsorption Measurement

The nitrogen adsorption isotherms of Eskişehir and Ankara clays in natural and acid activated forms are given in Figure 5.6. and 5.7, respectively. Also, the characteristics of acid activated clay samples are given in Appendix A.1. The shapes of isotherms are of type II according to the IUPAC classification. As seen from the figure the isotherms are concave to the p/p^o (relative pressure) axis at low relative pressure, then almost linear and finally convex to the axis.

Figure 5.6. Nitrogen adsorption isotherms of the natural and representative acid activated Eskişehir clays and Tonsil (T).

From the Figure 5.6, the increase in the N_2 amount adsorbed with increasing acid concentration can be seen. The acid treated clay (E5-1) having the higher surface area than Tonsil was obtained. The BET surface area of Eskişehir clay (E5-1) and Tonsil (T) were found as $269.67 m^2/g$ and $242.07 m^2/g$, respectively.

The N_2 amount adsorbed by Ankara clay are significantly higher than that of Eskişehir clay. With acid activation of Ankara clay, the N_2 amount adsorbed increases with increasing treatment time.
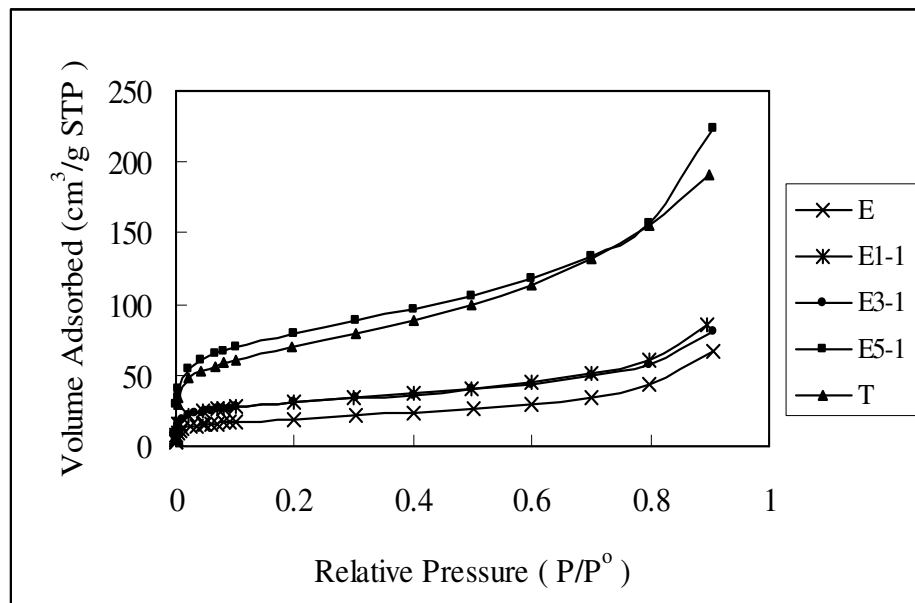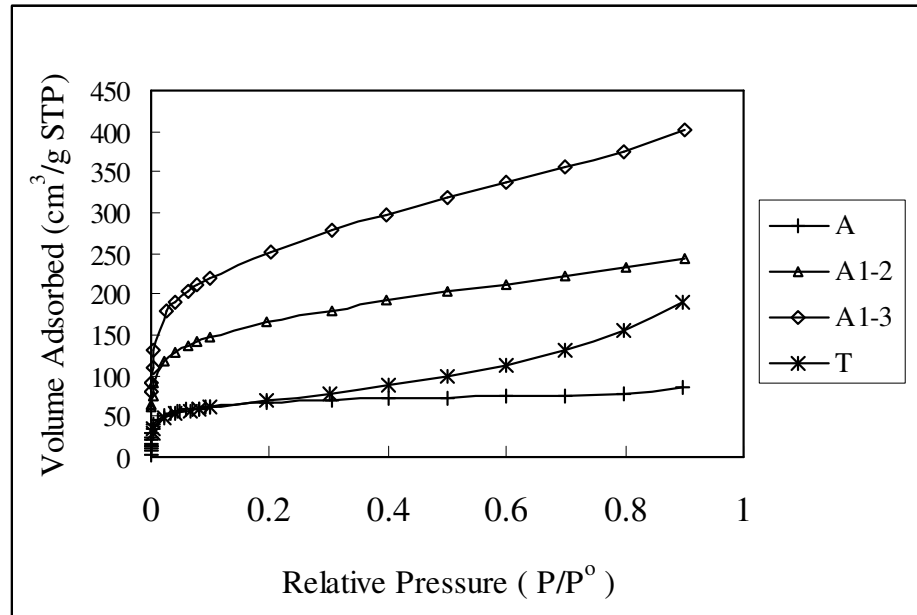
Figure 5.7. Nitrogen adsorption isotherms of the natural and representative acid activated Ankara clays and Tonsil (T).

The surface area was calculated by using the adsorption data in a relative pressure (p/p°) range from 0.05 to 0.20. The surface area calculated for Eskişehir and Ankara clays in natural and acid activated forms are given in Figure 5.8. and 5.9, respectively.

Surface area of acid activated Eskişehir clay was increased by time for 1 N and 3 N HCl treatment. Maximum point was reached at 5 N 1h HCl (E5-1) treatment then surface area decreased with increasing time. Maximum surface area was determined to be 269.67 m^2/g. For bleaching of sunflower oil, three different acid activated clays (E1-1, E3-1 and E5-1) were selected as adsorbents used in bleaching of sunflower oil to compare their bleaching efficieny with acid activated bleaching clay, Tonsil.
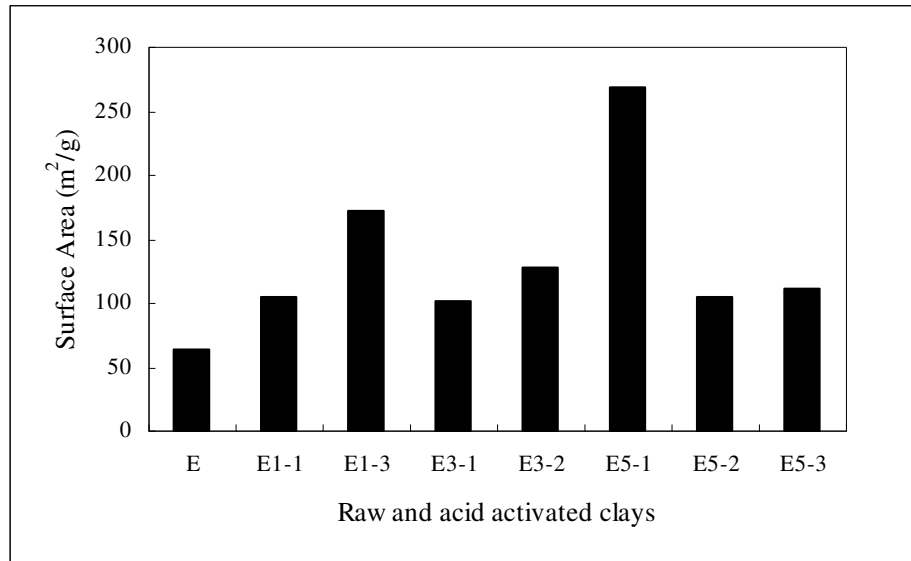
Figure 5.8. Surface area of raw and acid activated Eskişehir clay.
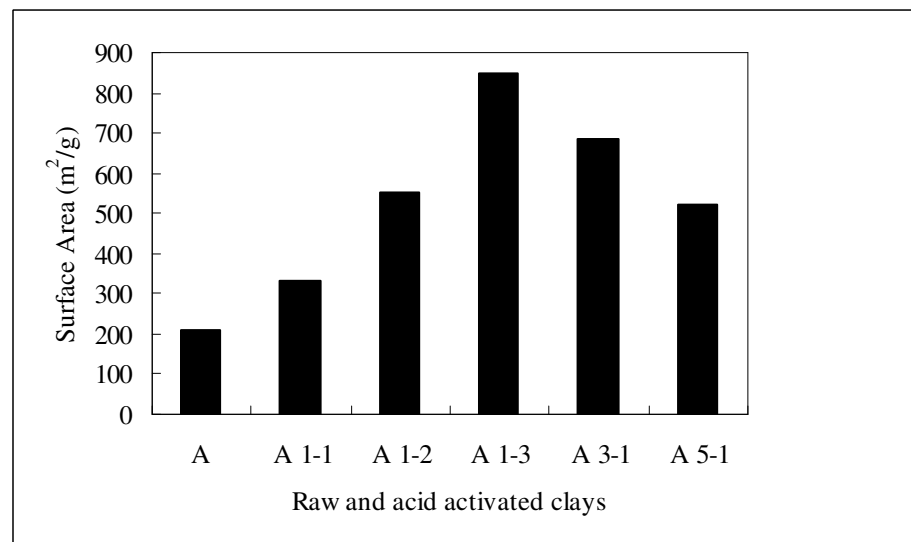
Figure 5.9. Surface area of raw and acid activated Ankara clay.

Surface area of acid activated Ankara clay increased with increasing time for 1N HCl treatment. Maximum surface area was achieved at acid treatment with 1 N HCl concentration for 3 hours treatment (A1-3) and was determined to be 849.09 m^2/g. Then surface area of it decreased with increasing acid concentration. According to the results of the surface area, two kinds of acid activated clays (A1-2 and A1-3) were selected as adsorbents used in bleaching of sunflower oil to compare their bleaching efficieny with Tonsil.

**5.1.4. Scanning Electron Microscopy and Energy Dispersive X-ray Analysis**

Scanning electron microscope (SEM) was used to take the microphotographs of the surface feature of clay samples. SEM microphotographs of natural form of the Eskişehir and Ankara clay samples are given in Figure 5.10. and 5.11, respectively.

Figure 5.10. SEM microphotograph of natural form of the Eskişehir clay.

Figure 5.11. SEM microphotograph of natural form of the Ankara clay.

Element distributions were taken in order to get information about the main elements in the different layers and then element forms were transfo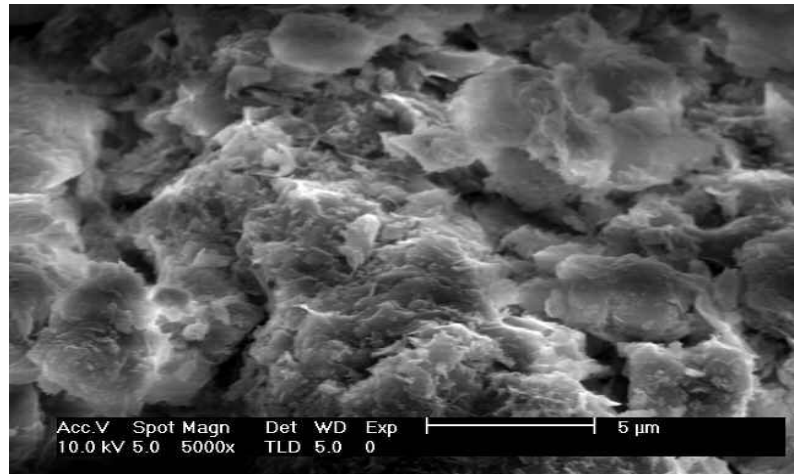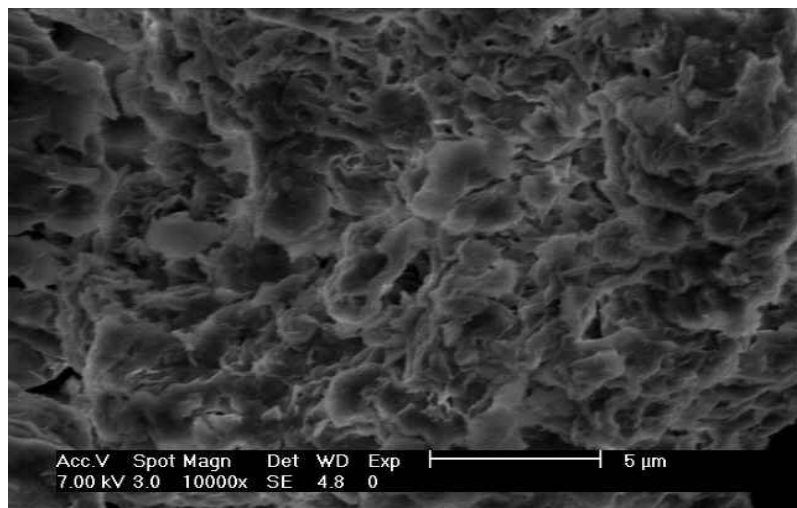rmed to oxide forms. As a result, SiO_2/Al_2O_3 ratio increases with increasing the period of time and acid concentration. Oxide forms of Si^{+4} and Al^{+3} cations of raw and acid activated Eskişehir and Ankara clay samples are represented in Table 5.1. and 5.2, respectively

Table 5.1. Chemical composition of raw and acid activated Eskişehir clays.

Oxides (wt%)	E	E1-1	E3-1	E5-1
SiO_2	77.3±4	81.5±0.1	82.9±1.5	84.7±1.2
Al_2O_3	12.8±1.4	12.6±0.3	12.0±0.6	11.3±0.5
SiO_2 /Al_2O_3	6.0	6.5	6.9	7.5

SiO_2/Al_2O_3 ratio was 6.0 for raw Eskişehir clay and increased to 6.5, 6.9 and 7.5 by treating the clay with 1 N, 3 N and 5 N HCl for 1 hour, respectively.

Table 5.2. Chemical composition of raw and acid activated Ankara clays.

Oxides (wt%)	A	A1-2	A1-3
SiO_2	65.2±0.6	74.5±0.9	74.9±0.9
Al_2O_3	24.2±0.5	19.7±0.7	19.4±0.7
SiO_2 /Al_2O_3	2.7	3.8	3.9

SiO_2/Al_2O_3 ratio was 2.70 for raw Ankara clay. Then, this ratio increased to 3.8 and 3.9 for 2 hours and 3 hours treatment with 1 N acid concentration, respectively.

Table 5.3. Chemical composition of acid activated Zeolite and commercially activated bleaching clay,Tonsil.

Oxides (wt%)	Tonsil	Zeolite
SiO_2	77.34±1.7	86.54±0.6
Al_2O_3	16.89±1.6	9.59±0.5
SiO_2 / Al_2O_3	4.58	9.02

As given in Table 5.3, SiO_2/Al_2O_3 ratio was observed 4.58 for commercially activated bleaching clay, Tonsil, and 9.02 for acid activated zeolite treated with 2N HNO_3 for 6h. SiO_2/Al_2O_3 ratio of Zeolite was found as 9.02 which is higher than the clay samples. It can be said that dissolving ratio of Al^{+3} cation from zeolite layers were higher than the clays with acid activation.

5.1.5. Determination of the Chemical Composition by ICP-AES

Chemical composition of the natural forms of the Ankara and Eskişehir clays were analyzed with ICP-AES. Element contents are given in Table 5.4.

Table 5.4. Chemical compositions of the Ankara and Eskişehir clay.

Oxides (wt%)	E	A
SiO_2	61.91	59.05
Al_2O_3	12.52	17.25
CaO	4.13	1.72
Na_2O	0.82	1.60
MgO	4.70	4.80
Fe_2O_3	7.00	6.24
K_2O	0.95	1.22

Acid activated clay suspension was washed by decantation with deionized water until it is Cl^- free (pH 3.5 - 4.0) and ICP was applied to first washing water of acid activated clay. The removal percentage of cations for Eskişehir and Ankara clays after activation are tabulated in Table 5.5. and 5.6, respectively. According to the ICP results for Eskişehir clay, the dissolving ratio of Ca^+, Na^+, Mg^{2+}, K^+, Fe^{3+} and Al^{3+} increases along with increasing of acid concentration. This case was observed with increasing the time for Ankara clay. Thus, the Si^{4+} content and the Si/Al ratio increased in the acid activated montmorillonites. Dissolving ratio of these metal cations are important and will be controlled to obtain high bleaching performance.

Table 5.5. The removal percentage of cations for Eskişehir clay after acid activation.

Cations (w/w%)	E1-1	E3-1	E5-1
Si	0.62	0.59	0.52
Al	16.9	23.97	33.42
Ca	80.87	88.24	101.02
Na	3.22	3.27	3.29
Mg	18.5	19.00	20.03
Fe	2.37	2.40	3.24
K	4.2	5.35	6.51

Table 5.6. The removal percentage of cations for Ankara clay after acid activation.

Cations (w/w%)	A1-2	A1-3
Si	0.57	0.53
Al	18.11	19.88
Ca	92.57	94.52
Na	2.17	2.41
Mg	20.51	20.60
Fe	12.17	12.75
K	16.81	17.81

Ca^{2+} is the most readily removed cation at low acid concentration among the cations. Because the element is present in the interlayered area and displaced by H^+ easily while Mg^{2+}, Fe^{3+} and Al^{3+} are settled in the octahedral area of montmorillonite which are dissolved with difficulty (Lu and Cui 2001).

5.2. Bleaching of Sunflower Oil

Generally the bleaching process uses bleaching earth at temperatures of 80-120°C for 15-30 minutes under vacuum (Baranowskyet al. 2001). The dosage of bleaching earths can vary between 0.5-2% on a weight basis depending on the oil type (Valenzulela Diaz and Souza Santos 2001). In this study, the bleaching experiments were done at 15 and 30 minutes contact time, 0, 0.5, 1, 1.5 % earth concentrations on a

weight basis and 100°C contact temperature at the laboratory conditions to observe color, peroxide value, free-fatty acid content and oil retention of bleached oil. The results were compared with bleaching efficiency of Tonsil. Characteristics of commercial and neutralized sunflower oil are given in Appendix A.2.
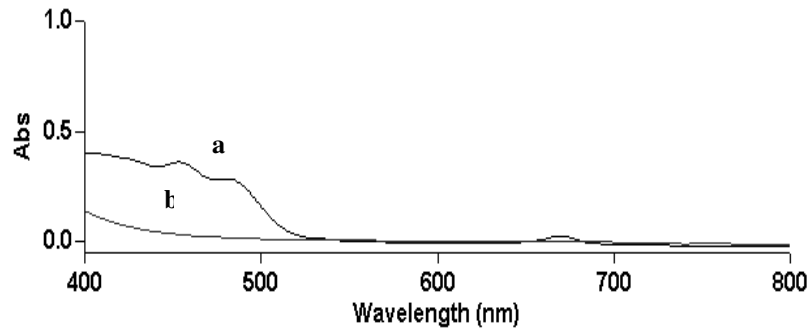

Figure 5.12. UV absorbance spectra of neutralized (a) and treated sunflower oil (b).

Visible absorption spectra of neutralized oil was recorded in the wavelength region between 400 and 800 nm. The absorption spectrum of neutralized oil gave a maximum at 455nm with two shoulders at 455 and 483 nm. These peaks were disappeared with treated of sunflower oil as seen in Figure 5.12.

Absorbance value of the neutralized sunflower oil was found 0.4290 at 455nm. Peroxide value and free-fatty acid content were found 16.8 meq/kg and 0.07%, respectively. When alkali-neutralized sunflower oil was kept at 100°C bleaching temperature, 15 and 30 minutes contact time without any acid activated clays, absorbance value increased from 0.422 to 0.442 and peroxide value also increased from 41.2 to 43.7 meq/kg with increasing contact time. Color value and peroxide value of oil were affected with increasing contact time inversely. As a result, clay is needed to achieve desired color and also peroxides and hydroperoxides are decomposed with acid activated clay and this catalytic activity reduces the peroxide value (Patterson 1992 and Nkpa et al. 1989).

As seen in Figure 5.13 and 5.14, absorbance value of oil bleached with Ankara clay decreased with increasing earth concentration. There were no obvious changes with increasing bleaching time. Maximum surface area of Ankara clay (A1-3) also affected this value positively according to 1 N 2h HCl treatment (A1-2). Absorbance value was

observed as 0.230 (0.5% earth concentration at 15 min. contact time) at the begining then decreased to 0.094 (1.5% earth concentration at 30 min. contact time).

With respect to the neutralized oil, bleached oil with acid activated Ankara clay had a peroxide value 46.2 meq/kg first, then decreased to 22.4 meq/kg with 1 N 3h HCl treatment clay (1.5% earth concentration at 30 min. contact times). There were no obvious changes with increasing time. However, decreasing of this value was observed in Figure 5.15. and 5.16. when the earth concentration increased (from 0.5% to 1.5). Because acid bleaching clays are able to decompose some of the oxidation products such as peroxides and this products are removed with bleaching process (Baranowsky et al. 2001). Thus, peroxide value of oil decreases.

Besides, there were no obvious changes for free-fatty acid contents. These value approximately observed around 0.08 %. However, with respect to the free-fatty acid content of neutralized oil, this value increased. An increase in clay dosages lead to an increase in free-fatty acid. Because the acidity of the surface activity of clays will increase with increasing treatment time. (Nkpa et al. 1989). As shown in Figure 5.17 and 5.18, this value increased with increasing time from 15 minutes to 30 minutes with increasing clay dosage from 0.5 % to 1.5 % .

Figure 5.13. Absorbance value of bleached oil with acid activated Ankara clay (A1-2).
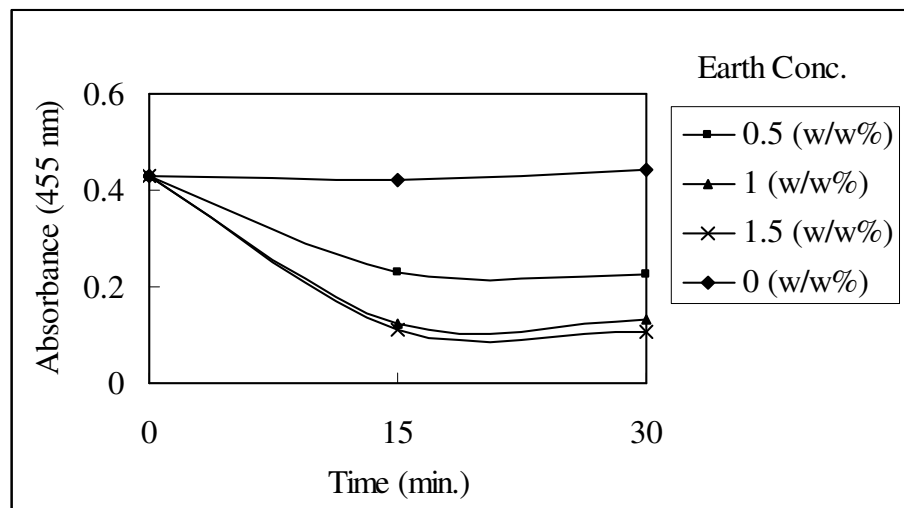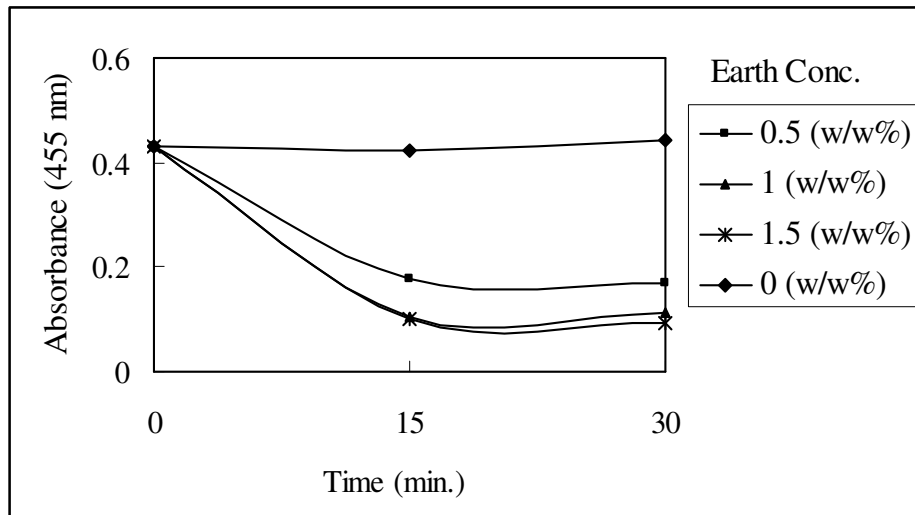
Figure 5.14. Absorbance value of bleached oil with acid activated Ankara clay (A1-3).
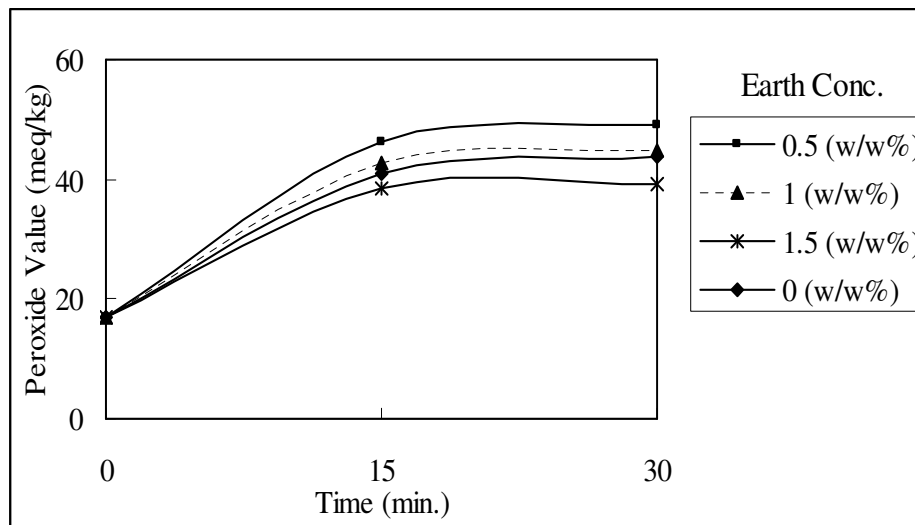

Figure 5.15. Peroxide value of bleached oil with acid activated Ankara clay (A1-2).
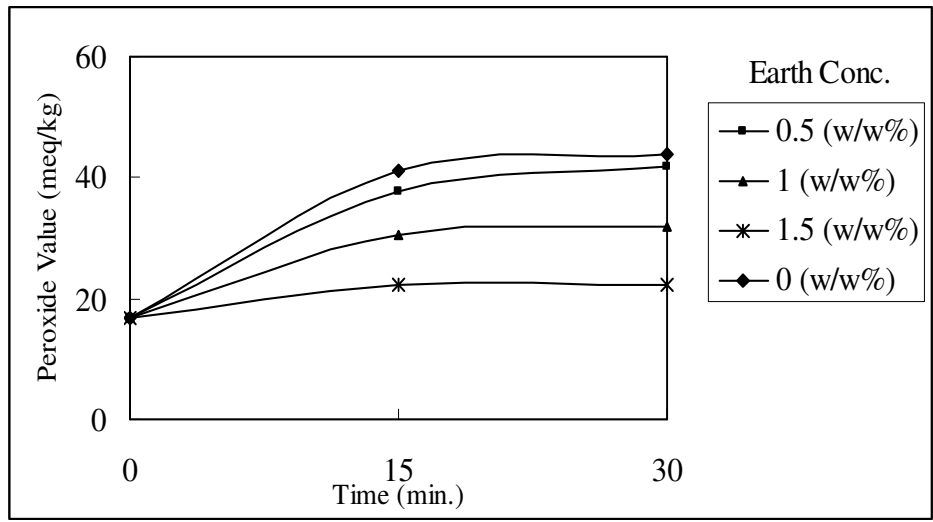
Figure 5.16. Peroxide value of bleached oil with acid activated Ankara clay (A1-3).
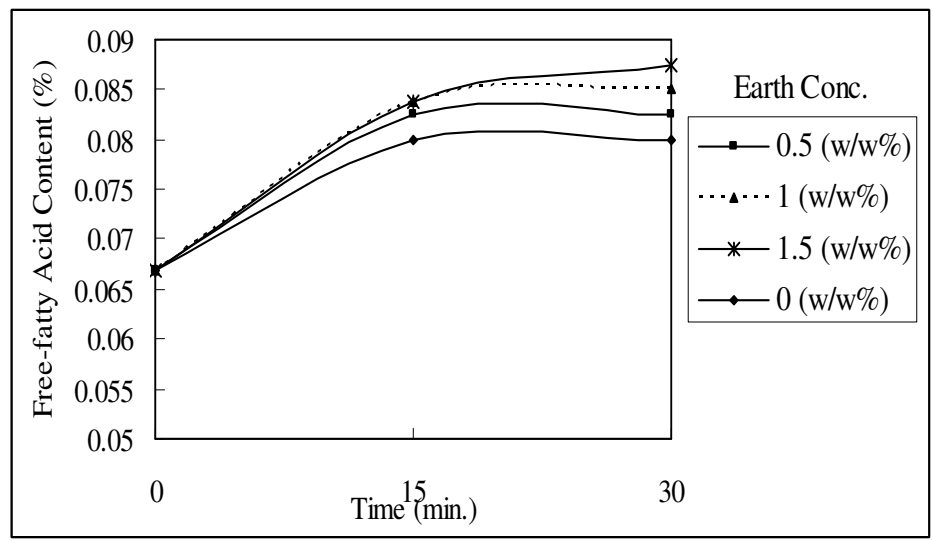

Figure 5.17. Free-fatty acid content of bleached oil with acid activated Ankara clay (A1-2).
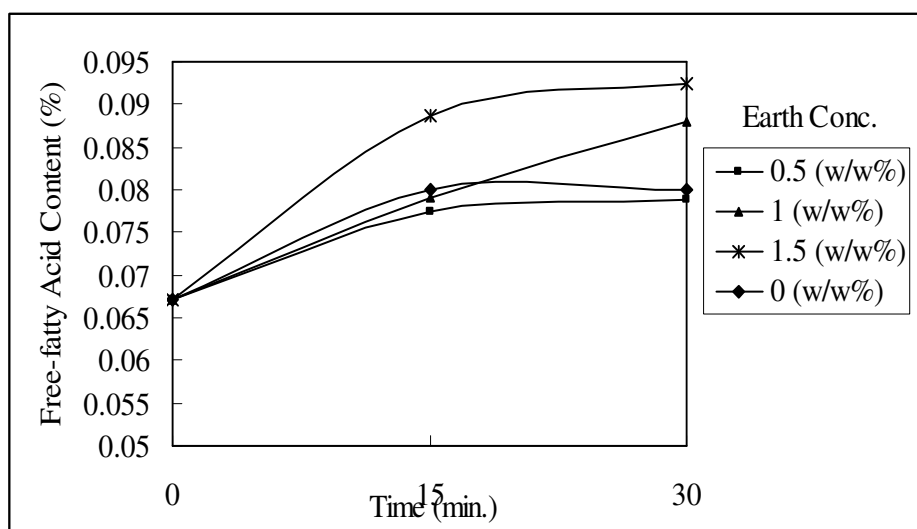
Figure 5.18. Free-fatty acid content of bleached oil with acid activated Ankara clay (A1-3).

As seen in Figure 5.19, 5.20. and 5.21, absorbance value of oil bleached with the acid activated Eskişehir clay with 15 minutes contact time decreased for all kinds of clay (1 N, 3 N, 5 N HCl treatment) but after 1 % clay concentration and 30 minutes contact time it started to increase again for each clay. Maximum absorbance value (0.084) was achieved with maximum surface area of Eskişehir clay with 5 N 1h HCl treatment.

Bleached oil with acid activated Eskişehir clay had a peroxide value 31.2 meq/kg first, then decreased to 3.7 meq/kg which was below peroxide value of neutralized oil (16.8 meq/kg). Decreasing of this value was observed in Figure 5.22, 5.23 and 5.24, when the earth concentration and time increased for all kinds clay (1 N, 3 N, 5 N HCl treatment) because of decomposing some of the oxidation products and removing with bleaching process (Baranowsky et al. 2001). Increasing earth concentration was observed to affect than increasing bleaching time to reduce peroxide value of bleached oil.

Free-fatty acid contents of bleached oil approximately observed around 0.09 %. There were no obvious changes between the bleaching conditions. However, according to the free-fatty acid content of neutralized oil, this value increased from 0.07 to 0.09 % due to increasing in clay dosages leading to an increase in free-fatty acid (Nkpa et al. 1989). With increasing earth concentration from 0.5% to 1.5%, free-fatty acid increased continuously. Free-fatty acid content of bleached oil with acid activated Eskişehir clay is represented in Figure 5.25, 5.26. and 5.27.

Figure 5.19. Absorbance value of bleached oil with acid activated Eskişehir clay (E1-1).

Figure 5.20. Absorbance value of bleached oil with acid activated Eskişehir clay (E3-1).

Figure 5.21. Absorbance value of bleached oil with acid activated Eskişehir Clay (E5-1).

Figure 5.22. Peroxide value of bleached oil with acid activated Eskişehir clay (E1-1).
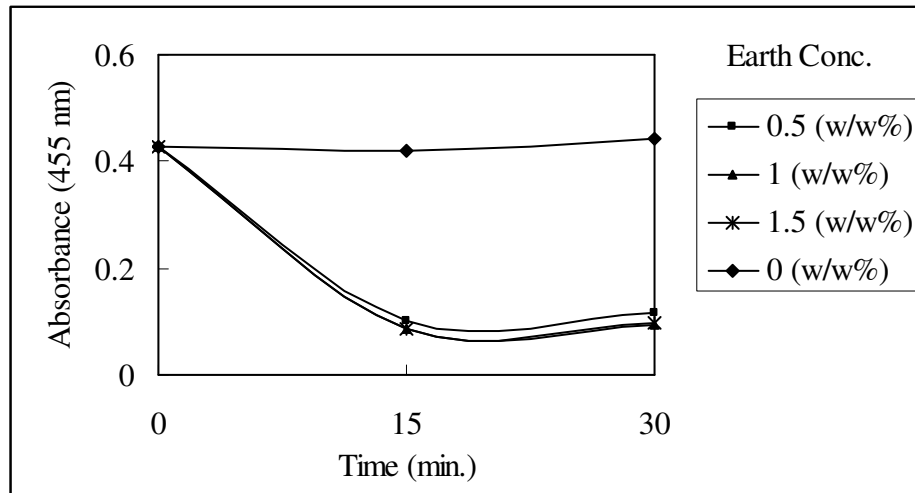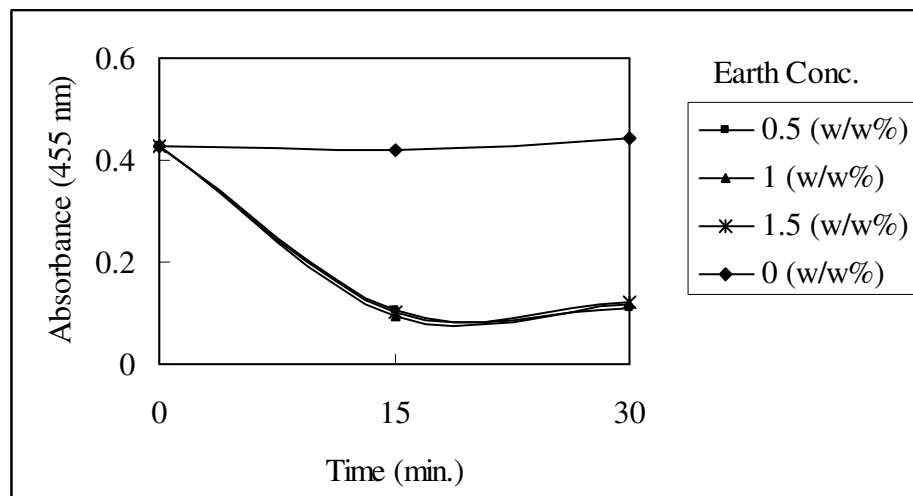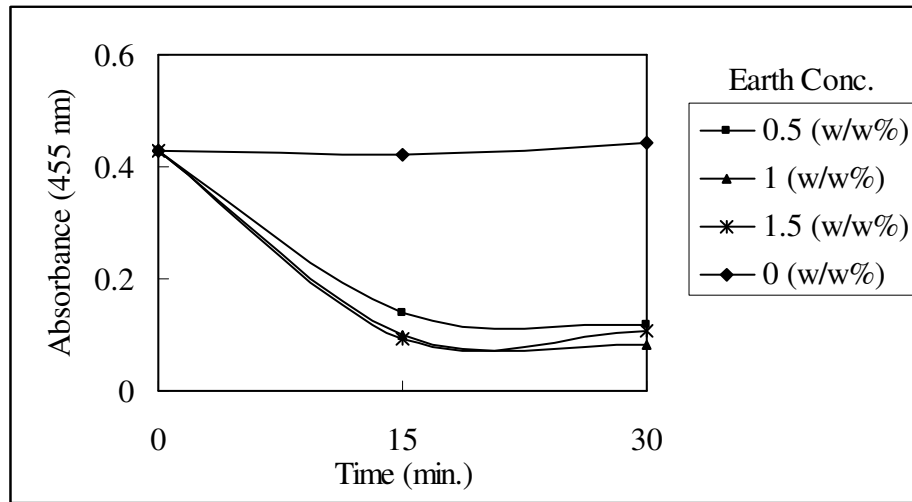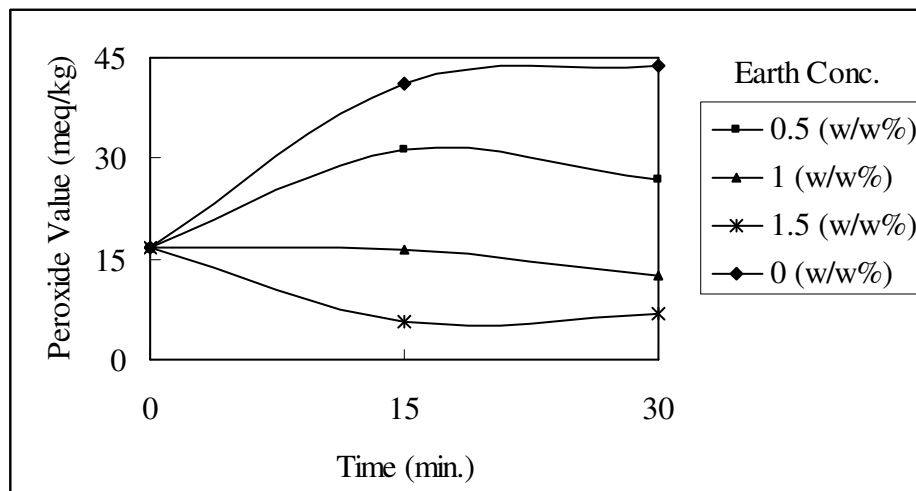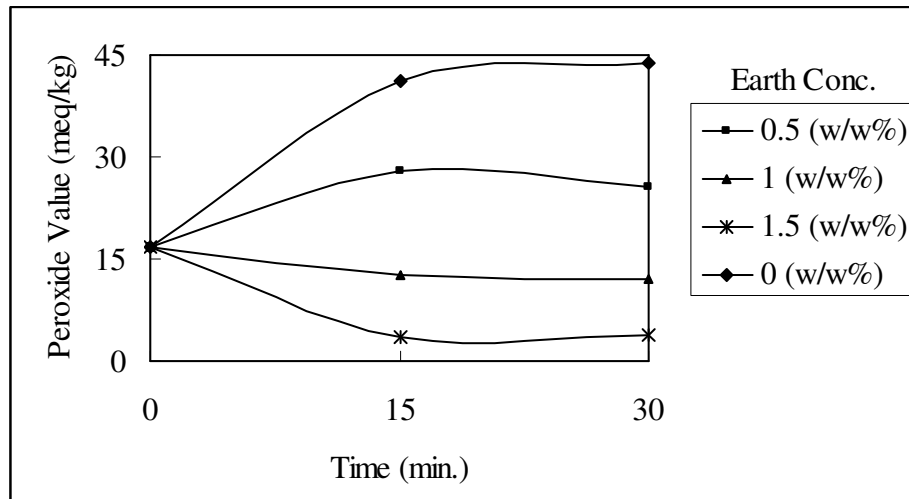
Figure 5.23. Peroxide value of bleached oil with acid activated Eskişehir clay (E3-1).
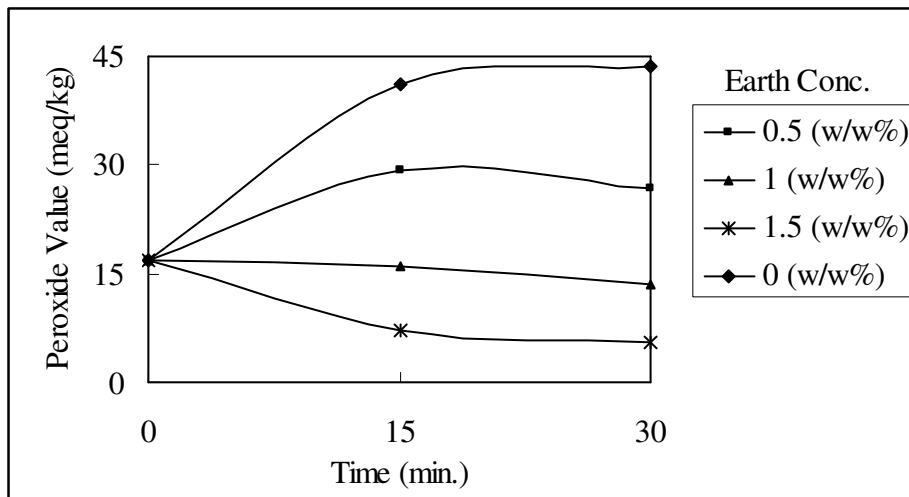
Figure 5.24. Peroxide value of bleached oil with acid activated Eskişehir clay (E5-1).
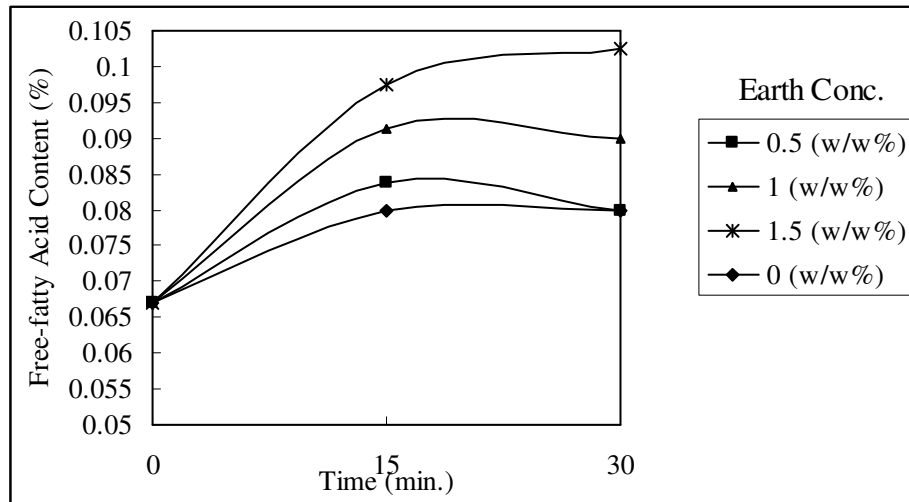
Figure 5.25. Free-fatty acid content of bleached oil with acid activated Eskişehir clay (E1-1).
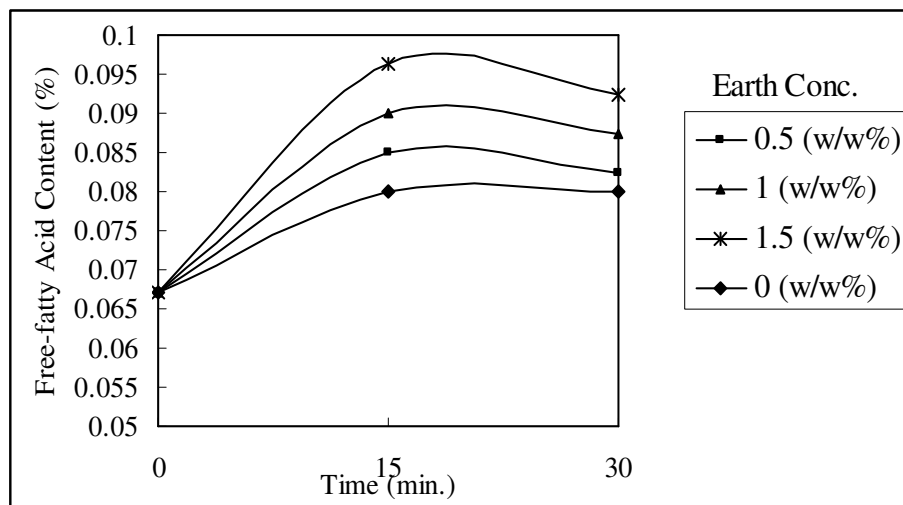
Figure 5.26. Free-fatty acid content of bleached oil with acid activated Eskişehir clay (E3-1).
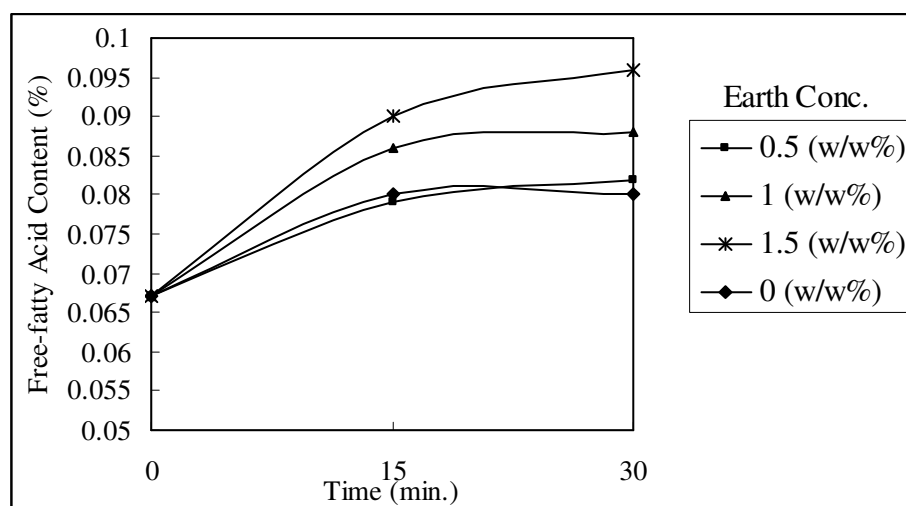
Figure 5.27. Free-fatty acid content of bleached oil with acid activated Eskişehir clay (E5-1).

The smallest value of absorbance was found 0.084 with Eskişehir clay and obtained with 1% earth concentration and 30 minutes contact time and this value was found 0.083 with Tonsil at the same conditions.

New color formation occurs by continuing oxidation and color increases by oxidation of pigments and due to stabilization of these oxidized pigments, adsorption of pigments prevented (Mounts 1981). Bleaching earths can catalyze these oxidation reaction. As a result, absorbance value starts to increase. It was observed in bleaching process treated with 1.5 % earth concentration for Eskişehir clay in this study.

Clays can adsorb peroxide and catalyze peroxide degradation into secondary oxidation products and also can adsorb oxidation products depending on clay concentration (Rossi et al. 2003). Bleaching to a normal color level reduces the peroxides and remaining peroxide decomposition products are removed by deodorization process. In this study, peroxide value were decreased with an increasing earth concentration. Minimum peroxide value was obtained 3.74 meq/kg with Eskişehir clay.

Bleaching earths are produced from acid activation of montmorillonite and the acidity of clay surface contributes free-fatty acid formation (Morgan et al. 1985). So, a rise in free-fatty acid occured due to acid activated clay. Those activated earths will produce or no change in the free-fatty acid content of the neutralized oil. Some of them may add 0.05-0.1 % to the free-fatty acid content (Mounts 1981). In this study free-fatty

acid content observed maximum around 0.09 % and as to the free-fatty acid content of neutralized oil, this value increased maximum 0.02 % value.

As bleaching parameters, 1 % earth concentration, 30 minutes contact time at 100 °C bleaching temperature were selected. At this selected point, Eskişehir clay, Ankara clay and zeolite were compared with Tonsil. Absorbance values of these minerals are given in Figure 5.30.

In this study, zeolite activated 2 M HNO_3 was tried to see their bleaching performance. At this activated point, zeolite showed maximum surface area.
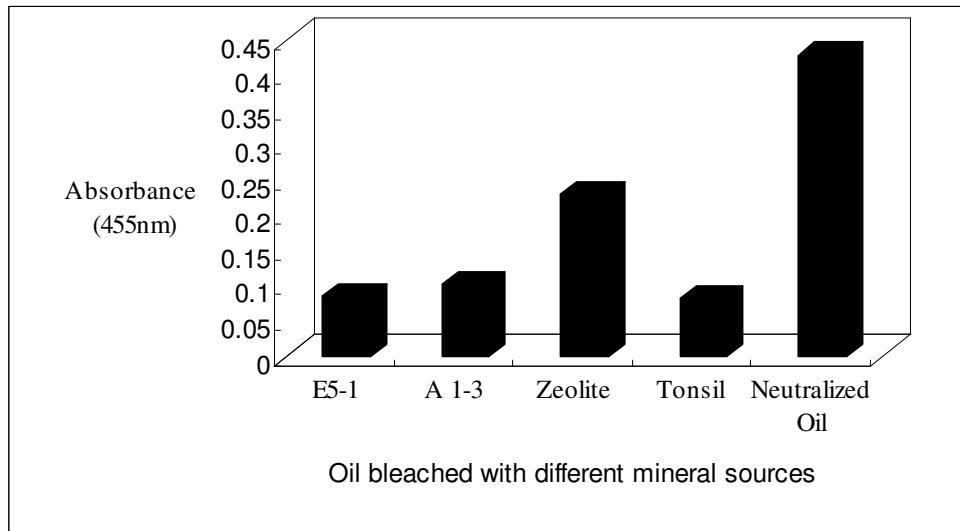
Figure 5.28. Absorbance value of bleached oil at selected point [(100°C, 30min., 1 (w/w%)]. Zeolite : acid activated with 2N HNO_3 at 6h, 60°C.

As a result, Eskişehir clay, Ankara clay, Tonsil and Zeolite was used to select suitable earth for bleaching of sunflower oil. Between different clays from different regions and zeolite as to reference earth (Tonsil), Eskişehir clay was selected due to its high bleaching efficiency. Absorbance value of Eskişehir clay and Tonsil showed approximately same value and their bleaching efficiency 80 % and 81 % respectively. The characteristics of bleached oils are given in Appendix A.3.

Bleaching efficieny was calculated by the following formula (Srasra et al. 1989) ;

$$\text{Bleaching efficieny [\%]} = \frac{A^o_\lambda(\text{neutral oil}) - A_\lambda(\text{treated oil})}{A^o_\lambda(\text{neutral oil})} *100$$

Where A is the absorbance value at wavelength λ, 455 nm for pigment uptake.

At selected bleaching point, lovibond red and yellow color of bleached oil indicated that Eskişehir clay and Tonsil were close to each other as bleaching performance. In American trading rules, maximum red color of bleached sunflower oil is 2.5 and maximum yellow color of bleached color is 25 (Rossell 1991). In this study, all of them, except zeolite showed under 2.5 red and 25 yellow color value.

Acid activated zeolite did not reach required bleaching efficiency. Its bleaching efficiency was found as 46 % and this value was 25 % with raw zeolite. In addition, red and yellow color were higher than the other earths as shown in Table 5.7.

Table 5.7. Lovibond red and yellow color of bleached oil at selected point [(100°C, 30 min., 1 (w/w %)] and neutralized, bleached & edible oils.

	Values of Lovibond Red & Yellow Color	
	Red Color	Yellow Color
Neutralized oil	3.1	40
Treated oil with E5-1	1.1	20
Treated oil with A1-3	2	12
Treated oil with Tonsil	0.8	20
Treated oil with Zeolite*	2.6	30
Refined, Bleached & Deodorized oil	0.9	10

*Zeolite : acid activated with 2N HNO$_3$ at 6h, 60°C.

The removal of color pigment is needed to obtain an acceptable finished edible oil. For this reason, the color pigments are removed at different steps in the conventional oil process. Especially during bleaching step, maximum reduction occur (85%) and then remaining thermally degradable color pigments are removed in the subsequent deodorization step due to high temperature processing (Subramanian 2001). Deodorization is the last step to improve the color, taste and the stability of the oil with the removal of undesirable substances. Lovibond results of deodorized oil 0.9 and 10 for red and yellow color, respectively and these value were lower than bleached oil because remaining color pigments from bleaching process are removed by deodorization step. Also remaining peroxide decomposition products are removed by this process that is, zero peroxide value is obtained (Mounts 1981).

Table 5.8. Oil retention values of representative acid activated clay samples and Zeolite.

Sources	*Oil Retention %
A1-3	52
E5-1	63
Tonsil	60
Zeolite	59

$$*\text{Oil retention} [\%] = \frac{W_{filter\ cake} - (W_{BE} - W_{H20})}{W_{filter\ cake}} * 100$$

W = Weight in g.

BE = Bleaching earth   (Baranowsky et al. 2001)

In the industrial bleaching process, the retention of oil is in the range of 30-70% of the weight of the activated clay (Subramanian 2001). Generally, oil lost to filter cake results oil loss in the bleaching process (Bera et al. 2004). As shown in Table 5.8, oil retention of Ankara and Eskişehir clay, Tonsil and Zeolite displayed in the range of 30-70% and oil loss of Ankara clay was lower than the others. This means that for each 100 kg of fresh bleaching earth 52 kg of oil are lost.

As a result, Eskişehir clay gave better decolorization effects according to Ankara clay and Zeolite. Maximum bleaching efficiency was achieved after 30 minutes contact time with 1 % earth concentration at 100°C bleaching temperature with 5 N 1h HCl treatment for Eskişehir clay.

CHAPTER 6

CONCLUSIONS

In this study, two clay samples from different regions (Eskişehir and Ankara) were used as adsorbent for bleaching of sunflower oil. Characterization studies were applied to determine structure and chemical composition of clay samples also to see changes after acid activation. Besides clay samples, acid activated zeolite also used as adsorbent for bleaching process.

By acid activation, partial dissolution of the raw materials occurred with mineral acid (HCl) and resulted in protonated clays and amorphous silica phases. This treatment provided an increase in surface area, porosity and acidity of the clays. Surface area of clays increased until maximum surface area was obtained and then decreased with increasing intensity of acid treatment. The chemical compositions of the solutions and clays after acid activation were determined using ICP and EDX analysis, respectively. According to the results, the SiO_2 content and the SiO_2/Al_2O_3 ratio increased with increase in acid concentration for the Eskişehir clay and with increasing treatment time for the Ankara clay. This ratio increased from 6.0 to 7.5 for acid activated Eskişehir clay, from 2.7 to 3.9 for acid activated Ankara clay.

Color, free-fatty acid content and peroxide value of bleached oil and oil retention by bleaching earths were determined to see oil quality after bleaching process. The peroxide value decreased with increasing catalytic activity of the bleaching earth. However, there were no obvious changes for free-fatty acid contents. Increase in clay dosage affected the peroxide value and free-fatty acid content of oil more than increasing treatment time of the bleaching process. According to resuts of oil analysis, 1% earth concentration and 30 minutes contact time at 100 °C bleaching temperature were selected among bleaching parameters,

The acid activated Eskişehir clay showed higher bleaching efficiency eventhough the acid activated Ankara clay had a higher surface area. The smallest absorbance value was found to be 0.084 with the acid activated Eskişehir clay and 0.083 with Tonsil at the same conditions. Bleaching efficiency was determined as 80 % and 81% for the acid activated Eskişehir and Tonsil samples, respectively. The absorbance value of bleached oil with acid activated Ankara clay was determined as 0.114 and its

bleaching efficiency was 73% at selected bleaching parameters. Bleaching efficiency of the acid activated Ankara clay was obtained to be lower compared to the Eskişehir sample.

Red and yellow color values of bleached oil with Eskişehir clay (5 N 1h HCl treatment) and Tonsil were determined to be close to each other. Red color values of bleached oil were 0.8 with Tonsil and 1.1 with Eskişehir clay. Their yellow color values were the same at 20. Red and yellow color values of the oil bleached with the Ankara clay (1 N 3h HCl treatment) were found to be 2 and 12, respectively. Red value of bleached oil with acid activated Ankara clay was higher than the others. However, this value is below the maximum set by the American trading rules (maximum 2.5 red).

The acid activated zeolite did not provide the required bleaching efficiency. Its bleaching efficiency was found to be 46 %, which was 25 % with the crude zeolite. In addition, results of red and yellow color values were higher than the other earths.

As a result, Eskişehir and Ankara clays can be used as bleaching earths, Eskişehir clay providing a better decolorization effects compared to the Ankara clay and Zeolite. Maximum bleaching efficiency was achieved after a contact time 30 minutes with 1 % earth concentration at 100°C bleaching temperature following 5 N 1h HCl treatment for Eskişehir clay.

As a result, bentonitic earths can be evaluated as adsorbent for using in bleaching of sunflower oil beside Tonsil in domestic market.

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APPENDIX

A.1. Characteristics of Acid Activated Clay Samples

Table A.1. Surface area and pore diameter of raw and acid activated Eskişehir clays.

	E	**E1-1**	**E1-3**	**E3-1**	**E3-3**	**E5-1**	**E5-2**	**E5-3**
BET surface area (m^2/g)	64.5	104.2	171.9	102.4	127.7	269.7	104.7	111.2
Langmuir Surface area (m^2/g)	90.6	148.0	243.2	145.2	181.6	379.9	148.3	156.5
Micropore area (m^2/g)	17.2	25.5	31.9	26.5	36.9	52.8	25.3	19.7
t-plot external surface area (m^2/g)	47.4	78.8	139.9	75.9	90.9	216.9	79.5	91.4
Median pore diameter (Å)	8.2	9.1	8.6	8.4	8.3	8.5	8.5	9.6

Table A.2. Surface area and pore diameter of raw and acid activated Ankara clays.

	A	A1-1	A1-2	A1-3	A3-1	A5-1
BET surface area (m^2/g)	209.7	332.5	551.0	849.1	686.5	523.4
Langmuir Surface area (m^2/g)	304.5	473.6	784.9	1246.6	955.2	728.3
Micropore area (m^2/g)	96.3	54.9	116.8	130.6	55.8	42.4
t-plot External surface area (m^2/g)	113.4	277.7	434.2	718.8	630.8	480.9
Median pore diameter (Å)	9.6	9.8	8.3	8.4	8.7	8.5

Table A.3. Surface area and pore diameter of Tonsil.

	Tonsil
BET surface area (m^2/g)	242.1
Langmuir Surface area (m^2/g)	334.3
Micropore area (m^2/g)	36.1
t-plot External surface area (m^2/g)	206.0
Median pore diameter (Å)	8.7

Table A.4. Surface area and micropore volume of acid activated Zeolite.

	Zeolite*
Langmuir surface area (m^2/g)	226
t-plot External surface area (m^2/g)	22.5
Micropore volume (cm^3/g)	0.068

*acid activated zeolite with 2 N HNO_3 at 60°C for 6 h (Becer 2003).

Table A.5. Moisture content of acid activated Eskişehir and Ankara clays.

	Moisture Content %
A1-2	14.0
A1-3	12.7
E1-1	9.3
E3-1	10.5
E5-1	10.4

A.2. Characteristics of Commercial and Neutralized Sunflower Oil

Table A.6. Characteristics of commercial (refined, bleached, deodorized and dewaxed) sunflower oil (Sontag 1979).

Moisture content %	0.10 % maximum
Free-fatty acid Content %	0.05 % maximum
Peroxide Value	2.0 meq/kg
Lovibond Red & Yellow Color	2.0 Red & 20.0 Yellow

Table A.7. Characteristics of neutralized sunflower oil before bleaching.

Moisture content %	0.03
Free-fatty acid Content %	0.07
Peroxide Value (meq/kg)	16.8
Lovibond Red & Yellow Color	3.1 Red & 40 Yellow
Spectrophotometric Color (Absorbance)	0.4290

Table A.8. Neutralized oil characteristics kept at 100°C bleaching temperature without any acid activated clays.

	Time (min.)	
	15 min.	30 min.
Free Fatty Acids (%)	0.08	0.08
Peroxide Value (meq/kg)	41.2	43.7
Spectro. Color (Abs.)	0.422	0.442

A.3. Characteristics of Bleached Oils

Table A.9. Results of bleaching experiments with 0.5 % earth concentration (w/w), at 100°C and 15 minutes.

	UV (Abs.)	Peroxide Value (meq/kg)	Free Fatty Acid %	Bleaching Efficiency %
A1-2	0.230	46.2	0.082	46
A1-3	0.175	37.7	0.078	59
E1-1	0.099	31.2	0.084	77
E3-1	0.106	27.9	0.085	75
E5-1	0.139	29.3	0.079	68

Table A.10. Results of bleaching experiments with 1 % earth concentration (w/w), at 100°C and 15 minutes.

	UV (Abs.)	Peroxide Value (meq/kg)	Free Fatty Acid %	Bleaching Efficiency %
A1-2	0.124	42.9	0.084	71
A1-3	0.104	30.6	0.079	76
E1-1	0.086	16.4	0.091	80
E3-1	0.094	12.7	0.09	78
E5-1	0.101	16.1	0.086	76

Table A.11. Results of bleaching experiments with 1.5 % earth concentration (w/w), at 100°C and 15 minutes.

	UV (Abs.)	Peroxide Value (meq/kg)	Free Fatty Acid %	Bleaching Efficiency %
A1-2	0.111	38.4	0.084	74
A1-3	0.100	22.2	0.088	77
E1-1	0.088	5.7	0.098	79
E3-1	0.100	3.5	0.096	77
E5-1	0.092	7.1	0.090	79

Table A.12. Results of bleaching experiments with 0.5 % earth concentration (w/w), at 100°C, 30 minutes.

	UV (Abs.)	Peroxide Value (meq/kg)	Free Fatty Acid %	Bleaching Efficiency %
A1-2	0.224	49.1	0.082	48
A1-3	0.168	41.9	0.079	61
E1-1	0.118	26.7	0.080	73
E3-1	0.108	25.7	0.082	75
E5-1	0.118	26.7	0.082	73

Table A.13. Results of bleaching experiments with 1 % earth concentration (w/w), at 100°C and 30 minutes.

	UV (Abs.)	Peroxide Value (meq/kg)	Free Fatty Acid %	Bleaching Efficiency %
Tonsil	0.083	10.9	0.093	81
A1-2	0.130	44.8	0.085	70
A1-3	0.114	32.0	0.088	73
E1-1	0.095	12.5	0.090	78
E3-1	0.117	12.1	0.088	73
E5-1	0.084	13.5	0.088	80
Zeolite crude	0.323	57.5	0.080	25
Zeolite 2 N (HNO_3 treated)	0.230	49.7	0.081	46

Table A.14. Results of bleaching experiments with 1.5 % earth concentration (w/w), at 100°C and 30 minutes.

	UV (Abs.)	Peroxide Value (meq/kg)	Free Fatty Acid %	Bleaching Efficiency %
A1-2	0.105	39.3	0.088	76
A1-3	0.094	22.4	0.093	78
E1-1	0.098	6.9	0.103	77
E3-1	0.120	3.7	0.093	72
E5-1	0.107	5.6	0.096	75