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SCHOOL OF CHEMICAL AND BIO-ENGINEERING

ACTIVATION OF RAW BENTONITE (AFAR REGION) USING SULFURIC ACID FOR RAPESEED AND NIGER SEED OIL BLEACHING

A Thesis in Process Engineering Stream

By Leena Shemsu

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Activation of Raw Bentonite (Afar Region) Using Sulfuric Acid for Rapeseed and Niger Seed Oil Bleaching

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This is to certify that the thesis prepared by Leena Shemsu, entitled: *Activation of Raw Bentonite (Afar Region) Using Sulfuric Acid for Rapeseed and Niger Seed Oil Bleaching* and submitted in partial fulfillment of the requirements for the degree of Masters of Science (Chemical and Bio Engineering) complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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DECLARATION

I declare that, this research work for the degree of Masters of Science at Addis Ababa institute of Technology is my own work. The work has not been presented elsewhere for assessment. Where material has been used from other sources it has been properly acknowledged / referred.

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ABSTRACT

In this study, a two-stage process was conducted. The first one was carrying out the activation process of raw bentonite at different conditions and the optimum parameter was chosen. The second process was bleaching of Niger seed oil and rapeseed oil using the chosen activated bentonite. The raw bentonite collected from Gewane in Afar region was activated by sulfuric acid and the design of various experiments in order to assess and simulate the effects of the acid activation of raw bentonite on the bleaching capacity of Niger seed oil is described.

Two key parameters of the acidic activation, namely acid concentration and activation temperature, were considered. The highest bleaching capacity was obtained around 3M acid concentration and at $90^{o}C$ *of activation temperature as optimal activation. The raw and activated bentonite at optimal condition was characterized by XRD, FTIR and SEM with EDS. The results of the XRD showed that the raw bentonite is composed of montmorillonite, quartz, muscovite, hematite, feldspar and cristobalit. X-ray and FTIR data confirmed that acid activation affects both the octahedral and the tetrahedral sheets. The results of the analysis by Energy Dispersive Spectroscopy (EDS), showed that, presence of silica, alumina and iron as major constituents, along with traces of sodium, potassium, magnesium, calcium, and titanium in the form of impurities. These exchangeable cations were removed partially by acid attack.*

Full factorial experimental design was employed to correlate the bleaching parameters (temperature, time and dosage of clay) to the percentage color reduction for Niger seed and rapeseed oil bleached. The result showed that the optimum condition for the bleaching process was a temperature of $90^{0}C$*, a period of 30 minutes and 4 % clay dosage which resulted in 94.37% bleaching of the Niger seed oil. For rapeseed oil, the maximum bleaching efficiency, which is 96.01%, was obtained at* $110\ ^{0}C$*, a time period of 45 minutes and 1% clay dosage. The experimental result was in agreement with the model prediction.*

Generally, the study has shown that the clay is a good adsorbent for the bleaching of both oils. This research has further established that acid activated bentonite has the power to remove not only pigments but also reduce the free fatty acid of unbleached oils.

Keywords: Bentonite, Acid activation, Characterization, Bleaching, Niger seed oil, Rapeseed oil

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LIST OF ACRONYMS

ABD	Apparent Bulk Density
ASTM	American Standard Test Method
CIF	Cost Insurance and Freight
CY	Calendar Year
EDS	Energy Dispersive Spectroscopy
ERCA	Ethiopian Revenues and Customs Authority
ETB	Ethiopian Birr
EUBA	European Bentonite Association
GAME	Gas Assisted Mechanical Extraction
FFA	Free Fatty Acid
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning Electron Microscopy
USD	US Dollar
VIS-UV	Visible-Ultra Violate
XRD	X-ray Diffraction

CHAPTER 1 INTRODUCTION

1.1 Background

Quality control and quality assurance testing are increasingly important at every point in the food supply chain, from manufacturing and packaging to distribution and retail sale. Vegetable oil is one of the basic food items which is consumed by almost every human being in this universe. Therefore, quality of vegetable oil is an important issue to consider in healthy life which is continually subjected to rigorous quality control and quality assurance testing.

In vegetable oil refining, there are four major steps involved which are degumming, neutralization, bleaching and deodorization. Among these steps bleaching is the very important and critical step, because it ensures the good color and odor of vegetable oil. Furthermore, appearance, taste and quality of vegetable oil are also depending on this step (*Usman et al, 2012*). And this process can be done by treatment with powdered substances called bleaching earth or bleaching clay. After heating and mixing, the bleaching clay is removed by filtration; the resultant oil is brighter, less colored and more stable.

Bleaching clay, bleaching earth, and fuller’s earth are all terms used to denote certain clay minerals that can be used in their natural or acid-activated states to clarify and reduce color intensity of fats and oils. Although there are 7 major clay groups and at least 33 different specific clay minerals, only 2, calcium montmorillonite (calcium bentonite) and a particular naturally occurring mixture of calcium montmorillonite and attapulgite called hormite, play a significant commercial role as bleaching clays (*Grimm, 1968*). However, these naturally occurring clays (raw bleaching clay), if not pretreated, are associated with poor adsorption capacity and hence low oil bleaching performance.

The adsorption capacity of bleaching clay can be enhanced by various treatment techniques. Among these techniques acid treatment is the most practiced technique in vegetable oil industries. Other techniques include alkali treatment and organic treatment, but these techniques are not effective enough for enhancing the adsorption capacity of fuller’s earth at desired level (*Kulkarni and Jatkar, 2013*). In acid treatment, normally sulfuric acid and hydrochloric acid is preferred and shows satisfactory results.

The preparation of acid-activated bentonite must be controlled in order to obtain maximum bleaching capacity (*Kirali and Laçin, 2006*). Some of important parameters which affect the treatment techniques are acid concentration, treatment time, temperature effect, Solid/liquid ratio and moisture content (*Noyan, Önal, and Sarıkaya, 2007*). And the major factors that affect the bleaching process, aside from the actual quality of incoming oil, are the conditions employed during the contact between oil and adsorbent. Assuming good quality oil (i.e., low in phospholipids, soaps, pigments and free fatty acids) and the proper choice of adsorbent, other important factors include moisture of oil, absence of air during bleaching and bleaching temperature and time.

This study will focus on the acid activation of Ethiopian bentonite and testing of its bleaching capacity for rapeseed and Niger seed oil by determining the optimal conditions. The effects of experimental conditions such as temperature, contact time and oil/activated bentonite ratio will be examined in order to get optimum experimental conditions.

1.2 Statement of the problem

Edible oil has now become an indispensable ingredient in the kitchen around the globe. The demand for edible oil is increasing with increasing world population and the improvement in buying power. But an edible oil is not just press from the seed or fruits of oil rich plant and then filled in the container. Crude vegetable oil in addition to triglycerides contains impurities like free fatty acids, phospholipids, hydroperoxides, trace metals and pigments. And these crude oil pass through a multistage treatment process that removes all undesired substances while maintaining the nutritional value and ensuring the quality and stability of the end product.

Ethiopia has a considerable potential for growing different types of oilseeds, including linseed, Niger seed, soybeans, cotton seed, sesame, groundnuts, sunflower seed, castor beans, and rapeseed (*Demissie, Taddesse, Mulatu and Beyene, 1991*). The oilseeds sector in Ethiopia however, is constrained by several factors and one of them is in the processing area. The domestic edible oil production is characterized by obsolete technology where most of the oilseeds are crushed locally without any refining and are predominantly characterized by inefficient and poor quality (crude oil) production. A number of local crushers have limited capacity with low hygiene standards. Only a few larger crushing or refining companies seem to have adequate safety and hygiene standards compared to European industry standards (*Wijnands, 2007*). Bleaching is one of the key processes in fats and oils refining, designed to remove not only pigments, but also a wide range of other impurities. The improvement in the color of the oil is due to the removal of organic compounds such as carotenoids especially beta-carotene and their derivatives, xanthophyll chlorophylls, tocopherols, pheophytin, gossypol and it degradation products that give undesirable color to the oils. These substances decrease the quality or process ability of oil through darkening, foaming, smoking, precipitation, development of off-flavor and decreasing oxidative stability. Therefore, those impurities limit the shelf life and the uses of the oils and due to these Ethiopian consumers are generally hardly attracted by tastes and preferences towards imported edible oil.

Bleaching process uses a substantial range of different bleaching agents in order to remove a wide range of specific impurities. Acid activated bentonites are the most preferable due to is high bleaching efficiency and higher absorbing capacity as well as low cost. Essentially all bentonite used within Ethiopia is imported, material coming from a range of countries like Egypt, Netherlands, Italy, China, South Africa and India. And these imported bentonite is used mainly in the decolorizing of edible oils and these processes probably account for 90% of bentonite consumption. There is no domestic development of bentonite clay but bentonite clays have been identified in two main areas of the Ethiopian rift valley (the main occurrences are in the Ledi, Gewane, and Warssisa areas in the Afar depression) and these deposits have not been worked to provide material for use by local industries. And to researcher’s knowledge, no one has studied the bleaching performance for edible oil using these bentonites which are available locally. Therefore, this study will solve the problem that comes from foreign currency in order to import the activated bentonite for bleaching process. Generally, its scope encompasses the improvement of the quality of local edible oils as well as the development of local materials likely to be used for the decolorization of edible oils.

1.3 Objectives of the Research

1.3.1 General Objective:

The general objective of the study is to prepare and characterize acid activated bentonite of local origin for the process of bleaching Niger seed and Rapeseed oil.

1.3.2 Specific Objectives:

- To characterize the physical properties of the Ethiopian bentonite, such as moisture content, bulk density, apparent density and swell index.
- To prepare different acid activated bentonites by varying H_2SO_4 concentration, and activation temperature.
- To characterize the selected raw and activated bentonite by XRD, FTIR and SEM.
- To study the bleaching performance of activated bentonite for two different type of edible oils which are Rapeseed and Niger seed oil.
- To investigate the effect of different operating conditions during bleaching such as oil/bentonite ratio, bleaching temperature and bleaching time in order to get optimum conditions.
- To determine physicochemical properties of bleached oil by analyzing percentage color reduction (%CR) and percentage free fatty acid (FFA) content before and after bleaching.

1.4 Significance of the Research

This study should be significant in the sense that it will:

- produce low cost bleaching agent (bentonite) which is available locally.
- add to the knowledge and understanding of the bleaching process of edible oil by acid activated bentonite.
- provide useful knowledge on factors that might have impact on the bleaching efficiency.
- Contribute the enhancement of edible oil quality and to the development of local technology for the production of bleaching rate.
- play a role in national research and development efforts to establish businesses henceforth creating job opportunities for small-scale edible oil producers to perform their production quality.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

An oil is a substance that is in a viscous liquid state ("oily") at ambient temperatures or slightly warmer, and is both hydrophobic (immiscible with water) and lipophilic (miscible with other oils, literally). This general definition includes compound classes with otherwise unrelated chemical structures, properties, and uses, including vegetable oils, petrochemical oils, and volatile essential oils.

Edible or cooking oil is fat of plant, animal or microbial origin, which is liquid at room temperature and is suitable for food use. Some of the many different kinds of edible vegetable oils include: olive oil, palm oil, soybean oil, canola oil, pumpkin seed oil, corn oil, sunflower oil, safflower oil, peanut oil, grape seed oil, sesame oil, argan oil and rice bran oil. Many other kinds of vegetable oils are also used for cooking. The generic term "vegetable oil" when used to label a cooking oil product refers to a blend of a variety of oils often based on palm, corn, soybean or sunflower oils. Edible oil of animal origin is e.g. fish oil. Microbial oil is also encompassed.

2.1.1 World edible oil production

Edible oil and oil crops are among the widely-traded commodities in the world. Production and export of oilseeds are however, dominated by a group of producing countries. The United States, China, Brazil, India, Argentina, the EU, and Canada are the world's largest producers, which account for about 70 percent of global oilseeds output (*Hoffman, 1999*).

There are different varieties of oilseeds produced by different countries. Commodities' share of world oilseed production shows that soybeans alone account 53.3 percent followed by rapeseed and cottonseed each accounting 12.1 percent while peanut and sunflower seed account 10 and 8.7 percent respectively. Other types of oilseeds account only 3.8 percent (*Hoffman, 1999*).

Demand for vegetable/edible oil has consistently been moving up due to consistent increase in consumption, which is in turn caused by the increasing population as well as increase in disposable income in developing economies. The entire oil and fat production worldwide currently stands at more than 100 million metric tons per year, while reliable forecasts indicate a further increase in production and demand over the decades to come.

2.1.2 **Local edible oil production**

The food and beverages sector is one of the main components of Ethiopia's manufacturing sector. Based on official industrial statistics, total employment can be estimated at some 53,000 while the value of sales is almost 7 billion Birr. Value added generated by the sector is in the order of Birr 3 billion, equivalent to little less than 2% of the GDP. The sector includes a wide variety of activities, mostly linked to the transformation of domestically produced agricultural products. In certain cases, reliance is made on imported products (*Roberto Zavatta and Samuel Feyissa, 2009*).

Ethiopia consists of different climate zones and a range of altitudes from below sea level up to more than 4,500 meters above sea level. This enables it to grow a wide range of oilseeds, in which it has a long tradition (*Wijnands, 2007*). Linseed, Niger seed, soybeans, Cotton seed, sesame, groundnuts, safflower seed, castor beans, and rapeseed are important types of oilseeds grown in Ethiopia (*Hailegiorgis, 2011*).

Local production of edible oil in calendar year (CY) 2016 is projected to reach 137,500 metric tons, up by 10 percent from the previous year. Three oils - Niger, cotton, and linseed account for approximately 44, 23, and 22 percent, respectively, of oil production. The remaining 11 percent is made up of sunflower, soybean and ground nuts.

Edible oil supply from Ethiopia's oil factories is less than 20 percent of the total consumption of the country. In addition to the 27 large and medium-scale edible oil processors in Ethiopia there are more than 1,000 edible oil micro-processors that operate in rural and urban areas in often using outdated technology to crush oilseeds which are sold to consumers as crude oil. The processors run their operations in their own backyard in residential areas where most of the oilseeds are crushed locally without any refining (*Wijnands, 2007*). Therefore, there exists a huge potential to work on import substitute activities.

Imports of edible oil have been rapidly increasing over the last five years, with annual growth during this period almost reaching 20 percent. Post expects this upward trajectory to continue with imports reaching 550,000 metric tons in CY16. Most of this imported oil will be palm because of its price competitiveness.

In CY15, Ethiopia imported 479,000 metric tons of cooking oil, valued at nearly $474 million dollars. Of this imported oil, more than 90 percent by volume was palm oil, most of which comes from Indonesia and Malaysia. The remainder of imported oil is made up of sunflower, soybean and olive oils. The leading supplier of soybean oil is Egypt, while Turkey is the largest supplier of sunflower oil. See tables 8, 9 and 10 below for breakdown of oil imports value/volume and origin.

Table 2-1 Edible Oil Import Volume (MT)

Imports	2010	2011	2012	2013	2014	2015
Palm Oil	212,686	228,209	292,797	139,899	373,763	442,536
Sunflower Oil	1,135	2,228	1,453	2,198	2,450	9,704
Soy Oil	713	6,755	654	2,001	656	6,746
Vegetable Fats & Oils	11,912	11,263	17,041	13,487	11,316	16,954
Olive Oil	86	166	174	253	308	758
Sesame Oil	5	390	14	5	16	13
Other Edible Oils	780	3,548	85	194	577	1,877
Total	**227,316**	**252,559**	**312,217**	**158,038**	**389,086**	**478,588**

Source: *ERCA*

Table 2-2 Edible Oil Import Value ('000 USD)

Imports	2010	2011	2012	2013	2014	2015
Palm Oil	216,763	322,786	382,278	145,832	403,198	419,636
Sunflower Oil	1,458	3,909	2,438	4,055	4,309	15,692
Soy Oil	1,009	11,956	1,203	3,109	1,083	8,787
Vegetable Fats & Oils	18,099	19,564	28,453	16,935	18,355	25,220
Olive Oil	209	529	510	660	1,066	1,840
Sesame Oil	7	430	30	26	47	71
Other Edible Oils	1,013	5,779	196	312	973	2,582
Total	**238,557**	**364,952**	**415,109**	**170,929**	**429,031**	**473,806**

Source: *ERCA*

2.1.3 Niger seed oil

Niger (Guizotia abyssinica (L.f.) Cass., Compositae) is an oilseed crop cultivated in Ethiopia and India. The evidences suggest that niger originated in the highlands of Ethiopia, north of 10'N latitude. From Ethiopia, the cultivated Niger is believed to have spread to India during third millennium BC along with other crops, such as finger millet. It constitutes about 50% of Ethiopian and 3% of Indian oilseed production. It represents also a minor oilseed crop in some other African countries (*Ramadan and Morsel, 2002*).

In Ethiopia, it is cultivated on waterlogged soils where most crops and all other oilseeds fail to grow and contributes a great deal to soil conservation and land rehabilitation. Besides cookery, Niger seed oil can be used in the manufacture of soap, paints, or as a lubricant or illuminant.

The major Niger producing areas in Ethiopia are characterized by moderate temperatures ranged between 16^oC and 20^oC during the growing season. In Ethiopia, Niger is cultivated at altitudes ranging from 500m to 2980m but mainly grown in mid-altitude and highland areas (1700–2200m) (*Getinet and Sharma,1996*).

2.1.3.1 *Composition*

The genus Guizotia consists of six species, of which five, including niger, are native to the Ethiopian highlands. It is a dicotyledonous herb, moderately to well branched and grows up to 2 m tall. The seed contains about 30% - 40% oil, 10% - 25% proteins, 12% - 18% soluble sugars, 10% - 20% crude fiber and 10% - 11% moisture. In general, the Ethiopian Niger meal contains less protein and more crude fiber than the Niger meal grown in India (*Chavan, 1961*).

Table 2-3 Fatty acid composition of Niger seed oil

Fatty Acid	Percentage
Myristic acid (C14:0)	**1.7%-3.4%**
Palmitic acid (C16:0)	**5.8%-13.0%**
Stearic acid (C18:0)	**5.0%-7.5%**
Oleic acid (C18:1)	**13.4%-39.3%**
Linoleic acid (C18:2)	**45.5%-65.8%**

Source: *Studies on niger (Guizotia abyssinica) seed oil. - Abstract*

Table 2-4 Physical and chemical characteristics specification of Niger seed oil

Characteristics	Requirements	
	Refined	**Grade I**
Moisture and insoluble impurities (%)	**0.10**	**0.25**
Iron(Fe), mg/kg	**1**	**1.5**
Cupper (Cu), mg/kg	**0.1**	**0.1**
Color on Lovibond scale in ¼” cell, expressed as Y+5R	**8**	**15**
Specific gravity at 30ºC	**0.917-0.920**	**0.917-0.920**
Reflective index at 40ºC	**1.4665-1.4691**	**1.4665-1.4691**
Butyro-refractometer reading at 40 °C	**61.0**	**65.0**
Saponification value	**189-193**	**189-193**
Iodine value	**110-135**	**110-135**
Unsaponificable matter (%)	**0.8**	**1**
Acid value	**0.5**	**5**
Bellier’s turbidity temperature in ºC	**25-29**	**25-29**

Source: *agmarknet.nic.in/vogmrule.htm*

2.1.4 **Rapeseed / Canola oil**

Rapeseed oil species used to produce canola oil and meal are from the Brassica genus in the cruciferae family. They were first cultivated in India almost 4000 years ago. Large-scale planting of rape oilseed was first reported in Europe in the thirteenth century. The Brassica species probably evolved from the same common ancestor as wild from the same common ancestor as wild mustard (Sinopis), radish (Raphanius) and arrugala (Eruca).

Early rapeseed cultivars had high levels of erucic acid in the oil and high levels of glucosinolates in the meal. The presence of these components was considered to be a health concern. The high level of erucic acid were blamed for producing fatty deposits in the heart, skeletal muscles and adrenals of rodents as well as impairing growth. Glucosinolates were also considered detrimental in rapeseed meal fed to poultry, swine and ruminants. Their hydrolyzed products, isothiocyanates and other sulfur-containing compounds, interfere with the uptake of iodine by the thyroid gland, contribute to liver disease, and reduce growth and weight gain in animals (*Roman Przybylski and Ted Mag, 1990*).

2.1.4.1 *Composition*

Edible oil and fats are composed primarily of triacylglycerol-esters of glycerol with molecules of fatty acids. The typical composition of canola and rapeseed oils is presented in Table 2-5.

Table 2-5 Constituents of canola and rapeseed oils

Component	Canola	Rapeseed
Triacylglycerol (%)	**94.4-99.1**	**91.8-99.0**
Phospholipids (%)		
Crude oil	up to 2.5	up to 3.5
Water-degummed	up to 0.6	up to 0.8
Acid-degummed	up to 0.1	-
Free fatty acids (%)	**0.4-1.2**	**0.5-108**
Unsaponifiables (%)	**0.5-1.2**	**0.5-1.2**
Tocopherols (ppm)	**700-1200**	**700-1000**
Chlorophylls (ppm)	**5-50**	**5-55**
Sulfur (ppm)	**3-25**	**5-35**

***Source:** Mag 1990 and Ying and DeMan 1989*

Canola oil is the only known edible oil containing one or more fatty acid with a sulfur atom as the integral part of the molecule. The structure of the proposed molecule of this fatty acid suggests the possibility of the formation or presence of many isomers (*Wijesundera and Ackman 1988*).

Table 2-6 Fatty acid composition of rapeseed oil

Fatty Acid	**Percentage**
Palmitic acid (C16:0)	**4%**
Stearic acid (C18:0)	**2%**
Oleic acid (C18:1)	**56%**
Linoleic acid (C18:2)	**26%**
Linoleic acid (C18:3)	**10%**
Others	**2%**

***Source:** Gunstone, F. Fatty Acid and Lipid Chemistry; Blackie: London, 1996*

2.1.4.2 *Pigments*

Pigments present in canola cause undesirable color in the oil. They promote photo-oxidation as well as inhibit catalysts used for hydrogenation. Chlorophylls without phytol, such as chlorophyllides and pheophorbides, may have nutritional effects because of their photo-toxicity which may be followed by photosensitive dermatitis (*Endo, 1992*). A bleaching step is necessary during oil processing to remove chlorophyll, chlorophyll derivatives, and other color bodies.

2.2 Edible oil processing operations

2.2.1 Raw material preparation

Most edible oils are obtained from beans or seeds, which generally furnish two valuable commodities – an oil and protein rich meal. Within the sources of edible oils, it is useful to distinguish three different types (*Gunstone, 2001*):

- **By products**: cotton and corn are grown primarily for fiber and cereal respectively and the oil is a byproduct. Soybean can also be included in this category because it yields two products (oil and meal) which represent approximately 18% and 79% respectively of the dried bean. It could also be argued that peanuts (groundnuts) should be included, since only about one half of the crop is crushed and the rest is consumed as nuts.
- **Tree crops:** palm, palm kernel, coconut and olive oils are obtained from trees that have to be planted and mature before they give a useful crop. One this stage is reached, the trees continue to provide crops for 25-30 years, in the case of palm, and longer than that for olive. These crops cannot be changed on a yearly basis.
- **Annual crops:** the third category are annual crops such as rape, sunflower and linseed. Appropriate decisions have to be made annually by the farmer or planter concerning which crops to grow. The choice is usually between oilseed crops and cereals, and the decision is based on agricultural and economic factors.

Most of the crops are produced annually at harvest time, which comes late in the CY in the northern hemisphere and early in the calendar year in the southern hemisphere. However, some equatorial crops like palm and coconut are harvested through all the twelve months of the year, through there is some minor seasonal variation in quality (*Gunstone, 2001*).

Before extraction the seed must be prepared and conventional seed preparation includes drying, cleaning, cracking, optional dehulling or decortication, conditioning and flaking of the seeds. The option of expanding after flaking is used to improve oil extraction, percolation and solvent drainage, and is accompanied by a doubling of the throughput. In another variation in seed preparation (hot dehulling), hulls are removed from the split seeds by alternate sloe and rapid heating before cracking and flaking. The Alcon process (*Penk 1986*) is a flake-heating treatment aimed to improve the degumming efficiency of the crude oil. A very low level of phospholipid in degummed oil can be achieved and therefore the oil can be physically refined.

2.2.2 **Oil extraction**

The main question next to the amount and quality of oil contained in the raw material is how to express as much as possible of that oil. This maximum possible oil extraction from the raw material is commonly said to be efficiency of expression. The efficiency of expression generally depends on the technology in use. However, the efficiency improvement can generally be made for that given technology at different stages in the process i.e. modifying raw material nature, control of operational parameters the pressing machine and improvement of machine design in order of its complexity.

Different oil extraction technologies are listed below:

2.2.2.1 ***Hydraulic Press***

In 1795, J. Bramah of England invented the hydraulic press for oil extraction (*Kirschenbauer, 1944 cited in Kemper, 2005*). For this press oilseeds were milled, cooked, and wrapped in filters cloths woven from horse-hair. The oilseeds wrapped in filter cloths were manually loaded into perforated, horizontal boxes below the head block and above the ram of the press. The boxes were pressed together using upward hydraulic pressure on the ram. The oil was pressed out through the filter cloths surrounding the oilseeds. The filter cloths and spent cake were manually removed from the hydraulic press. The residual oil in spent cake was approximately 10%. Since its discovery various modifications and advancements had been made to hydraulic press from its simplest form to the most advance one. Today, hydraulic press is used only for olive oil and cacao butter pressing (*Kemper, 2005*).

2.2.2.2 *Screw Press Extraction*

Valerius D. Anderson (Anderson International Corp., Cleveland, Ohio) developed continuous screw press in 1900. He used a continuous press design in 1876 and tested a serious of screw-conveyer like devices that had perforated walls and a flapper-type choke at the discharge end. He later on made a breakthrough discovery providing interruptions to the screw flight i.e. mounted on a central shaft so as to have some unflighted space between the segments. This solved the problem of the product spinning with the shaft every time the choke is closed. The shaft is placed in a cylindrical housing with holes drilled throughout to allow oil to escape upon pressing (*Kemper, 2005*).

2.2.2.3 *Solvent Extraction*

Solvent extraction is a process in which a solvent (such as hexane) is used to separate the oil from the oil-bearing materials. It is a demanding process, using highly inflammable chemicals, and it is only practiced at a relatively more sophisticated industrial scale. The advantage of solvent extraction is the high efficiency of extraction that can be obtained economically with this method (>99wt. %). But can be at the expense of reduced oil quality resulting from residual solvent chemicals if the technology is not high level (*Willems, 2008*). And also, it demands high initial investment and skilled technician. Therefore, it is less recommended where the technology is not well refined and the skill is not reliable.

2.2.2.4 *Recent Developments in Oil Extraction/Expression*

In a more advanced approach supercritical fluid extraction following prepress is also under investigation (*del Valle, 2006*). Gas assisted oilseed pressing technology is also becoming interesting where dense gas is used so that there would be lower residual oil content during solid-fluid mechanical separation. The gas is contacted with the oilseed before or during pressing in order to achieve high efficiency. Review of recent developments (*Dijkstra, 2009*) has shown the progresses in the area including evaluation on gas assisted mechanical extraction (GAME) that the high-pressure CO_2 released at the nozzle of the press, escapes and dissolves in the oil and thereby reduces its viscosity and entrains so much oil that the residual oil content of the press cake is less than 3%.

A wet extruder can be used to enhance the performance of solvent extraction on soybeans and cottonseed, and a dry extruder can be used to enhance the performance of a full press.

2.2.3 Oil refining process

2.2.3.1 *Why do we need to refine crude oil?*

Most crude oils and fats consist for more than 95% of mixtures of triacylglycerol. The non-triacylglycerol fraction contains variable amounts of phosphatides, free fatty acids, oxidation products, unsaponifiable matter (tocopherols, sterols, hydrocarbons etc.) and other so-called impurities the quantities of these minor components in crude oils vary with the oil source, extraction process, season and geographical origins. They can have different effects on the nutritional, functional and organoleptic properties of the oil.

The general objective of refining is to remove those components that have an adverse effect on the overall oil quality with the least possible damage to the triacylglycerol. At the same time, minor components with a known positive impact have to be retained as much as possible in the oil (*Farhoosh, 2009*). Some components like fatty acids, mono and diacylglycerols and phosphatides are the glyceride origin. Although phosphatides protect the crude oil from oxidation, they need to be removed because of their negative effect on the color, taste and oxidative stability of the oil. Other minor components can be isolated in the unsaponifiable fraction.

The main components of the unsaponifiable fraction (0.3-2%) include sterols, tocopherols, hydrocarbons, pigments and vitamins. The potential possible impact of some components of the unsaponifiable fraction, on health receives a lot of attention. Tocopherols for example are the most important natural antioxidants of phenolic nature protecting the edible oils from oxidation (*Lu & Liu, 2002*). On the other side, tocopherols are also biologically active substances with a generally accepted vitamin activity in the human body. Phytosterols are desired because they may reduce blood cholesterol levels.

Steps of processes of refining will be discussed as follows:

2.2.3.2 *Degumming*

Degumming is frequently the first processing step for crude oils which contain relatively high amount of hydratable phosphatides which are soluble in triglycerides (*Karleskind &Wolff, 1996*). Hydratable phosphatides can be removed from oil by adding the proper quantity of water, mixing thoroughly, allowing time for the hydration to occur, and separating by centrifugation. For this process, water is injected into the crude oil feed stream in proper proportion to the quantity of water-hydratable phosphatides. After sufficient hold time in a surge tank, the process stream is fed to centrifuges for separation of the hydrated phosphatides (gums) from the oil stream.

The crude oil feed stream is filtered to remove particulate matter if the subsequent gum recovery is for producing lecithin. Properly designed and operated water degumming process can achieve at least 90% of the ideal. Consequently, achieving the typical trading rule specification of 200 ppm phosphorous maximum is usually not a problem (*H. Yesim Karasulu, 2011*).

Degumming provides the advantages of producing lecithin and reducing the phosphatide removal load in caustic refining. If physical refining is subsequently employed, it is essential to degum oils high in phosphatides for both economic and product quality purposes. With the very best degumming, some water-hydratable phosphatides are left in the oil.

2.2.3.3 ***Neutralization***

The purpose of caustic refining (neutralization) is to remove free fatty acids, phosphatides and other materials including protein meal, glycerol, carbohydrates, resins and metals. In addition, some color reduction (pigment removal) is achieved.

Crude oil, degummed oil or mixtures of crude and degummed oil are fed to the refining process. Caustic soda (sodium hydroxide) is fed in the proper strength and quantity to react with the free fatty acids and phosphatides to form soapstock and hydratable gums. Having polar and hydrophilic properties, the soapstock produced is effective in removing some of the other impurities from the oil stream. Soapstock and other impurities are separated from the oil by centrifuges (*H. Yesim Karasulu, 2011*).

The processing endpoint for caustic refining varies according to the quality of the crude or degummed oil. It could be free fatty acid, phosphatide or color level. The impurity most difficult to remove in meeting the in-process oil specification determines the refining endpoint.

Caustic soda is not completely selective in reacting with the targets of free fatty acid and phosphatides; therefore, some triglycerides are hydrolyzed and saponified (broken down and converted to soap). Thus, selecting the proper strength caustic soda and the caustic-oil exposure time are key considerations to maximize the yield of refined oil (*Smallwood, 2001*).

2.2.3.4 ***Bleaching***

The main purpose is to remove residual soap and gums, pigments and oxidized components. This process is applied under vacuum with the addition of bleaching earth. Sometimes other absorption agents, such as active carbon or silicate, are added to promote better removal of unwanted minor components.

Bleaching is known as a mass transfer process that involves the partial removal of the oil soluble, non-triglyceride components from the oil stream by changing the physical state to a solid, separating the solids from the oil stream by filtration. Specifically, the non-triglyceride components in a liquid state are changed to a solid state by adsorption on to the surface of the solid bleaching earth particles added to the oil stream.

To optimize the performance of edible oil bleaching, the process design and the operating variables involved must be selected to drive the equilibrium toward maximum adsorption within the required product quality and operational equipment restraints. The process is carried out by adding the proper amount of clay to the refined oil stream. Typical bleaching conditions include a minimum of 20-40minutes contact time between the clay and the oil, a temperature range 80 to 120 °C and a vacuum of 50 mmHg absolute. Subsequently, the spent clay is filtered out of the bleached oil. On filtration process there are several factors that must be considered and some of them are the filter medium, filtration time and speed, and pressure drop during filtration.

Quality of the oil feed to the bleaching process is another critical determinant of bleaching performance. If impurities are present in the oil which covers the clay surface features necessary for adsorption, the bleaching effect mass transfer will be proportionally reduced.

The processing endpoint for bleaching is determined by the most difficult of the factors to achieve in meeting the bleached oil specification (color, soap, oxidation products, metal or phosphatide). In theory, properly bleached oil should have a zero-peroxide value (*Bailey, 1996*). In practice, it does because the sample taken for analysis is usually exposed to the atmosphere (air); thus, the presence of peroxide will be found typically < 1.0 meq/kg.

2.2.3.5 *Deodorization*

Deodorization is the final step in the processing sequence of converting crude vegetable oil or fat to an acceptable product for human consumption. In the deodorization process, the remaining impurities are either removed or reduced to a sufficiently low level for the production of acceptable flavor and functional edible oils and fats. While oils and fats do not harbor the growth bacteria and other organisms, one of the benefits of deodorization is to completely sterilize final product (*Bockisch, 1998*).

With deodorization, relative bland flavor and odor, essentially complete removal of residual herbicide and pesticide residue, low free fatty acid content, removal of oxidation products (zero peroxide content), low moisture content (about 0.05%), color reduction through heat bleaching of the carotene pigments improvements achieved.

Normally, a chelant, like citric acid, is injected into the deodorized oil stream for reacting with any residual metals. The metal salts formed are subsequently removed from the oil by filtration (*H. Yesim Karasulu, 2011*).

Deodorization is carried out in batch, semi-continuous or continuous systems. The deodorization principles are the same regardless of the system used. By heating the oil up to a temperature in the range (230-260°C) under a vacuum of 2 to 10 mmHg absolute, the non-triglyceride components and steam (vapor steam) are removed from the deodorization vessel by the vacuum system.

2.3 Edible oil bleaching process

Bleaching is one of the key processes in fats and oils refining, designed to remove not only pigments, but also a wide range of other impurities. Most crude fats and oils contain impurities that have to be removed for both commercial and health reasons. Modern industrial bleaching technologies are the way to do this.

The bleaching of fats and oils is normally carried out after either alkaline refining or degumming, and prepares the oil for the final deodorization process. In the case of crude palm oil, bleaching is the initial stage of the whole refining process.

At first glance, bleaching seems a relatively simple process that consists of mixing the oil with a powder, stirring for some minutes and then removing the powder again. However, this process is quite complex both in theory and in practice. And the term “bleaching” is in fact a somewhat misleading description for a complex refining process in which the removal of pigmentation is no longer the most important purpose.

The prime focus in modern bleaching processes is now on the removal of a wide range of different impurities, of which pigmentation is only one. Such impurities can virtually all be removed using new processes in which combinations of different bleaching agents are used to bind specific impurities. These are then removed when the bleaching agent is subsequently filtered out.

Efficient bleaching makes it possible to

- remove certain pigments such as carotenoids and chlorophyll
- decompose and partially remove oxidation products
- remove contaminants such as soaps and trace metals
- remove traces of phosphatides
- remove polycyclic aromatic hydrocarbons and other pollutants.

All these substances can have adverse effects on both the quality and stability of your final product, and therefore have to be removed to ensure that the product is commercially attractive.

Bleaching also reduces the number of substances that can affect the taste and smell of the fats and oils.

2.3.1 **Colors and pigments in edible oils**

There are three major types of color in vegetable oil (*Rich, 1964*):

- Organic color pigments of known composition.
- Organic degradation products.
- Color formed by oxidation of colorless precursors.

In the unoxidized state, the principal organic color pigments of known composition are quite readily adsorbed by bleaching clays. Pigments in the most common vegetable oils are:

- **Alpha, Beta Carotene ($C_{40}H_{56}$):** The carotenes are yellow to red, and structurally consist of highly unsaturated hydrocarbon chains arranged in various cyclic configurations. An important characteristic of the carotenoid pigments from the standpoint of bleaching is that they are unstable to heat and, as oxidation progresses, they gradually fade practically to a colorless state.
- **Xanthophyll ($C_{40}H_{56}O_2$):** Xanthophyll is colored yellow, and it is structurally similar to the carotenes except for an extra oxygen in the cyclic ring at each end of the hydrocarbon chain.
- **Chlorophyll A and B ($C_{55}H_{72}\dot{M}gN_4O_5$) and ($C_{55}H_{70}\dot{M}gN_4O_6$):** The chlorophylls are green, and structurally are unsaturated magnesium containing pyrrole derivatives and esters of the unsaturated primary alcohol phytol. Unlike the carotenoid pigments, the chlorophylls do not fade appreciably on heating. They are more readily adsorbed by clay with low pH (*Pritchett, W.G. Taylor and D.M. Carroll, 1947*) because alkali tends to stabilize chlorophyll, whereas acid decomposes it.
- **Gossypol Pigments:** The gossypols are the complex system of red, yellow, etc. pigments in cottonseed oil.

The organic degradation products are brown in color, and are present in vegetable oil, usually from damaged seeds. They generally are composed of degraded proteins, carbohydrates, mucilaginous matter, and phospholipids, and normally are present as positive colloid dispersions rather than being oil soluble as are the organic color pigments mentioned above. This type of color is usually difficult to remove by adsorption.

Color formed in oil by oxidation of colorless precursors, such as dark red ehroman-5, 6-quinones (*Bailey, Alton E. 1946*) from gamma tocopherol, is difficult to remove by adsorption. It has been known for some years that as a vegetable oil or animal fat ages, it becomes progressively more difficult to bleach; i.e., more clay is required to bleach oil to the same color. If the aged oil is darker than it was when fresh, the decrease in bleaching response is probably due to the formation of new color which is difficult to adsorb. On the other hand, if the oil is lighter in color upon aging, the color pigments have become fixed, or nonresponsive to adsorption, in all probability by oxidation.

Thus, it is evident that bleaching is a complex mechanism, and involves more than simple adsorption of color pigments. Some of the color bodies, such as the carotenoids, tend to fade out in bleaching if oxidized by heating. Other new color may form, also by oxidation, and some of the existing color pigments may become fixed (or non-responsive to adsorption) by oxidation which gives the same effect as a poorer bleach.

2.3.2 **Types of bleaching**

2.3.2.1 ***Dry bleaching***

Dry bleaching is the method traditionally used for fats and oils. Although most common in Europe and Asia, it is a process that industry experts throughout the world are familiar with, and provides a viable solution in many processing situations.

Before it is mixed with bleaching earth, the oil is heated. If the process requires it, a citric acid solution is mixed with the hot oil to bind trace metals and decompose any residual soaps.

After this treatment, the oil is mixed with bleaching earth, activated carbon or a mixture of these two. This is done under vacuum to prevent oxidation, and in the presence of sparing steam. This process is called dry bleaching, because the bleaching reactor operates at a vacuum of about 70torr, which greatly reduces the humidity in the oil.

After bleaching, the bleaching agent is normally removed using pressure leaf filters. Naturally, the filter cake that accumulates here still contains oil. Much of this can be recovered by steam-blowing the contents of these filters.

2.3.2.2 ***Wet bleaching***

As the name implies, wet bleaching is a bleaching process in which water is added to the oil while it is in contact with the bleaching agent in the bleaching reactor. The presence of small amounts of water results in more efficient use of the relatively expensive bleaching earth. This greater efficiency results in lower earth consumption as well as reductions of total oil losses. This makes wet bleaching an attractive solution on account of the overall economics of the process, even though the investment costs are slightly higher.

The water present during wet bleaching is introduced in the form of a citric acid solution, or by taking wet oil from the separation line. Adjustment is carried out by careful control of the operating vacuum in the bleaching reactor to determine how much of the water subsequently evaporates. Even tiny amounts of water – anything in excess of 0.5% – remaining in the mixture after this will cause filtration problems later on. The oil therefore has to be dried before filtration.

In terms of the equipment used, the basic difference between wet and dry bleaching installations is therefore whether or not a dryer is located between the bleaching reactor and the filtration system.

2.3.2.3 *Two-stage bleaching*

The two-stage bleaching process is essentially a combination of wet and dry bleaching, combined with highly efficient two-step filtration. The main idea behind two-stage bleaching is to ensure that the dosing and filtration of the necessary adsorbents take place between each stage of treating the oil. This means that the adsorption process can be made significantly more efficient. This is because adsorption takes place on a continuous basis until there is equilibrium between the concentration of pigments and other impurities on the surface of the adsorbent and the concentration remaining in the oil. As soon as this equilibrium is reached, the adsorbent is filtered out of the oil. At the second stage, fresh adsorbent is then added to the treated oil until a new state of equilibrium is reached. This oil then passes through a second filtration stage.

Two-stage bleaching is particularly relevant if you wish to use synthetic amorphous silica compounds as an adsorbent. These are particularly effective for removing phosphatides, trace metals, gums and soaps. Using synthetic silica also makes it possible to cut back considerably on wastewater effluent from refining edible oils. The best performance using synthetic silica compounds normally require the presence of small amounts of water. This means that it is possible to extend a wet bleaching plant by adding a synthetic silica dosing system upstream.

Table 2-7 Comparative advantages of different types of bleaching

Types of bleaching	Advantages
Dry bleaching	✓ lower initial investment compared with other types of bleaching ✓ the use of plate heat exchangers for heating and cooling means lower consumption of utilities compared with shell-and-tube solutions. This results in lower operating costs. ✓ easy, straightforward control and operation ✓ only a minimum of space is required for installation ✓ minimal energy consumption
Wet bleaching	✓ more efficient use of the bleaching earth ✓ easy to combine with a silica treatment process ✓ highly flexible ✓ low consumption of bleaching earth ✓ reduced oil loss during filtration.
Two-stage bleaching	✓ possibilities for using cheaper bleaching agents and first-stage adsorbents, thus reducing operating costs ✓ reduced bleaching agent loading, resulting in lower costs ✓ high degree of flexibility.

In this researcher, dry bleaching type was used due to several advantages compared to others as mentioned above.

2.3.3 Bleaching mechanism and process options

During the bleaching process adsorption occurs via many different mechanisms involving various physical and chemical interactions (*Berbesi, R. 2011*); most of them improve the quality of the oil, but some of them may reduce it. These mechanisms include the following:

- **Adsorption:** mechanism by which the sorbent binds a contaminant. This can occur in three different ways:
    - ✓ Physically through surface attraction involving van der Waals' forces
    - ✓ Chemically by “chemisorption” by electrochemical bonding to the surface of the clay
    - ✓ By molecular sieves which trap contaminants under pressure inside the pores of the clay during filtration
- **Absorption:** mechanism by which the intra-granular pores are filled with some fluid, mainly oil and in turn whatever contaminants came along with it.

- **Filtration:** mechanism of trapping or physically removing suspended contaminants: the physical act of filtering out the suspended clay that simultaneously removes the minor contaminants adsorbed to the clay particles. Filters used in the bleaching process include processing filters (horizontal and vertical leaf filters) and polishing filters (bag, cartridge, paper).
- **Catalysis:** mechanism by which contaminants are degraded by interaction with the surface of the clay. For example, peroxides are effectively reduced (polymerized and/or decomposed into volatile oxidation by-products) by clay/oil interaction. With excessive heat and oxidation, pigments can form color compounds that are difficult to remove or said to be “fixed.” In the event of color fixation, red color is more difficult to remove by bleaching clays alone and resistant to thermal degradation leading to higher red color after deodorization.

2.3.3.1 *Process Options*

The bleaching process configurations have advanced from the slow, less efficient batch process to the highly efficient countercurrent process options including true countercurrent and lead-lag or double pass bleaching systems currently offered.

Batch bleaching systems continue to be the process of preference for those who process many different products per day in small quantities. Countercurrent bleaching systems (*Transfeld, P., Schneider, M. and Börner, G. 1998*) find more favor in modern facilities because they maximize bleaching efficiency by utilizing the spent clay to exhaustion, which results in substantial savings (up to 40% reported) with 20-30% reported clay reduction (*Waranica, G.*).

2.3.4 **Bleaching agent and its treatment techniques**

The most commonly used way to bleach fats and oils is to treat them with surface active surfactant powdery materials. These bind (also known as “adsorb”) the pigmented substances in the oils to the extensive surface area provided by them being in powder form. The adsorptive capacity of sorbent minerals depends on their mineralogical structure and adsorptive properties, such as surface area, particle size distribution, porosity, and surface acidity. Modern bleaching processes use a substantial range of different bleaching agents in order to remove a wide range of specific impurities, in addition to the pigments. The agents normally used include (*Rohani, 2006*):

- natural bleaching earths (used with only limited color-reducing effect but are particularly useful in treating animal fats)
- activated bleaching earths (widely used for removing all kinds of impurities)
- activated carbon (used to remove polyaromatic hydrocarbons and ensure removal of a wide range of specific pollutants)
- synthetic amorphous silica compounds (used largely in wet bleaching, with a focus on selectively removing phosphatides, trace metals and soaps).

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite andsepiolite. In the process of refining vegetable oil, bleaching clays have been used extensively as adsorbent in vegetable oil refining.

Adsorption capacity of fuller's earth is enhanced by various treatment techniques. Several reviews have been made on clay activation for vegetable oil bleaching (*Farihahusnah and Mohamed 2011*), the reports of these researchers were focused on structural and surface properties of the clay mineral, textural characteristics, surface chemistry, modification techniques and parameters that influence the activation method.

2.3.4.1 ***Effect of activation on clay structure***

The crystal clay structure is one of the important factors that contribute to clay adsorptive property. The crystal structure with a few exceptions consists of sheets. Individual layer consists of two, three or four sheets. The sheets are formed by tetrahedrons $(SiO_4)^{4-}$ or octahedrons Such as $[AlO_3(OH_3)]^{6-}$. When an octahedral sheet is linked to one tetrahedral sheet, the clay layer is called two sheet phyllosilicate and is referred to as 1:1-layer type. Similarly, when the ratio of tetrahedral sheet to octahedral sheet is 2:1, it is called three-layer phyllosilicate. The octahedral sheet is sandwiched between the two tetrahedral sheets (*Konta J. Clay and man 1995*).

Isomorphic substitution is an important characteristic of clay which generates negative charge on clay layers. It involves replacement of constituent metal ion of the lattice by cation of lower charge thus producing a negative charge (*Matocha CJ. 2006*). Example of such substitution includes Al^{3+} for Si^{4+} in the tetrahedral sheets. This negative charge is balanced by the interlayer exchangeable cation. Another special future of clay mineral is the presence of Lewis and Bronsted acidity site which is one of the active site that determines the chemical reactions in the clay structure. *Sposito et al. (1999)* reported that, when isomorphic substitution occurs in the octahedral sheet, the negative charge is more delocalized and the Lewis base character (electron donor) of the siloxane surface is enhanced.

The negative charge that results from isomorphic substitution is balanced by the presence of exchangeable cations which are Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} ions. The excess negative charge smeared over all the superficial oxygen and makes the clay surface highly acidic. This subsequently have great impact on the sorption of polar and charged organic compounds.

2.3.4.2 ***Types of clay activation***

2.3.4.2.1 Acid activation

Natural clays are purified and treated with mineral acids. These acids include hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, organic acid such as acetic, citric, oxalic and lactic. Among these acids, hydrochloric acid and sulfuric acid are the most widely used in acid activation, because they give good result regarding the specific surface area, porosity and adsorption capacity of the activated clay (*Valenzuela Diaz FR, Souza Santos P. 2001*).

Acid activation of clay results in leaching of cation from tetrahedral and octahedral sheets and replaces the exchangeable cation with hydrogen ion. Acid treatment of clay also opens the edges of the platelets and as a result, surface area and pore diameter increases (*Fransisco RV, Persio de Souza Santos. 2001*).

Generally, the process of acid activation involves purification of the clay and grinding to very fine particles. The grinded clay mixed with known amount of acid and the resulting mixture heated to a temperature of between 60 and 100ºC under continuous stirring for a period ranging from 2-6 hours. The clay suspension is then washed in distilled water before filtration and drying process to recover the solid acid treated clay.

2.3.4.2.2 Alkaline Activation

Very few studies were reported on the effects of alkaline treatment of bleaching earth on the adsorption bleaching of vegetable oils capacity. *Okwara and Osoka (2006)*, studied the influence of caustic activation of Nigerian clays for palm oil bleaching. The clay samples (kaolin, bentonite and fuller's earth) were activated at 80-85ºC for 35-45 minutes using caustic soda (NaOH) at concentrations of 1M, 2M, 3M and 4M respectively. The alkaline activated clays were used to bleach palm oil. They discovered that alkaline activated clay could remove reasonable amount of unwanted pigment in vegetable oil.

However, the use of alkali activated clay is still receiving research attention because no conclusive information has been drawn on its effect on the general properties of vegetable oils.

2.3.4.2.3 Thermal Activation

Heat treatment is a physical method of clay modification. Clay structure and composition can be modified by heating at high temperature (*HellerKallai L. 2006*). Thermal activation involves dumping an already pulverized sample of the adsorbent such as clay in a high temperature enclosure (oven), maintaining its temperature within the range 400-600^{0}C for about three hours before cooling to room temperature. Dehydration of clay sample at such elevated temperature causes a drastic alteration in the clay structure, its plastic properties are lost and the clay is said to be dead.

Valenzuela Diaz and Souza Santos (2001) stated that thermal treatment is a method of alteration of chemical composition and/or crystalline structure by the effect of temperature. Heat treatment of clay results in loss of all or substantial proportion of chemically held water in the clay. Many impurities are also lost during heat treatment.

Regina OA, (2012) modified the physio-chemical properties of Uri (Nigeria) clay minerals to enhance its adsorptive capacity. The author modified the samples by thermal activation at temperatures ranging from 100ºC to 500ºC. Such heat-treated clays were used to bleach palm oil for its adsorptive capacity test.

2.3.4.2.4 Microwave Activation

Microwave heating can be used to significantly modify the adsorption properties of bleaching earth. *Gunawan et al. (2010)* investigated the effect of organo-bentonite for the purification of vegetable oils by using normal heating and microwave irradiation method. The authors discovered that the amounts of free fatty acid (FFA) removed during bleaching process by microwave irradiation method are higher than the conventional heating. The results also show that there was a significant decrease in peroxide value (PV) for both methods.

Korichi et al. (2009) studied the effect of acid activation under microwave irradiation on the textural and structural properties of a smectite from Algeria. The results showed that, the specific surface area, micropore and mesopore of smectite increased with increasing irradiation time. The authors also reported that the temperature and time required by the microwave heating for adsorbent preparation are far shorter than the conventional thermal activation method.

Their findings indicated that, the method is simple, economic, time saving and energy efficient. However, this method of modification has not been optimized hence, its adoption in manufacturing and industrial synthesis is not yet feasible.

2.3.4.2.5 Pillaring

Pillaring is another method of clay modification which involves combination of both chemical and physical treatment. It involves the insertion of inorganic polycation of nano dimension to the clay interlayer and subsequent thermal treatment. These polycationic metals also known as pillars can be intercalated into the interlayer of the clay to produce thermally stable activated clays.

Falaras et al. (2000), investigated the bleaching properties of Alumina-pillared activated montmorillonite on cotton seed oil. The Ca-rich montmorillonite was treated with sulfuric acid and pillared with a poly cation called Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{+7}$ at a calcinations temperature of 500ºC.

2.4 Bleaching of edible oil using acid-activated bentonite

2.4.1 Raw bentonite

2.4.1.1 *Nature and occurrence*

Bentonite is the name used for a range of clays that can swell and gel when dispersed in water. Although the bentonite industry is slightly over 70 years old, the name bentonite was applied as early as 1848 by Knight to a highly plastic clay material occurring near Fort Benton, Wyoming (*Grim, 1953, p. 361*). According to *Chisholm (1960, p. 30)* the first commercial bentonite was shipped in 1888 under the name "Taylorite". From this modest beginning, in which production amounted to only a few tons per year, bentonite production now exceeds a million tons per year.

The origin of bentonite is attributed to the alteration of volcanic ash, or glass, but common use of the term is often extended to include material of primarily a montmorillonite composition which may have formed in another manner. Bentonite from ash falls and other sources occurs worldwide in strata spanning a broad range of ages, but is most abundant in Cretaceous or younger rocks. Accordingly, its major component, montmorillonite, occurs abundantly as dust at and near surface deposits of bentonite and is dispersed widely by air and moving water. Montmorillonite is thus ubiquitous in low concentrations worldwide in soil, in the sediment load of natural waters, and in airborne dust (*Parker, 1988*).

According to information got from Geological Survey of Ethiopia, world production of bentonite is currently approaching 17,000 million tons per year, with the USA by far the largest single producer at 7600 Mt/yr. Approximately 90% of world bentonite production is concentrated in 13 countries: the USA, Greece, the Commonwealth of Independent States, Turkey, Germany, Italy, Japan, Mexico, Ukraine, Bulgaria, Czech Republic, South Africa, and Australia. The USA, Greece, and the Commonwealth of Independent States account for roughly 55% of the annual world production of 10 million tonnes. The largest single use of bentonite is in foundry molding sand (24%), followed by drilling mud (21%) and iron ore pelletizing (15%). Various absorbent uses together account for a further 23% of world production.

2.4.1.2 *Bentonite in Ethiopia*

Bentonite clay resources are found in the Afar and Oromia regions. They are easily accessible, as they are located near the main road. The main occurrences in Afar are located at Ledi, Gewane, Hadar and Warseiso. The bentonite beds are part of a thick sequence of lacustrine sediments, which consists of clays, silts, sands, calcareous grits, gravels, conglomerates, basaltic flows, and ashes. These sediments were deposited near the western margin of the central part of the Afar depression, which throughout the Tertiary and Quaternary was an area of subsidence and intermittent volcanism. The bentonite clays are probably the result of alteration of glassy igneous materials (*Mengistu*, *1987*). The total resource in the Afar region is estimated to be 170 million tonns. The bentonite beds are well exposed and the overburden consists of loamy gravel and sandy clay.

Bentonite clay of Pleistocene age occurs at Gidicho Island (bottom locality on map below), Lake Abaya, in association with diatomite, with a total estimated resource of five million tons (*Knot, 1983*).

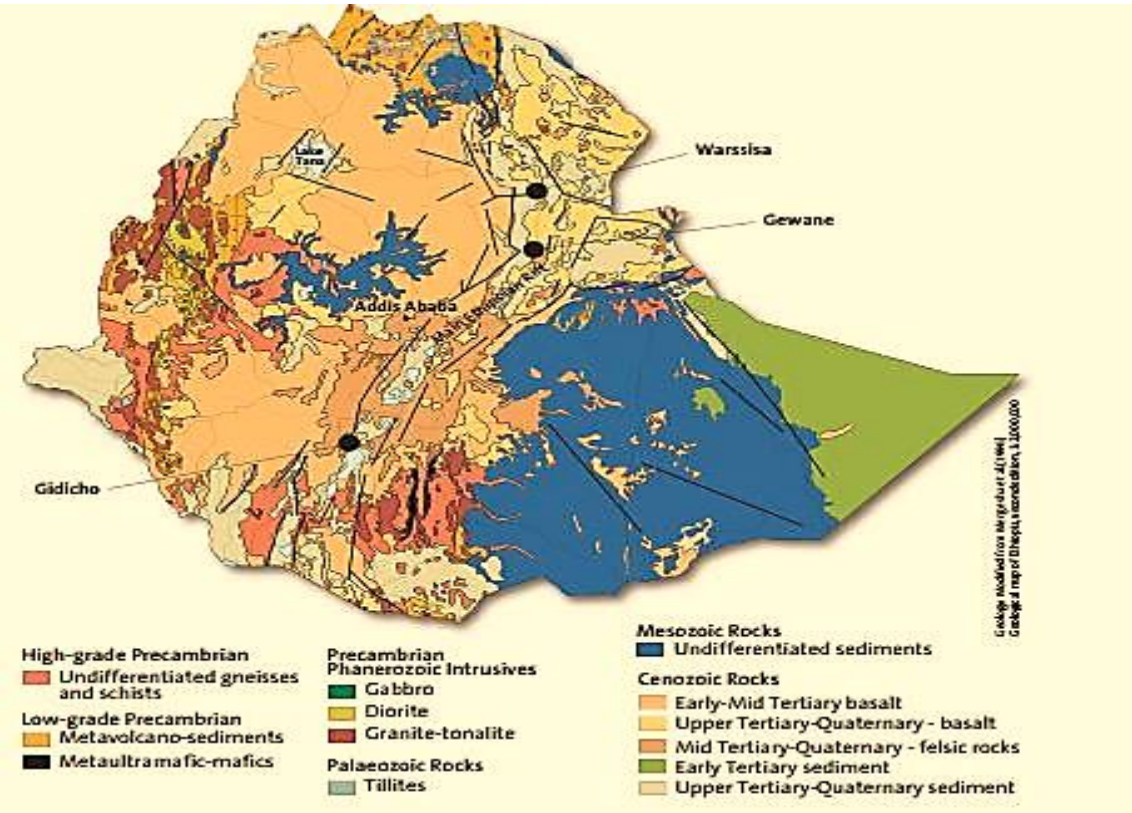


Figure 2.1 Simplified geological map of Ethiopia showing bentonite deposits

Source: *www.mome.gov.et (Ministry of Mines of Ethiopia)*

Table 2-8 Location and resource of bentonite deposit of Ethiopia

Area (province)	Name of deposits	Easting	Northing	Resource (million tons)
Afar	**Gewane Bentonite**	**40° 38' 05"E**	**10° 17' 50"N**	**126**
Sidamo	**Gidicho Bentonite**	**37° 56' 00"E**	**06° 24' 00"N**	**5**
Afar	**Warsissa Bentonite**	**40° 39' 00"E**	**11° 22' 20"N**	**10.5**

Source: www.mome.gov.et *(Ministry of Mines of Ethiopia)*

Although testing of bentonite clays from these localities has indicated suitability for drilling mud, iron ore pelletizing and, possibly, foundry use, apart from minor and sporadic exceptions, these deposits have not been worked to provide material for use by local industries. Essentially all bentonite used within Ethiopia is imported, material coming from a range of countries.

The main use of this imported bentonite is in processing of edible oil. Other outlets are in drilling, metal casting and for filtering beer. Currently there are numerous small-scale edible-oil producers who do not bleach their products, but forthcoming Government regulations may make this mandatory. This should lead to an increase in demand for bleaching-grade bentonite.

Table 2-9 Bentonite import data of Ethiopia in 2016

Country	Net Weight in KG	CIF Value USD	Total Tax USD
India	503000	84986.72	20184.34
United Kingdom	515	1043.5	0
Italy	4561	9164.54	2176.57
France	501.33	4817.33	999.59

Abbreviation CIF: Cost insurance and freight

Source: *http://www.ethiopianimporter.com/ethiopia-import-data/edible-oil.html*

2.4.1.3 *Structure and composition*

Bentonite and fullers earth are terms used for any clay materials belonging to the smectite group, of which the most common mineral species is montmorillonite. Bentonite, in addition to montmorillonite, contains a small portion of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum, or pyrite. Bentonite varieties are distinguished on the basis of their principal exchangeable cation, hence sodium-, calcium-, magnesium- (saponite), potassium- (meta-bentonite) and lithium- (hectorite) bentonite.

Natural sodium bentonite is characterized by very high swelling ability, high liquid limit and low filter loss. Natural calcium bentonite**,** where calcium is the predominant exchangeable cation, is mined world-wide. It has much lower swelling ability and liquid limit, and much higher filter or fluid loss than natural sodium bentonite.

Chemically, montmorillonite is described as a hydrous aluminum silicate containing small amounts of alkali and alkaline-earth metals. Structurally, montmorillonite is made of two basic building blocks, the aluminum octahedral sheet and the silica tetrahedral sheet. Chemical composition of pure montmorillonite is used as the reference in assessing analytical data of the studied bentonite samples. *Neaman et al. (2003)* give the following stoichiometric formula for purified montmorillonite:

$$Na_{0.18}Ca_{0.10}\,(Si_{3.98}Al_{0.02})\,(Al_{1.55}Fe^{3+}_{0.09}Fe^{2+}_{0.08}Mg_{0.28})\,O_{10}(OH)_2\cdot nH_2O$$

Exchangeable **Tetrahedral** **Octahedral site** **H_2O^+** **H_2O^-**

A single montmorillonite unit cell consists of two silica tetrahedral sheets, between which is an aluminum octahedral sheet. Lengths and widths of montmorillonite flakes are from 10 to 100 times the thicknesses. The montmorillonite lattice is negative in charge, owing primarily to isomorphous replacements of ions within the structure. This negative character is balanced by cations which are held on the surface of the flakes. Cations held in this fashion by the clay can be readily exchanged.

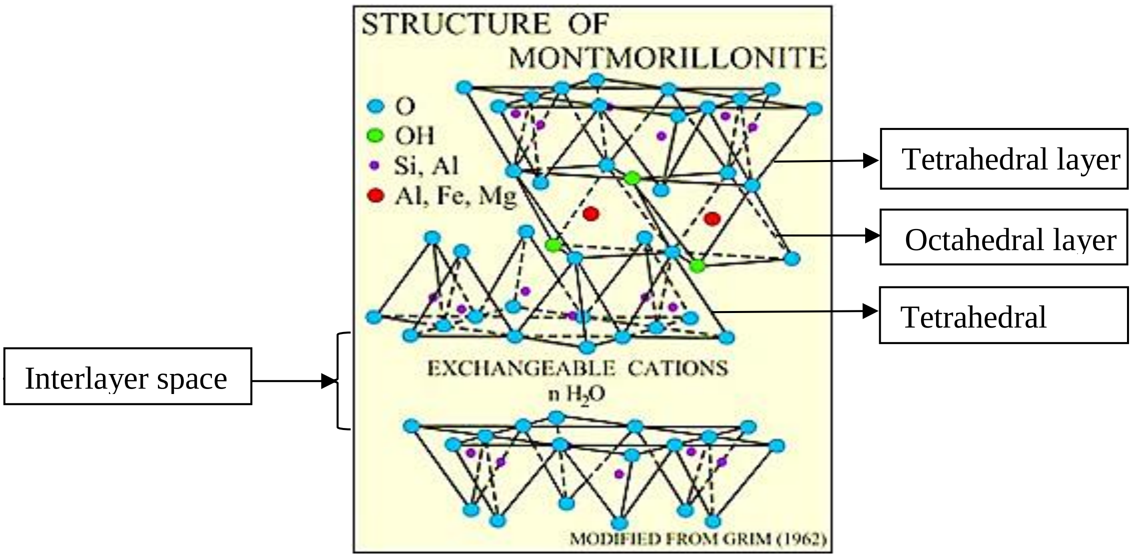


Figure 2.2 Diagrammatic sketch of the structure of montmorillonite (*after Grim, 1962*)

2.4.1.4 *Bentonite properties*

The most important properties of bentonite for which it is employed in many different industries are the following (*Farndon, John. 2006*):

- **Water absorption and swelling**

A fundamental property of bentonite is to absorb water and expand. However, not all bentonites have the same absorption capacity. Its level of hydration and swelling depends on the type of exchangeable ions contained, with different hydrophilic and solvating power. Swelling is mainly due to two factors which are water absorption at platelet surface level, and osmotic repulsive forces, forcing platelets to detach and open up like a “stack of cards”. Sodium bentonite, with sodium cation prevalence (Na^+) allows water to penetrate through the platelets, forcing them apart, thus leading to swelling. Conversely, calcium bentonite, with calcium cation prevalence (Ca^{2+}), while getting hydrated in much the same way, due to its strong positive charge, has lower absorption properties, not permitting water to penetrate through the platelets. In this latter case, platelets flake off rather than swell.

- **Viscosity and thixotropy of aqueous suspensions**

when bentonite is dispersed in water, highly stable colloidal suspensions are formed with high viscosity and thixotropy. At high enough concentrations, these suspensions begin to take on the characteristics of a gel. Suspensions are formed when water molecules penetrate into platelet interlayers. Here, hydrogen bridge bonds are formed by the hydrogen atoms contained in the water molecules. Platelets become isolated from each other, while bonded through interposition water. When left still, a mesh is formed which, by incorporating water, jellifies.

Conversely, under mechanical stress, these bonds partially break, thus allowing platelets to move more freely. Viscosity under these conditions is lower than at rest. This reversible sol-gelsol process is known as thixotropy. These properties shown by bentonite aqueous suspensions are mainly exploited in drilling slurries.

- **Colloidal and waterproofing properties**

when water is absorbed by bentonite, a semisolid gel is formed with strong hydrostatic pressure resistance. A montmorillonite platelet can be figured out as a thin packet of negatively charged layers. Due to their negative charge, they repel each other while letting water through. In this way, while the packet swells, a stable shell is formed around the platelet. When saturated, this shell will repel water, even under pressure. For all these properties, bentonite is employed in ponds and docks, to seal off soil infiltrations, and line the base of landfills.

- **Binding property**

This bentonite property is mainly exploited to produce green molding sand. In this application, bentonite with a suitable moisture content covers quartz sand grains and acts as a connective tissue to the entire mass. Under this homogenous coating, even at maximum compression, water will remain in a highly “rigid” state, binding the sand grains and lending maximum resistance to the sand mould. Bentonite vitrification temperature is higher than other clays. Therefore, when used as an additive, it makes green sand more durable, and, in particular, more resistant to heat stress.

- **Surface properties (coagulation– absorption – adsorption)**

Bentonite absorption – adsorption properties are determined by the high specific surface and free charges present on each micelle. Coagulation occurs through the adsorption of ions of opposite charge to that of colloidal particles.

2.4.2 **Industrial Use of Activated Bentonite**

2.4.2.1 ***Wastewater treatment***

Wastewater treatment can be achieved by chemical precipitation, ion exchange, adsorption, membrane filtration, and electro dialysis. Among these methods, chemical precipitation is the most common technique. But adsorption is an alternative technology for metal separation from aqueous solutions. Activated clay is used in the removal of heavy metals and dyes from wastewater (*Resmi, 2012; Qingliang, 2013*); for example, it has been used to remove cobalt from wastewater (*Al-shahrani, 2013*).

It has been shown that acid activated bentonite clay can also be used in petrochemical wastewater pre-treatment for the removal of ammonium compounds and phosphorous ions. Such ions-saturated bentonite can be used as a mineral fertilizer or as an additive for cattle fodder (*Buic and Zelic, 2009*).

2.4.2.2 ***Catalyst***

Activated montmorillonite is used to catalyze various chemical reactions such as cracking of petroleum to increase the yield and the quality of gasoline from petroleum. In addition, the montmorillonite is used as an alkylation catalyst of phenols and as delicate pH adjuster (*Hartwell, 1965*). *Vijaykumar et al., (2009)* have reported high efficient catalyst for esterification of various carboxylic acids with phenol alcohols made from acid activated Indian bentonite.

2.4.2.3 ***Edible Oils refining and food markets***

In vegetable fats and oils industries, bentonite is utilized in the removal of impurities, where its adsorptive properties are crucial (EUBA, 2011). Besides removing pigments and other impurities such as soap, trace metals and phosphatides, the clay also reduces the oxidation products (*Langmaack and Eggers, 2002*). Bentonite is also used as a clarification agent in drinks such as beer, wine and mineral water and in products like sugar or honey (*EUBA, 2011*).

2.4.2.4 ***Pharmaceutical, cosmetics and medicine***

Due to its adsorptive properties, bentonite is used as a filler in pharmaceuticals because it allows paste formation. In medicine, it is used as an antidote in heavy metal poisoning. Bentonite is also used in production of personal care products such as sunburn cream, baby and face powder, etc. (*EUBA, 2011*).

2.4.2.5 *Paper*

Bentonite is crucial to paper making for pitch control and in paper recycling where it offers useful de-inking properties. In addition, acid activated bentonite is used in the manufacture of carbonless copy paper as active component (*EUBA, 2011*).

2.4.2.6 *Construction and civil engineering*

Bentonite is traditionally used as a thixotropic, support and lubricant agent in diaphragm wall, foundation and pipe jacking. It is also used in cement and mortars due to its viscosity and plasticity (*EUBA, 2011*). It is conventionally used as mud constituent in oils and water well drilling mainly to seal the borehole walls, to remove drill cuttings and to lubricate the cutting head.

2.4.2.7 *Pelletizing*

Bentonite is used as a binding agent in the production of iron ore pellets. Through this process, iron ore fines are converted into spherical pellets, suitable as feed material in blast furnaces for pig iron production, or in the production of direct reduction iron (DRI).

2.4.2.8 *Cat Litter*

Bentonite is used for cat litter, due to its advantage of absorbing refuse by forming clumps (which can be easily removed) leaving the remaining product intact for further use.

2.4.2.9 *Agriculture*

Bentonite is used as an animal feed supplement, as a pelletizing aid in the production of animal feed pellets, as well as a flow ability aid for unconsolidated feed ingredients such as soy meal. It also is used as an ion exchange for improvement and conditioning of the soil. When thermally treated, it can be used as a porous ceramic carrier for various herbicides and pesticides.

2.4.2.10 *Detergents, Paints, Dyes and Polishes*

Laundry detergents and liquid hand cleansers/soaps rely on the inclusion of bentonite, in order to remove the impurities in solvents and to soften the fabrics.

Due to its thixotropic properties, bentonite and organoclays function as a thickening and/or suspension agent in varnishes, and in water and solvent paints. Its adsorption properties are appreciated for the finishing of indigo dying cloth, and in dyes (lacquers for paints & wallpapers).

2.4.3 Basic factors affecting bleaching capacity

Determination of optimum parameters for achieving highest bleaching efficiency is important to prevent formation of undesirable compounds in the final product. Therefore, it is necessary to consider the following effects:

2.4.3.1 *Effects of a Clay's Properties*

- **Moisture Content:** Bleaching clays normally contain from 8-18% free moisture. The most generally accepted conception of the clay structure is that the montmorillonite molecules are arranged in aggregates in the form of parallel layers, somewhat like a cake. The water molecules lie between and around the layers, and serve as a support to keep the layers apart. The color bodies cannot be adsorbed to the maximum capacity of the clay until all the water has been removed, or to express it simply, the color bodies cannot come in until the water goes out.
- **Clay Acidity:** Natural clay has a normal pH range of 4.0-7.0, and activated clay 2.5-4.0. Chlorophyll-rich oils such as soybean, require a low pH, i.e. substantial acidity, for optimum adsorptive capacity. It is one reason why natural clay, with its high pH and near neutrality, is relatively ineffective on this type of oil. There is an inverse ratio between clay pH and free fatty acid increase in the oil during bleaching. The hydrogen ions cause some hydrolysis of the oil glycerides to form free fatty acid and glycerin. For this reason, an optimum balance must be observed by the clay manufacturer between a low pH for maximum adsorptive capacity on the chlorophyll type oils, and a high pH for minimum hydrolytic effect on any fat or oil.
- **Apparent Bulk Density (ABD):** It means the wt./unit volume of clay when it has been tapped to constant volume in a graduated cylinder. The ABD of a clay is one of its most informative properties, such as the ABD is inversely proportional to the adsorptive capacity and to the clay's filtration rate. Its most significant correlative value is as a measure of the clay's oil retention because the ABD depends upon the air void space in the clay, which in turn measures directly the amount of oil the clay will retain as a filter cake.
- **Oil retention and filter rate**

- **The particle size distribution:** It is one of the essential properties of the bleaching earths and obtaining the desired particle size distribution, will help to become a bleaching earth with high activity and, at the same time, excellent filtration properties. An earth size of 100-200 mesh is convenient for experimental work.

2.4.3.2 *Effects on treatment techniques*

- **Type of activation:** *Regina OA. (2012)* determined the adsorptive capacity of Udi modified clays on palm oil. The author modified Udi clay by thermal and acid activation and discovered that bleaching efficiency increased from 29.67% to 75.3% and 92.74%, for thermally and acid activated samples, respectively.
- **Types of acid:** Natural clays are purified and treated with mineral acids. These acids include hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, organic acid such as acetic, citric, oxalic and lactic. Among these acids, hydrochloric acid and sulfuric acid are the most widely used in acid activation, because they give good result regarding the specific surface area, porosity and adsorption capacity of the activated clay (*Valenzuela Diaz FR, Souza Santos P. 2001*). *David (1991)* in a United State patent titled ‘oil bleaching method and composition for same reported that sulfuric acid is preferred because it does not evaporate during the acid activation step or at the beginning of the final drying process, thus permitting a more complete activation of the clay.
- **Acid concentration:** Bleaching efficiency increases proportionally to the removal of octahedral cations from bentonite structure. Dissolution of octahedral cations (Mg^{2+}, Fe^{2+}, Al^{3+}) increased continuously with increasing acid concentration. As a result, acid activation of the clay sample with high concentration of acid yielded an adsorbent material which are highly efficient in the bleaching of the oil. *Salawudeen (2007)*, evaluated the performance of acid treated Nigerian clay for palm oil bleaching. The maximum percentage color reduction of 89.46% was achieved in H_2SO_4 activated clay at 2M acid concentration. Further increase in concentration of H_2SO_4 has no significant effect.
- **Treatment time:** According to *Ma & Withrow (1930)* decolourization takes place almost immediately after good contact of earth and oil is obtained. Time of contact is unimportant after thorough contact has been obtained and usually for a period ranging from 2-6 hours.

- **Temperature effect:** Generally, the process of acid activation takes place at a temperature of between 80 and 100ºC under continuous stirring. According to *Didi (2009),* a fine bentonite suspension in water (320 g dry clay per liter) was put in contact with pure H_2SO_4 (98%) at various temperatures (60–120 °C), for various contact times (6–12h). The highest bleaching capacity was found to be 99%, under optimum activation conditions, namely: acid concentration (34%), contact time (7 h) and temperature (90 °C).
- **Solid/liquid ratio*:*** *Girgin (1996)* studied oil decolorization properties of the Emirler elinoptilolite. In these tests, clinoptilolite samples were mixed with 100ml of hydrochloric acid solutions of 0.01 to 12 M for obtaining different solid/liquid ratios that are 1/2, 1/5, 1/10, 1/20 and 1/30 agitated by a magnetic stirrer for a specified time, filtered through Whatman 42 filter paper, and the residues were washed with distilled water until the filtrates become neutral. Then they were dried at 105^{0C} for 2 h and used in the bleaching experiments. Taking into consideration all the data obtained from the bleaching experiments on acid activated clinoptilolite samples, it was concluded that reasonable results could be achieved at the following optimum conditions: HCI concentration of 1 mole/l, solid/liquid ratio of 1/20, temperature of 25^{0C} and agitation time of 1 hr.
- **Moisture content and method of drying:** After washing and filtering, activated clays must be dried to facilitate handling and to maximize bleaching power. In addition to drying the clay to a specific moisture content level, the method of drying is significant. It has been determined that speed of drying affects bleaching power.

2.4.3.3 *Effects on bleaching process*

- **Atmospheric and vacuum bleaching:** Bleaching with clay, besides adsorption, also involves other reactions of oxidative nature occurring during the bleaching period. These oxidative reactions result in a balance between the fading of some color pigments which lightens the color, and the formation of new non-absorbable color plus the fixation of others which darken the bleached color. The effect of the oxidative reactions is most strikingly demonstrated when comparing atmospheric to vacuum bleaching. It will be noted that natural clay bleached better in the atmosphere, whereas activated clay, in a majority of eases, bleached better under vacuum (*Rich, 1960*).

- **Dosage of bleaching clay:** The dosage of bleaching clay is variable depending on both the process and the oil type. Chemical refining uses 0.5-2% on weight basis while physical refining consumes about 0.25-2%. However, the dark oil and fats may require as much as 2-4% to meet final color requirement (*Fransisco RV, Persio de Souza Santos. 2001*). *Dubravka et al. (2012)* studied the optimization of bleaching parameter for soya bean oil. Their result showed that the amount of clay had the greatest influence on bleaching efficiency. Temperature and clay dose significantly increased oxidative stability while increased clay dose reduced the tocopherol content of the bleached oil.
- **Bleaching time:** One important point is the contact time between oil and clay which should be between 20 and 40 min, depending on the quality of oil and the amount of clay used for the processing. Within this time, an equilibrium between coloring compounds adsorbed by the clay and coloring compounds remaining in the oil should be reached, whereas the ratio should be moved in the direction of coloring compounds adsorbed by the clay. By intensive mixing of the slurry, which improves the contact between oil and clay, this equilibrium can be reached within a relatively short time. After reaching this point, no more coloring compounds are absorbed from the oil by the clay.
- **Bleaching temperature:** The bleaching process is carried out under a vacuum with typical contact temperature in the range 80ºC - 130ºC. According to *Berbesi (2006),* bleaching temperature typically ranges from 90-125^{0}C and he stated that the contact time for effective bleaching typically ranges from 15 to 45 minutes, with 20 to 30 minutes being most common. He also noted that oil viscosity decreases with increasing temperature resulting in better dispersion of particles, improved clay oil interactions, and flowability. *James et al (2008)* reported that the optimum bleaching temperature is specific for a particular adsorbent and oil which is between 100 – 120^{0}C for palm oil.
- **Effect of adding Clay to “Hot” Oil and adding it to "Cold" Oil:** Adding clay to hot oil means that during the upbeat the oil is unprotected against oxidation, and hence some color fixation occurs. It reduces its adsorptive capacity because the moisture of the clay is driven off rapidly, causing collapse of the day's lattice structure, which in turn lowers its surface area before the clay has had an opportunity to adsorb color.

CHAPTER 3 MATERIALS AND METHOD

3.1 Materials

3.1.1 Equipment and Instruments

The following equipment's were used for the final research.

Table 3-1 List of equipment's and instruments

Instrument	Model	Use
Jaw crasher		Size reduction (1st)
Attrition mill	DIETZ-motoron kg 7311	Size reduction (2nd)
Mortar and pestle	5657 HAAN	Size reduction (3rd)
Sieve	Retsch, AS200	To sieve sample
Plastic bags	Falcon	To put samples
Drying oven	Memmert 100-800	To dry sample
Desiccator		To store the sample during cooling
Crucibles		To hold the sample
Balance	EP214C	To weigh sample
Measuring cylinder		To measure volume and to calculate swelling index
WiseStir® MSH-D Hotplate Magnetic Stirrer	MSH-20D	To activate raw bentonite with acid
Condenser and chiller		To prevent acid loss
Vacuum filter		To filter washed activated bentonite
pH meter	Jenway 3505	To measure pH
Rotary evaporator	RVO 400	To carry out bleaching process
Centrifuge	UNIVERSAL 320 R	To separate bleached oils
VIS-UV spectrophotometer	UVD-3200	To measure absorbance
Digital reading pipettes	ACURA 825/835	To take sample in small scale
Pycnometer	DURAN 50	To measure density
X-ray diffractometer	D8 Avance Brucker	To identify crystalline mineral phases of raw and activated bentonite
FTIR spectrometer	PerkinElmer	To obtain qualitative group for raw and activated bentonite
SEM	JSM-IT300	To identify the shape and surface morphology of raw and activated bentonite

3.1.2 Chemicals and reagents

Table 3-2 List of chemicals and reagents

Chemicals and Reagents	Use
Distilled water	Used for washing raw bentonite and activated bentonite, preparation and dilution of solution
Sulfuric acid	Used for activation of raw bentonite
Sodium bicarbonate	To adjust pH
Bentonite (local)	Used as bleaching agent
• Neutralized Niger seed oil • Neutralized Rapeseed oil	To carry out bleaching experiments
Hexane and petroleum ether	Used as a reference and to dilute oils for measuring absorbance
• Phenolphthalein • Potassium hydroxide • Ethyl alcohol	To determine acid value and free fatty acid

3.2 Methods

3.2.1 Collection and Characterization of Clay and Oil Samples

3.2.1.1 *Collection of neutralized Rape and Niger seed oil samples*

Pretreated and neutralized Niger seed oil and rapeseed oil was supplied by kibe Lemene edible oil factory, Ethiopia.

3.2.1.2 *Raw bentonite collection and pretreatment*

Bentonite was used as adsorbent precursor for the proposed study. Bentonite was collected from Ethiopian Mineral, Petroleum and Biofuel Corporation. This bentonite was originally came from Afar region Gewane. Sample was crushed, milled, screened, washed with distilled water and dried at 105ºC for 12hr to remove moisture and volatile organics from the clay. Then the dried raw bentonite was milled again using attrition mill and further size reduced using mortar and pestle. The powdered raw bentonite was sieved and the particle size between 74µm (200 mesh) to 150µm (100 mesh) was retained, weighed and preserved in an air tight plastic bag for the next step.

3.2.1.3 *Characterization of raw bentonite*

3.2.1.3.1 Moisture content determination (Loss on Drying- LOD method)

To determine the % moisture contents of the raw bentonite, 2g raw bentonite sample (m_1) was taken in crucible and weighed (m_2) and kept in an oven at 105ºC for 1hrs. Then the sample was transferred to desiccators to cool and weight, again it was transferred in to an oven until constant weight obtained (m_3) and % moisture content was determined by following the formula:

$$\%\, moisture\ content = \frac{m_2 - m_3}{m_1} * 100\% \qquad (1)$$

Where m_1= mass of sample, g, and

m_2= initial mass of sample and crucible, g.

m_3= final mass of sample and crucible, g.

3.2.1.3.2 Bulk Density Determination

The mass of empty 10ml graduated cylinder was measured and recorded (m_{ec}). Then a known amount of raw bentonite was transferred to the cylinder. The cylinder was tamped using rubber pad while the sample was being added until there was no further settling produced. After all sample was transferred, final mass of the cylinder was weighed (m_{sc}) and recorded. Finally, the bulk density of raw bentonite was calculated as follows:

$$\rho_B = \frac{m_{sc} - m_{ec}}{V_{cyl}} \tag{2}$$

Where ρ_B = Bulk density of raw bentonite, g/ml

m_{sc}= mass of sample and cylinder, g,

m_{ec}= mass of empty cylinder, g, and

V_{cyl}= volume of cylinder, ml.

3.2.1.3.3 Apparent Density Determination (ASTM D 1895 – 96)

The mass of empty pycnometer was measured (m_{ep}). Then approximately full of the pycnometer was filled with the sample using funnel. After all the sample was passed through the funnel, the excess on the top of the cup was immediately scraped off with a straightedge without shaking the cup. Then the weight was measured and recorded (m_{sp}). Since the pycnometer has definite volume the apparent density was calculated as follows:

$$\rho_A = \frac{m_{sp} - m_{ep}}{V_p} \tag{3}$$

Where ρ_A = Apparent density of raw bentonite, g/ml

m_{sp}= mass of sample and pycnometer, g,

m_{ep}= mass of empty pycnometer, g, and

V_p= volume of pycnometer, ml.

3.2.1.3.4 Swell index determination (ASTM D 5890 – 95)

Powdered raw bentonite was tested after drying to constant weight at 105°C and grounded using mortar and pestle to pass through a 100 mesh U.S. Standard Sieve. 2g of dried and finely ground sample was weighed. 90mL of reagent/distilled water was added to the clean 100mL graduated cylinder. Not more than a 0.1g increment of sample was removed with a volumetric spoon from weighing paper and carefully dusted it over the entire surface of water in the graduated cylinder over a period of approximately 30s. Then the inserted raw bentonite was allowed to wet, hydrate, and settle to the bottom of the graduated cylinder for a minimum period of 10min. The above procedures were continued until the entire 2g sample was completed. After the final increment, distilled water was added until it reached 100mL mark. After the minimum 16hr hydration period from the last increment addition, the volume level was recorded. And temperature of the slurry at the start and completion of the test was also recorded.

3.2.2 Preparation of Acid Activated Bentonite (Bleaching Earth)

The acid activation was carried out according to the method described by *N. Yildiz, Z. Aktas and A. Calimli (2004)*. Acid (H_2SO_4) activation of the bentonite was conducted in a hot plate magnetic stirrer. A reflux condenser was attached to prevent loss of acid and water. Acid concentrations were prepared as 1, 3, and 5 M. The ratio of the mass of clay to the volume of acid solution was 0.05 g/ml (1:5). The mixture of acid solution and the bentonite in the activation vessel was heated to 60, 75 and 90^0C with continuous stirring at 150rpm. The activation operation was completed in 4hr. After activation, the solid residue was filtered under vacuum, repeatedly washed with distilled water until reaching a neutral pH or free of $SO4^{2-}$. The samples were dried at 105°C for 4hr and grounded using mortar and pestle that would pass through a 74µm (200 mesh) sieve, weighed and stored in air tight plastic bag for further experimental purpose. Activated samples were designated as B_1, B_2, B_3, B_4, B_5, B_6, B_7, B_8 and B_9 where the numerical values indicate the run order. Yield percent was calculated using equation (1).

$$Y = 1 - \frac{(m_b - m_a)}{m_b} * 100\ \% \tag{4}$$

Where m_b= mass of raw bentonite before activation, g,

m_a= mass of raw bentonite after activation, g,

Y = yield, %.

Experimental Design

All the laboratory experiments related with activated bentonite preparation were based on a full factorial design where the different activation treatment factors were analyzed for different combination of their test levels. Using response surface method, the optimum combination of the operational factors was determined.

In this study a total of nine (9) bleaching activated bentonite samples were prepared. Randomization of experimental runs as well as appropriate analysis techniques were ensured through proper utilization of software package 'Design Expert'. Results from the analysis will help to make conclusion about the research.

Table 3-3 Experimental factors and levels for acid activation

Factors	Coded factor	Levels		
		Low (-1)	**Medium (0)**	**High (+)**
Sulfuric acid concentration (M)	**A**	**1**	**3**	**5**
Activation Temperature (^{0}C)	**B**	**60**	**75**	**90**

3.2.3 Investigation of effect of bentonite activation operating condition on the bleaching performances of adsorbent samples

To determine optimum activation conditions (acid concentration and activation temperature) a series of bleaching experiments were done with the chosen optimum condition of bleaching process and treated oil. Bleaching of the Niger seed oil with the prepared 9 activated bentonite samples was carried out according to the procedure reported by *Nde-Aga, Kamga, & Nguetnkam (2007).* 30ml of degummed, neutralized Niger seed oil was poured into a 250ml round bottom flask and heated up to a required temperature for the reaction on rotary evaporator under continuous stirring at 150rpm. When the rotary evaporator reached the set temperature, the activated bentonite clay sample was added. The reaction was carried out at 110^{0}C and the reaction times was 30min with dosage of 2%. At the end of the reaction, the bleached oil was separated using centrifuge under 6000rpm for 20 min. A total of 9 oil bleaching experiments were performed in order to screen the prepared samples and select the best one.

3.2.3.1 *Analysis of bleached oil and bleaching performance measurement*

The color of raw and bleached oil was measured using UV-Visible spectroscopy. The absorbance of the oil was measured as follows: 0.1g of bleached Niger seed oil was diluted in 7.5ml of petroleum ether and the absorbance of the sample determined at 445nm wavelength using petroleum ether as reference (*Nde Aga et al, 2007*). The percentage of oil bleached was calculated as follows:

$$\%CR = \frac{(Ab_o - Ab_x)}{Ab_o} * 100\ \% \tag{5}$$

Where $\%CR$ = percentage color reduction, %,

Ab_o = absorbance of the unbleached oils, and

Ab_x = absorbance of the bleached oils.

The best activated bentonite with high bleaching oil performance was selected for further bleaching experiments and clay characterization.

3.2.4 Characterization of raw and selected activated bentonite samples

3.2.4.1 *X-ray diffraction (XRD)*

XRD was used to determine the mineralogical composition of the raw and activated bentonites. X–ray diffraction (XRD) patterns was recorded with D8 Avance XRD of Brucker powder diffractometer with Cu-Kα (λ=1.540593-1.544414 Å, 40 KV and 15 mA) radiation having a continuous scanning mode with speed of 10 deg/min. X-ray diffractograms of raw and activated bentonite powders were obtained for the 2θ angles ranging from 10^0 to 70^0 with scan step 0.02^0. Diffraction peaks of crystalline phases were compared with those of standard compounds. This XRD analysis was performed in college of natural science, department of chemistry, AAU.

3.2.4.2 *FTIR spectra*

To obtain qualitative group and complementary evidence for the intercalation of H^+ ions into the bentonite minerals, FTIR spectra were performed in the region of 400-4,000 cm^{-1}. FTIR spectra were obtained using Spectrum 65 FT-IR (PerkinElmer), with samples prepared by the conventional KBr disc method. All the spectra were recorded and processed using IR solution software. This FTIR analysis was performed in college of natural science, department of chemistry, AAU.

3.2.4.3 *Scanning Electron Microscopy and Energy Dispersive Spectroscopy*

Scanning Electron Microscopy (SEM) aims to look at the structure and shape of the surface of bentonite, while to know the composition of the building blocks of bentonite used Energy Dispersive Spectroscopy (EDS). Morphological characteristics of the bentonite were examined using a JSM-IT300 SEM at accelerating voltage of 20 kV, beam size 3.0, working distance 12.1 and magnification of 1000. The samples were coated with carbon under low vacuum before analysis to prevent the accumulation of static electric charge on the surface of the bentonite particles. Semi quantitative chemical analysis of raw and activate bentonite was also obtained using an EDS (Acquisition Parameter: 20.0 kV, 7.47500 nA and energy range 0-20 keV) attached to a SEM. This SEM analysis was performed in Leather Industry Development Institute (LIDI).

3.2.5 Investigating the effects of operating parameters on bleaching performance of activated bentonite for Niger and Rape seed oil

3.2.5.1 *Bleaching Experiment*

An appropriate type of oil (30ml) was measured and transferred in to a round bottom flask and heated to a temperature of about 50˚C. A known weight of activated clay was added to the preheated oil under continuous stirring at 150rpm in a rotary evaporator. The oil-clay mixture was gradually heated to a specific bleaching temperature for specific time (according to the design of experiment). After the bleaching process, the oil treatment, the sludge was separated by centrifuge and the bleached oil samples was put into sample holder. The process was carried out for both Niger seed and rapeseed oils. The bleached oils were designated as N_1-N_{27}(Niger seed oil) and R_1-R_{27} (Rapeseed oil) where the numerical values indicate the run order.

Experimental Design

The bleaching experiment was based on a full factorial design resulting total of 29 randomized experimental runs for each type of oil.

Table 3-4 Experimental factors and levels for testing belching performance

Factors	Coded factor	Levels		
		Low (-1)	**Medium (0)**	**High (+)**
Activated bentonite/oil ratio (w/v %)	**A**	**1**	**2.5**	**4**
Bleaching Temperature (^{0}C)	**B**	**90**	**110**	**130**
Bleaching time (min)	**C**	**15**	**30**	**45**

In order to compare the bleaching performance, the bleaching process was also carried out using raw bentonite for both Niger seed and rapeseed oil at center point (0,0,0) of design expert.

3.2.5.1 *Analytical techniques for determination of Physicochemical Properties of Bleached Oil*

3.2.5.1.1 Percentage Color Reduction

The percentage color reduction of the oil before and after bleaching was determined using VIS-UV spectrophotometer. A full absorption spectrum was made over all the wave lengths, between 320 nm and 670 nm. The maximum absorbance of the samples was observed at the maximum wavelength 450 nm using hexane as reference. The samples were diluted in n-hexane in the proportion 0.1 g of oil to 2 ml of solvent. The bleaching capacity of the adsorbent was determined using equation (5).

3.2.5.1.2 Acid Value and Percentage Free Fatty Acid (ASTM D 1980 – 87)

The acid value is the number of mg of potassium hydroxide required to neutralize the free acid in 1 g of the substance. Acid value and free fatty acid content of the oil before and after bleaching was determined using titrimetric method. First 10 g/L phenolphthalein indicator solution was prepared by dissolving 1 g of phenolphthalein in 100 mL of ethanol (95 %). Then 0.1N potassium hydroxide stock solution was prepared and allowed to cool and settle in a stoppered bottle for 5 days. 5g of oil sample was weighed and transferred in 500mL flask. Then 100mL of hot ethyl alcohol and 0.5mL of the phenolphthalein indicator solution was added. After addition of the solution, it was titrated immediately while shaking with 0.1N KOH solution to the first pink color that persists for 30s. Finally, the acid value and FFA was calculated as follows:

$$Acid\ Value = \frac{56.11 * V * N}{M} \tag{6}$$

Where V = the volume of Potassium hydroxide used, ml,

N = the exact normality of KOH solution, N, and

M= the mass of oil sample, g.

$$\%\ FFA = 0.503 * acid\ value \tag{7}$$

Where $\%\ FFA$ = percentage free fatty acid, mg KOH/g oil.

CHAPTER 4 RESULT AND DISCUSSION

4.1 Proximate Composition and Some Characteristics of Raw Bentonite

Table 4-1 Results of physical characterization of raw bentonite

Characteristics	Result
Moisture content (%)	**8.209**
Bulk density (g/cm^3)	**1.4067**
Apparent density (g/cm^3)	**0.8179**
Swell index (mL/2g)	**13**

The moisture content for the clay lies within 8–18% recommended by *Wiedermann (1981)* as being appropriate to ensure that the clay structure does not buckle and loses its adsorptive capacity. The moisture content of the raw bentonite used in this study was found to be 8.209% using three replications and it was laid in the specified range. Constant weight of samples was obtained after 4 hrs. This indicates that in addition to free water, interlamellar space of the raw bentonite contains variable amounts of water molecules, which are electrostatically bound and form hydrates with the exchangeable cations. The result of the moisture was obtained at minimum of the range. It can conclude that the raw bentonite loses its moisture contain due to the period that stayed after collection.

Bentonite density when dry varies depending on the quality, and may range from 2.2 to 2.8 g/cm^3. Bentonite apparent density, when quarried and piled under natural moisture conditions, ranges from 1.5 to 1.8 g/cm^3. The apparent density of milled bentonite products varies depending on mill fineness, ranging from 0.7 to 0.9 g/cm^3. The result shows that it lies in the range. The bulk density of a clay is one of its most informative properties, such as the bulk density is inversely proportional to the adsorptive capacity and to the clay's filtration rate.

Swell Index test is an index method that enables evolution of swelling properties of materials containing expansive clay minerals. Output of this method is also a rough estimate of the smectite content in the sample and used to identify the type of bentonite. The result for swelling index of the raw bentonite was obtained around 13 ml/2g and similar as Ca-bentonite (non-swelling type) in *Ahonen et al. (2008)* and *Kumpulainen and Kiviranta (2010).*

4.2 Bleaching performances of different activated bentonite prepared using different activating protocol

4.2.1 Statistical analysis on acid activation

In order to determine the maximum bleaching capacity and yield with a model for acid activation of bentonite, a general full factorial design was used. Sulfuric acid concentration (A) and activation temperature (B) were chosen as independent variables to model and optimize according to previous experiments. The design matrix for two variables is varied at three levels (+1, 0 and -1).

Initially, the full factorial experimental designs were used to obtain first-order model with interaction terms effective on bleaching capacity and yield of different activated bentonites. As usual, the experiments were performed in random order to avoid systematic error. As the analysis of variance reveals that quadratic and linear terms were effective on bleaching capacity and yield of activated bentonite respectively.

The result of analysis of variance (ANOVA) for response surface quadratic model for bleaching capacity is shown in Table 4.2. The P values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables. The larger the magnitude of F-test value and the smaller the magnitude of P-values, the higher the significance of corresponding coefficient. Values of P less than 0.05 indicate that the model terms are significant. In this case, B, AB and A^2 are the significant model terms.

The fitness of the model equation was also expressed by the coefficient of determination, R^2. The adequacy of the model was tested by analysis of variance. The value of R-squared for the developed correlation is 0.9819. It implies that 98.19% of the total variation in the percentage of color reduction is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Appendix B.

Table 4-2 Design expert output (ANOVA) for bleaching capacity

```
Response 1:   % color reduction
ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares]
                Sum of                 Mean           F
  Source       Squares      DF       Square       Value         Prob > F
  Model         251.50       5        50.30       32.61           0.0081  significant
      A      2.817E-003      1   2.817E-003  1.826E-003           0.9686
      B         195.51       1       195.51      126.75           0.0015
    A^2          34.58       1        34.58       22.42           0.0179
    B^2           0.38       1         0.38        0.25           0.6520
     AB          21.02       1        21.02       13.63           0.0345
Residual          4.63       3         1.54
Cor Total       256.13       8

Std. Dev.          1.24                   R-Squared       0.9819
   Mean           72.77               Adj R-Squared       0.9518
   C.V.            1.71              Pred R-Squared       0.7910
  PRESS           53.54              Adeq Precision       17.598

Final Equation in Terms of Coded Factors:

 % color reduction =
           +75.84
           -0.022 * A
            +5.71 * B
            -4.16 * A^2
            -0.44 * B^2
            -2.29 * A * B
```

The result of analysis of variance (ANOVA) for response surface linear model for the second response (yield) is shown in Table 4.3. In this case, only A and B are the significant model terms. The regression model obtained is also found in this table.

Table 4-3 Design expert output (ANOVA) for yield response

```
Response 2:       yield
ANOVA for Response Surface Linear Model
Analysis of variance table [Partial sum of squares]
               Sum of             Mean           F
  Source      Squares     DF     Square       Value       Prob > F
  Model        429.43      2     214.72       37.53         0.0004  significant
      A        120.69      1     120.69       21.10         0.0037
      B        308.74      1     308.74       53.96         0.0003
Residual        34.33      6       5.72
Cor Total      463.76      8
```

Std. Dev.	2.39	R-Squared	0.9260
Mean	76.09	Adj R-Squared	0.9013
C.V.	3.14	Pred R-Squared	0.8149
PRESS	85.85	Adeq Precision	16.884

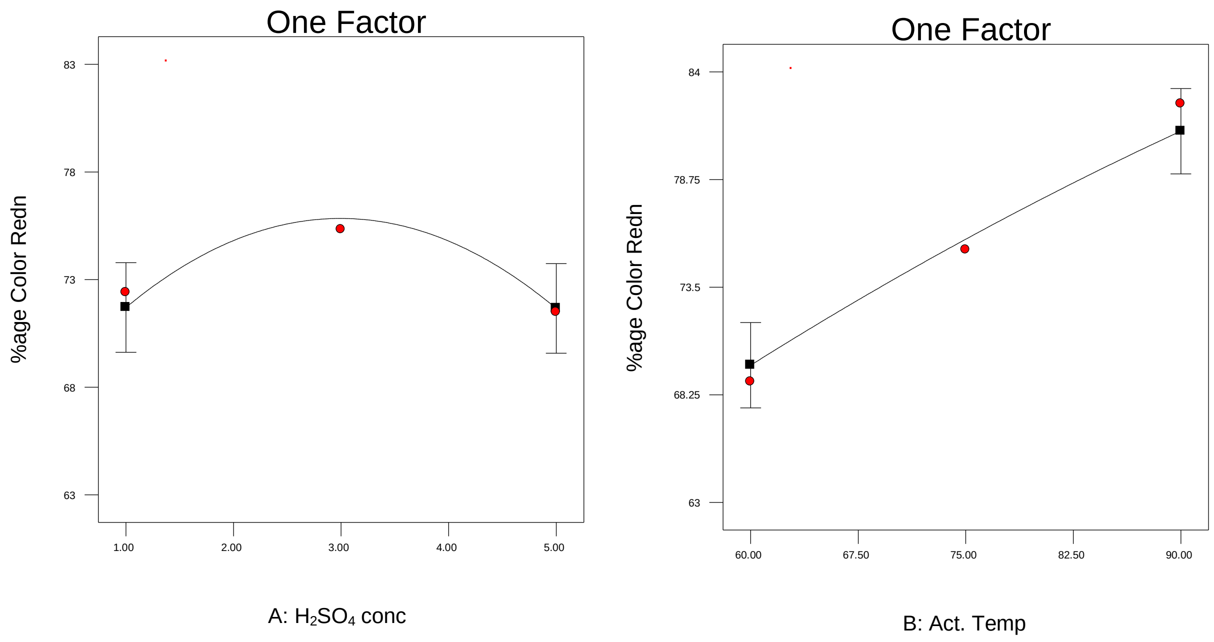
Final Equation in Terms of Coded Factors:

yield =
+76.09
-4.49 * A
-7.17 * B

4.2.2 Effect of individual parameters on percentage color reduction and yield

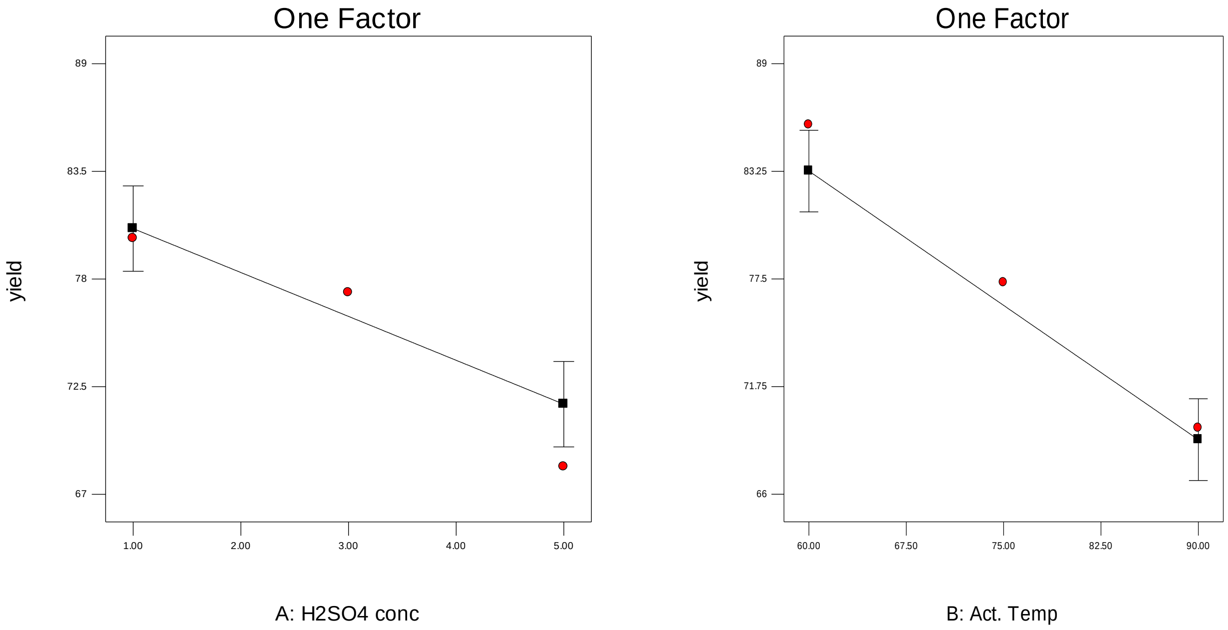
It is seen from the figures that bleaching capacity increased with increase in activation temperature and acid concentration. As expected, the individual effect of the activation temperature is almost stronger than that of the acid concentration.

From figure 4.2, it can be said that percentage yield is negatively affected by increase in temperature as well as acid concentration. This is due to the bentonite powder dissolves in high amount of acid concentration and temperature in addition to loss during washing and filtration process.



(A) **(B)**

Figure 4.1 Individual effect on color reduction (A) Acid concentration effect at 75^{0}C (B) Temperature effect when acid concentration 3M



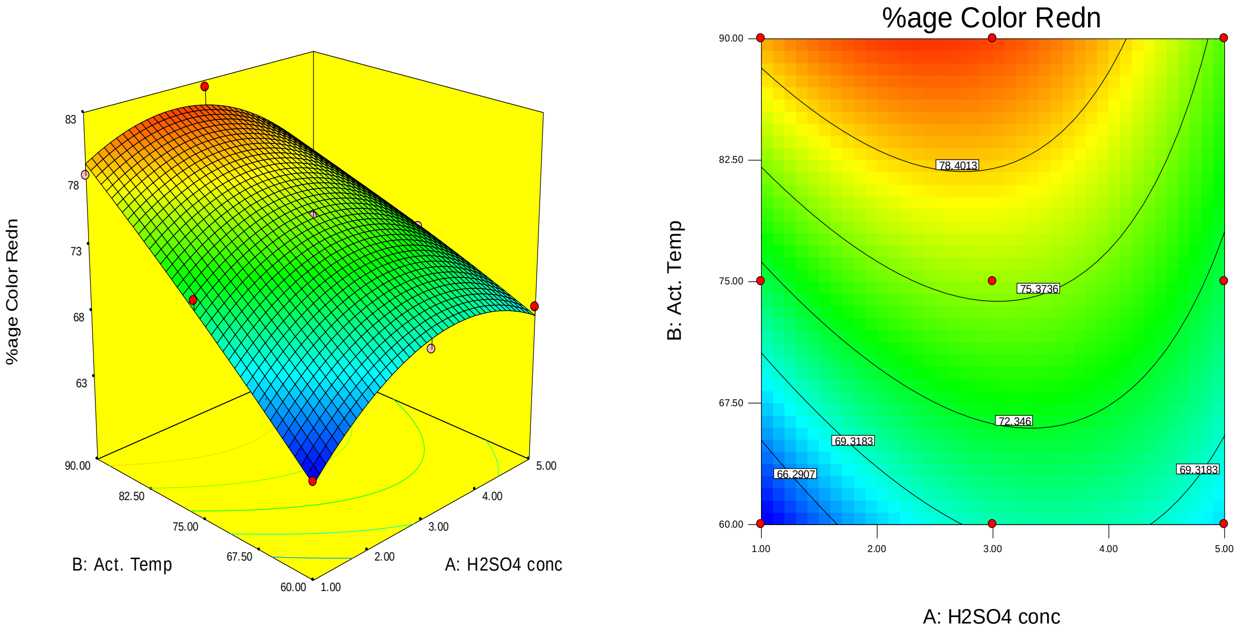
(A) **(B)**

Figure 4.2 Individual effect on yield (A) Acid concentration effect at 75^{0}C (B) Temperature effect when acid concentration 3M

4.2.3 Interaction effects on percentage color reduction

The study of the effects of the combinations of two factors were discussed and some important results described in the contour diagrams and 3D response surface plots shown below (figure 4.3). Since there is no interaction effect on yield there is no need to discuss.

There is interaction effect between acid concentration and activation temperature. But it was observed that above 3M, there was decrease in the bleaching efficiency. Further increase of the concentration of the acid solution used for clay activation did not increase the bleaching power of the adsorbents. This was attributed to the fact that the increase in the surface area is due to the formation of silica but the surface area of H-clays almost constant over strong acid leaching and silica has very poor bleaching power of oils.



(A) **(B)**

Figure 4.3 (A) 3D Response surface plot of temperature vs acid concentration and (B) Contour plot of temperature and acid concentration [Response: color reduction]

4.2.4 Optimal acid activation parameters to prepare efficient bleaching bentonite

Preliminary observations show that bleaching capacity varies significantly according to the experiment parameters, reaching values of 63.45-82.44% under certain operating conditions. A clear evidence for the judicious choice of the parameters range is that the highest bleaching capacity is obtained around 3M acid concentration and at 90°C of activation temperature. Considering the other response, highest percent yield is obtained at minimum acid concentration and temperature. But the main objective of this research is to find the optimum activation parameters for the highest performance of bleaching. The bleaching parameters were optimized subject to constraint shown in Table 4.4. Four solutions were found and the solution with the highest desirability was chosen. In other to verify the optimization results, the selected parameters were validated in the laboratory with suggested values as shown in Table 4.5. The result from the experiments confirmed the selected solutions.

Table 4-4 Optimization constraints and solutions for activation parameter

Constraints

Name	**Goal**	**Lower Limit**	**Upper Limit**
H_2SO_4 conc	is in range	1	5
Temp	is in range	60	90
% color redn	maximize	63.45	82.44
yield	is in range	67.23	88.27

Solutions

Number	**H_2SO_4 conc**	**Temp**	**% color redn**	**yield**	**Desirability**	
1	2.45	90.00	81.4308	70.1584	0.947	Selected
2	2.41	90.00	81.4299	70.2285	0.947	
3	2.53	90.00	81.4239	69.9796	0.946	
4	3.56	90.00	80.1266	67.6508	0.878	

Table 4-5 Validation result for sulfuric acid activated clay

Parameters	**Model predict**	**Experimental result**
H_2SO_4 conc. (M)	2.45	3
Activation temperature (^{0}C)	90	90
%age color reduction (%)	81.4308	82.44
Yield (%)	70.1584	69.53

After selecting the best activated bentonite with high bleaching oil performance further bleaching experiments and clay characterization was conducted.

4.3 Characterization results of raw and activated bentonite

After determining the optimum acid activation parameters, additional 50gm of raw bentonite activated (B_2) at optimum conditions (3M sulfuric acid concentration and at 90^oC). Then instrumental characterizations which are XRD, FTIR and SEM were done for raw and activated bentonite and the results discussed as follows.

4.3.1 XRD result

Mineral compositions of raw and activated bentonite clay were determined by XRD studies. The occurrences of minerals in clay were identified by comparing 'd' or 2theta values. Characterization of XRD patterns for raw bentonite indicates the presence of montmorillonite (Mo), cristobalite (Cr), quartz (Q), muscovite (Mu), hematite(H) and feldspar (F) as the major phases.

Table 4-6 Description on indicated minerals

Mineral name	Formula	Crystal system
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$	Monoclinic
Quartz	SiO_2	Trigonal (hexagonal axes)
Hematite	Fe_2O_3	Hexagonal
Cristobalite	O_2Si	Tetragonal
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$	Monoclinic
Feldspar	$KAlSi_3O_8$ – $NaAlSi_3O_8$ – $CaAl_2Si_2O_8$	Triclinic

In comparison with the diffraction pattern of the raw material, the changes in the diffractogram of the activated material, shown by a decrease in the intensities of all reflections except quartz and feldspar, indicating that they are resistant to acid attack. It can be seen that, the acid treatment affected mainly the montmorillonite phases. This means that the process favors the production of amorphous phase by decomposing montmorillonite structure. On the other hand, since the montmorillonite peak is still present after acid treatment, it can be assumed that the structure has been partially destroyed. Generally, this change is expected to have a positive impact on the adsorption efficiency of the activated clay.

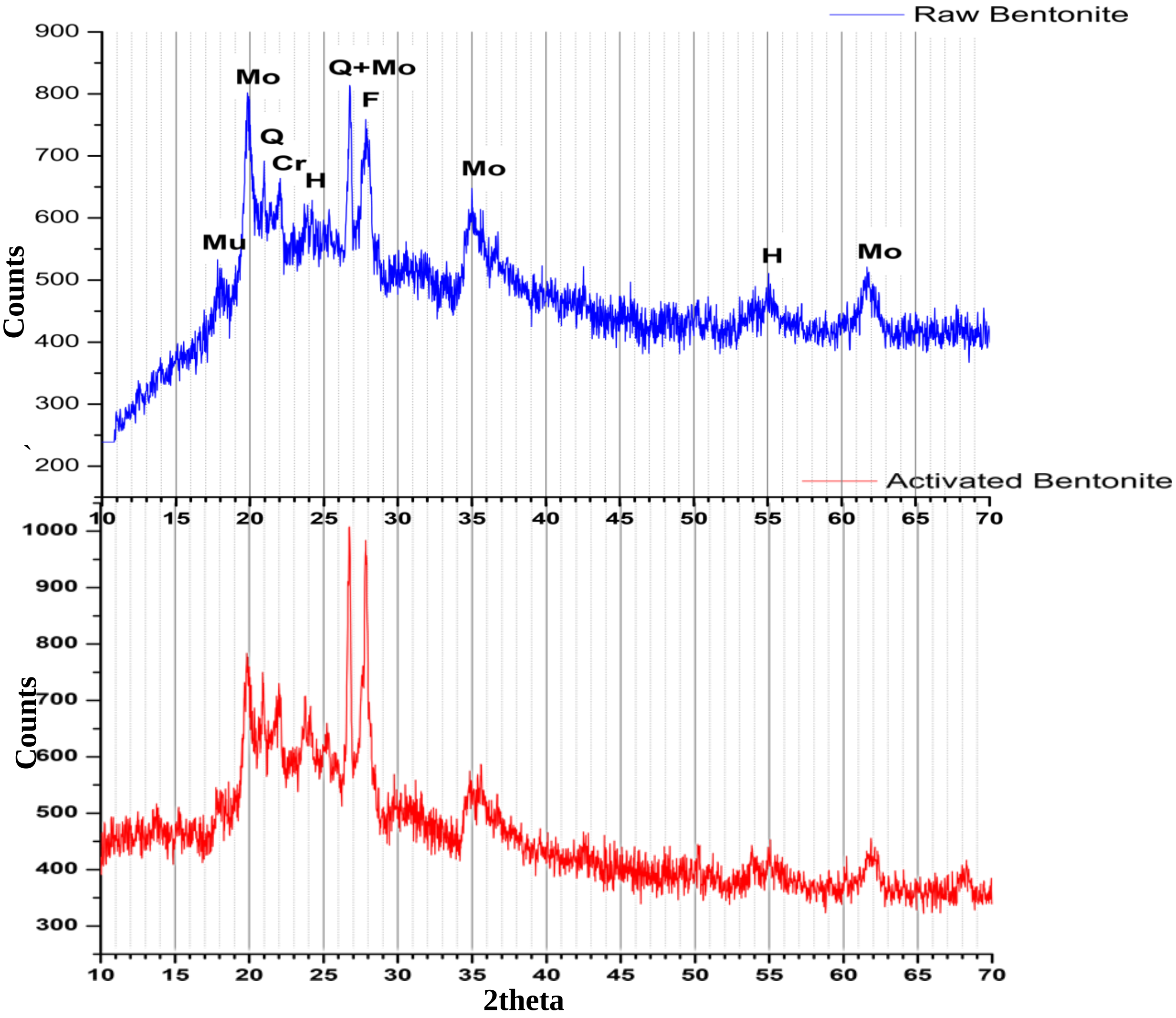


Figure 4.4 X-ray diffraction patterns for raw and activated bentonite

4.3.2 FTIR result

To recognize mineral species and identify characteristic bands of the raw and activated bentonite, the FTIR spectra were performed in the range from 4000 to 400 cm^{-1} to investigate the effect of activation on the chemical composition of the bentonite. Nevertheless, observed bands (in the range, 4000–500 cm^{-1}) have been tentatively assigned. Published collections of spectra of clay minerals as those reported by *Palanivel and Velraj* (2002) are very useful for identification and characterization of the bentonite mineral. Figure 4.5 shows that there are three main absorption regions: 3000–3800 cm^{-1}, 1300–1800 cm^{-1}, and 500–1200 cm^{-1}, and sharp differences could be found in each region of the bentonite samples.

The IR spectrum of raw bentonite indicates that montmorillonite is the dominant mineral phase in this bentonite. The KBr curve of raw bentonite was characteristic of montmorillonite with a single sharp band at 3620 cm^{-1} and a broad band at 3435 cm^{-1} of the OH stretching vibration of structural hydroxyl groups and water. The absorption band at 1635 cm^{-1} was attributed to the OH deformation mode of water. The 692 cm^{-1} band corresponded to coupled Al–O and Si–O out-of-plane vibrations. Quartz was present as indicated by the bands at 791 cm^{-1} and 538 cm^{-1}, in agreement with XRD result.

FTIR is very sensitive to the structural changes which occur in the clay upon acid treatment (Breen et al., 1995) and the IR data recorded herein suggest that both the octahedral and tetrahedral sheets were susceptible to acid attack. The intensity of stretching bands observed at 3620 cm^{-1} (Al–OH–Al along with the Al–Mg–OH stretching vibrations) decreased after acid activation. Activation with acid also resulted in the decrease of the peaks of the bands associated with the adsorbed water at 3435 (H–O–H stretching) and 1635 cm^{-1} (H–O–H bending). It is due to the removal of octahedral cations, causing the loss of water and hydroxyl groups coordinated to them. After acid leaching, the intensity of the band at 1035 cm^{-1} increases due to the formation of three–dimensional networks of amorphous Si–O–Si units. The intensity of band at 692 cm^{-1} (Al–OH–Si bending) almost disappeared with acid activation, signifying the partial dissolution of aluminum ions present in the octahedral sheet of bentonite. The raw bentonite leads to the formation of amorphous silica, indicated by the increased intensity of the peak, which may provide more adsorption sites.

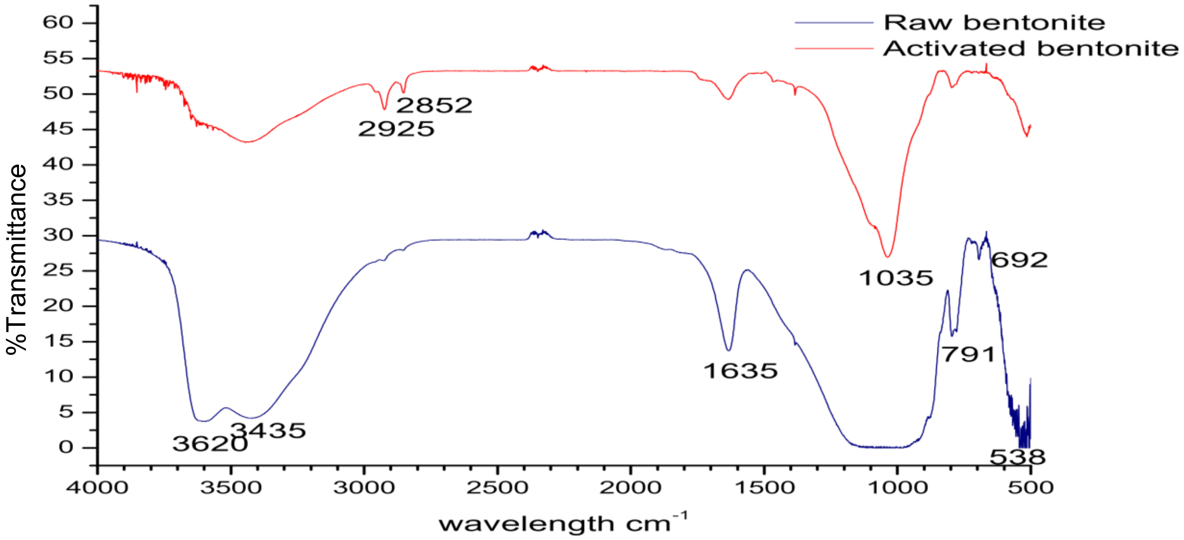
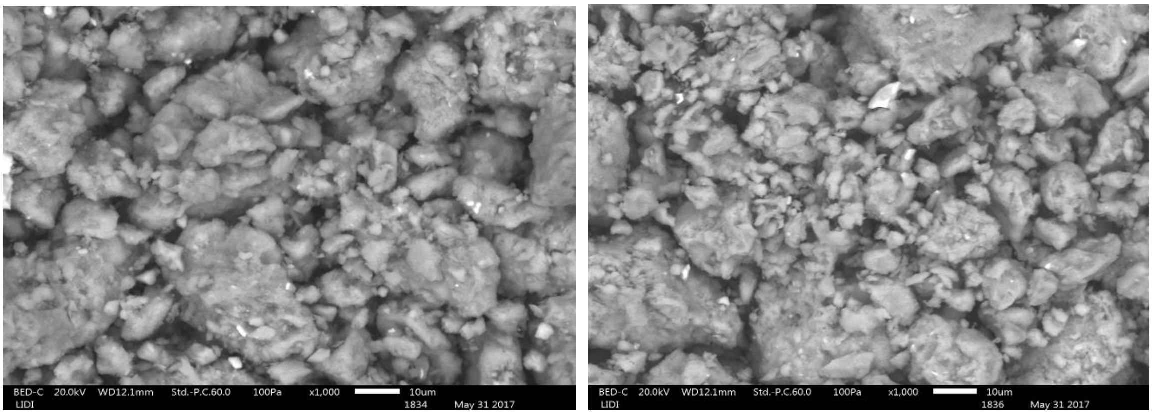


Figure 4.5 FTIR spectra of raw and activated bentonite

4.3.3 SEM and EDS result

The SEM examination was carried out to assess the effect of the activation protocols on the surface morphology of the bentonites. The surface morphology of the raw and activated bentonite which are magnified 1000 times, as shown in figure 4.6. From the figure, the result shows activating the bentonite makes the clay surface a little bit more porous. Acid can create new pore so that it will increase the acidity of its surface by cation substitution such as Al^{3+}, Fe^{3+} and Ca^{2+} with H^+ *(Ejikeme,2013*).



(A) **(B)**

Figure 4.6 SEM images (A) Raw bentonite and (B) Activated bentonite

In semi quantitative EDS microanalysis in SEM, the mass fractions and weight percent of the elements present in the raw and activated bentonite was calculated. ZAF method standardless quantitative analysis, given in Table 4.7, indicates the presence of silica, alumina and iron as major constituents, along with traces of sodium, potassium, magnesium, calcium, and titanium in the form of impurities and mass fraction percent of carbon and oxygen also detected. The result showed that some interlayer cations were removed as a result of the activation indicating that more active sites are generated on the clay surface. Acid treatment dissolves some $A1^{+3}$, Fe^{+3} and Mg^{+2} from the lattice structure and causes the exchange of K^+, Na^+, Ca^{+2} by H^+ in the interlamellar spaces (*Girgis and Ishak 1978; Clarke 1985*).

The amount of Ca^{2+}, Na^+, Mg^{2+} and K^+ removal by acid treatment corresponds to the exchangeable cations which are located out of the montmorillonite lattice (between layers), so that they dissolve easily under mild condition. However, a considerable amount of these elements is still found in the activated clays due to the presence of impurities, mainly, feldspar that has calcium, sodium and potassium, and is resistant to acid attack. Dissolution of Al^{3+} and Fe^{2+} cations is less than exchangeable cations this indicates that they need stronger condition to be removed from montmorillonite structure.

The Si^{4+} cations at tetrahedral sites of smectite are not dissolved by acid activation. The increase in relative content of these cations occurs as a result of depletion of the cations from the interlayer and octahedral sheets of the montmorillonite. In the 2:1 clay minerals, the tetrahedral cations are generally the most resistant to acid attack, followed by the octahedral cations, with the exchangeable cations the most vulnerable (*M. M. Kashani, A. A. Youzbashi and Z. Amiri, 2011*).

Table 4-7 ZAF Method Standardless Semi Quantitative Analysis for Raw and Activated Bentonite

Element	KeV	Mass% (Raw)	Mass% (Activated)
C K	**0.277**	**8.38**	**6.17**
O K	**0.525**	**48.83**	**52.56**
Na K	**1.041**	**0.80**	**0.32**
Mg K	**1.253**	**1.49**	**0.79**
Al K	**1.486**	**6.72**	**5.48**
Si K	**1.739**	**21.79**	**26.00**
Cl K	**2.621**	**0.26**	**-**
K K	**3.312**	**1.76**	**1.25**
Ti K	**4.508**	**0.98**	**1.53**
Ca K	**3.690**	**1.53**	**0.91**
Fe K	**6.398**	**7.47**	**4.99**
Total	**-**	**100%**	**100%**

4.4 Bleaching performance of selected activated bentonite on Niger and Rapeseed oil under different bleaching parameters

4.4.1 Statistical Analysis on Bleaching Performance

Optimization of the bleaching parameters was done using the chosen activated bentonite sample (B_2). Optimization was carried out using full factorial design with three factors (clay dosage percent, the bleaching time and bleaching temperature) and one response (%CR). Statistical analysis was carried out to determine correlation coefficients of the model as a function of the responses. The statistical summary of the design and the Experimental Design are shown in Appendix B.

Table 4.8 and table 4.9 show sequential model sum of squares for percentage color reduction of Niger seed and Rapeseed oil bleached respectively. The models were chosen because of their high correlation coefficient (actual and adjusted) value as shown in Appendix B.

Table 4-8 Sequential Model Sum of Squares for %CR of Niger seed oil

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p value Prob > F	
Mean vs Total	2.307E+005	1	2.307E+005			
Block vs Mean	3.24	1	3.24			
Linear vs Block	141.85	3	47.28	8.16	0.0006	
2FI vs Linear	76.02	3	25.34	8.45	0.0007	Suggested
Quadratic vs 2FI	0.73	3	0.24	0.070	0.9751	
Cubic vs Quadratic	28.34	7	4.05	1.31	0.3296	Aliased
Residual	33.94	11	3.09			
Total	2.310E+005	29	7965.15			

Table 4-9 Sequential Model Sum of Squares for %CR of rapeseed oil

Sequential Model Sum of Squares [Type I]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	2.637E+005	1	2.637E+005			
Block vs Mean	3.47	1	3.47			
Linear vs Block	8.77	3	2.92	7.89	0.0008	
2FI vs Linear	5.46	3	1.82	11.14	0.0001	
Quadratic vs 2FI	1.20	3	0.40	3.24	0.0465	Suggested
Cubic vs Quadratic	1.09	7	0.16	1.51	0.2602	Aliased
Residual	1.14	11	0.10			
Total	2.637E+005	29	9093.14			

4.4.2 Test for Significance and Accuracy of the Model

The levels of significance of the models were tested using the p-value. As shown in Table 4.10 and Table 4.11 p-value less than 0.05 indicate the model terms are significant and p-values greater than 0.1 indicate model terms are not significant.

For Niger seed oil, it can be seen that the model terms A, C, AB, AC and BC are significant. A, B and C represents bleaching temperature, bleaching time and clay dosage respectively. It can be inferred from this test that varying the clay dose and bleaching temperature will have effect on the percentage color reduction of the bleached Niger seed oil. But bleaching time has no significant effect and interaction effect between all the factors are significant.

For rapeseed oil, it can be seen that the model terms B, AB, AC, BC and A^2 are significant. This indicate that, bleaching time has more effect on percentage color reduction of rapeseed oil compared to others and quadratic effect of bleaching temperature is significant. And also, interaction effects between all factors are significant.

The significance of the model was tested further by plotting the actual experimental values against the model prediction values as shown in Appendix B. It can also be observed from the plots that some points lie on the 45˚ line while others are not too far from it showing that the model predictive.

Normal probability plots of the residuals are shown in Appendix B. Since the residuals lie approximately along a straight line, any problem was not suspect with normality in the data. There are no indications of severe outliers.

Table 4-10 Analysis of variance for response surface 2FI model for %CR of Niger seed oil

Response : %age CR
ANOVA for Response Surface 2FI Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	3.24	1	3.24			
Model	217.87	6	36.31	12.10	< 0.0001	significant
A-B.Temp	118.32	1	118.32	39.44	< 0.0001	
B-B.Time	3.13	1	3.13	1.04	0.3185	
C-Dosage	20.39	1	20.39	6.80	0.0165	
AB	13.25	1	13.25	4.42	0.0478	
AC	44.39	1	44.39	14.79	0.0009	
BC	18.38	1	18.38	6.12	0.0219	
Residual	63.01	21	3.00			
Lack of Fit	60.72	20	3.04	1.33	0.6046	not significant
Pure Error	2.29	1	2.29			
Cor Total	284.11	28				

Table 4-11 Analysis of variance for response surface quadratic model for %CR of rapeseed oil

Response: **%age Color Redn.**
ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Block	3.47	1	3.47			
Model	15.44	9	1.72	13.85	< 0.0001	significant
A-B.Temp	0.45	1	0.45	3.67	0.0714	
B-B.Time	8.24	1	8.24	66.57	< 0.0001	
C-Dosage	0.072	1	0.072	0.58	0.4550	
AB	1.29	1	1.29	10.40	0.0047	
AC	2.42	1	2.42	19.56	0.0003	
BC	1.76	1	1.76	14.18	0.0014	
A^2	0.79	1	0.79	6.40	0.0210	
B^2	0.30	1	0.30	2.42	0.1374	
C^2	0.11	1	0.11	0.91	0.3540	
Residual	2.23	18	0.12			
Lack of Fit	2.14	17	0.13	1.36	0.5971	not significant
Pure Error	0.092	1	0.092			
Cor Total	21.13	28				

4.4.3 Development of regression model equation

The equations generated from the fitted surface response 2FI and quadratic models for the bleaching operation of Niger seed and rapeseed oil are shown in Equations (8) and (9), respectively. These equations are mathematical representation of the experimental results and can be used to determine the bleaching parameters required to achieve a particular color reduction of oil prior the experiment. *Kumar et al. (2008)* stated that when regression coefficient has a positive sign, the increase of the associated factor causes an increase in response and a negative sign would cause a decrease in the optimization parameter.

$$\%CR = 89.76 - 2.56\,A + 0.42\,B + 1.06\,C - 1.05\,AB - 1.92\,AC - 1.24\,BC \tag{8}$$

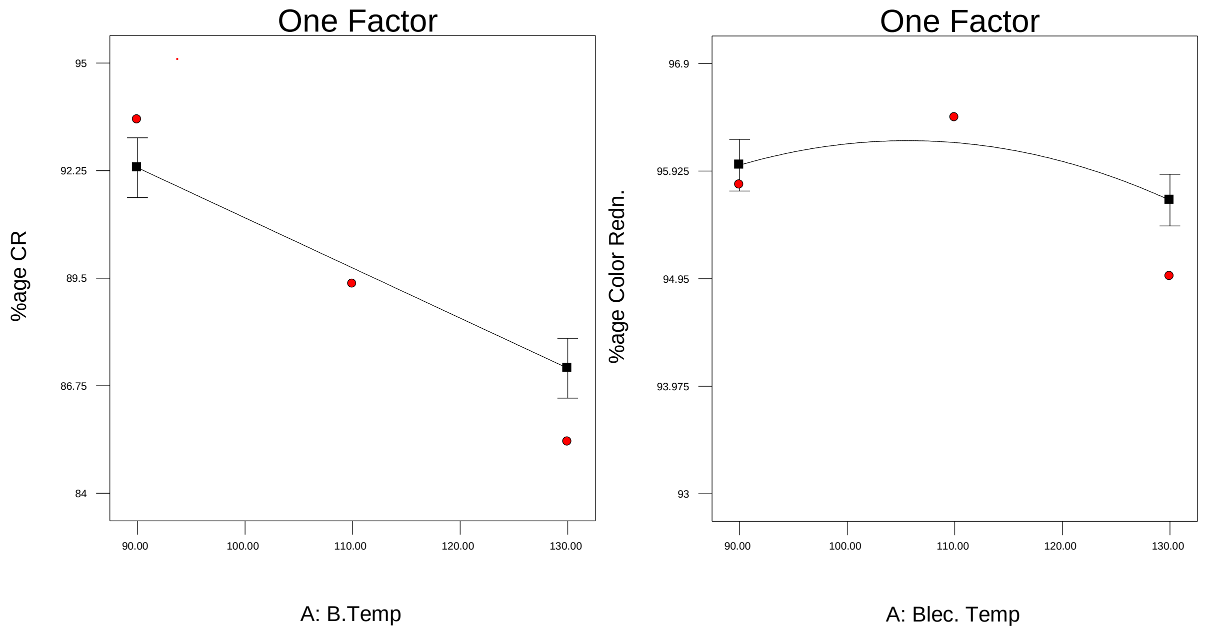
$$\begin{aligned}\%CR = 96.18 - 0.16\,A + 0.68\,B + 0.063\,C - 0.33\,AB - 0.45\,AC \\ - 0.38\,BC - 0.36\,A^2 - 0.22\,B^2 - 0.14\,C^2\end{aligned} \tag{9}$$

4.4.4 Effect of Individual Parameters on Color Reduction

Figures 4.7- 4.10 show the effect of individual parameters on color reduction of Niger seed and rapeseed oil. It is observed that the bleaching power of the adsorbent and effect of each factor varies from one type of oil to the other.

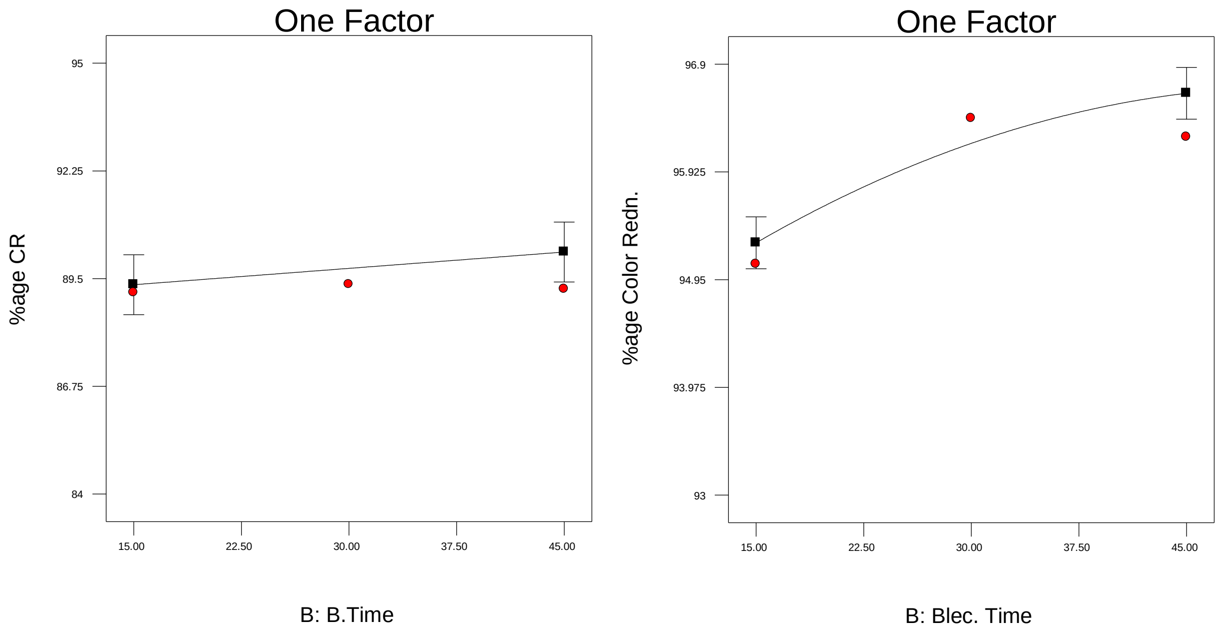
The bleaching performance of the Niger seed is negatively affected by temperature. As temperature increase the percentage color reduction decreases. The decolorization of the oil is fast in the first 30 min and progresses much more stable and reaches equilibrium thereafter. It is also observed that the bleaching power increases with the increase in clay dosage. This result is in line with the work of *Durbrvka et al. (2012)* which stated that high clay content enhances the removal of impurities in oil.

From figure 4.8 (B), it can be shown that the bleaching power of rapeseed oil is mainly affected by bleaching time and it has a positive effect. The percentage color reduction reaches equilibrium almost after 40 min. It is also observed that the bleaching power increased with the increase temperature up to the value of 110^0C. At this value the bleaching power is greater than 95%. Beyond 110^0C there is no more appreciable improvement in the bleaching power. The clay dosage was varied from an adsorbent oil ratio of 1% to 4%. It was observed that increasing the clay dosage increased the bleaching efficiency however, the results clearly indicate that the bleaching efficiency increases to an optimum value from which further increase in the adsorbent dosage has no significant effect on them.



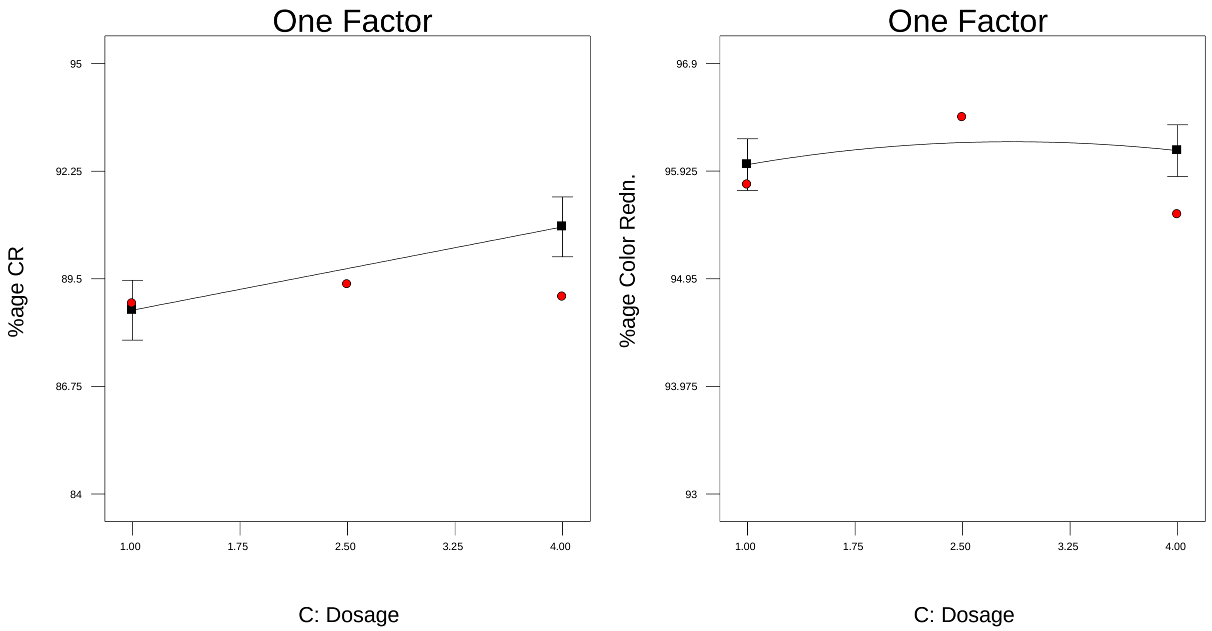
(A) **(B)**

Figure 4.7 Effect of temperature when time is 30min and clay dosage 2.5% for (A) Niger seed oil and (B) Rapeseed oil



(A) **(B)**

Figure 4.8 Effect of time at 110^{0}C and clay dosage 2.5% for (A) Niger seed oil and (B) Rapeseed oil

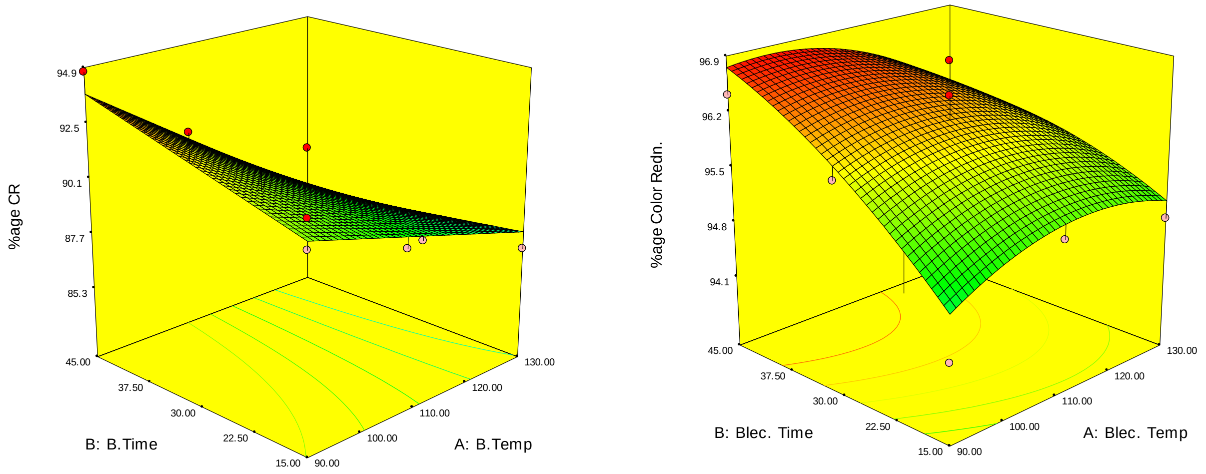


(A) **(B)**

Figure 4.9 Effect of clay dosage at 110^{0}C and time 30min for (A) Niger seed oil and (B) Rapeseed oil

4.4.5 Effect of interaction between process variables

3D response surface plots which are the graphical results of interactive effects are shown in Figures 4.10 – 4.12. The contour plots are shown in Appendix (B). Figure 4.10 represents the response for the interactive factors – bleaching temperature and time on Niger seed oil and rapeseed oil. From Figure 4.10 (A), bleaching temperature has negative effect for color reduction on Niger seed oil. Increasing time will increase the bleaching efficiency but to some extent due to the first most significant factor being the temperature and to its effect being negative. It is seen from the figures that percentage color reduction on rapeseed oil increased with increase in temperature and time. It was observed that above 110^{0}C, there was decrease in the bleaching efficiency. This can be seen from Figures 4.10 (B) since the area above this value indicates lesser bleaching efficiency compared to the darkest red region which has bleaching efficiency (> 96%).

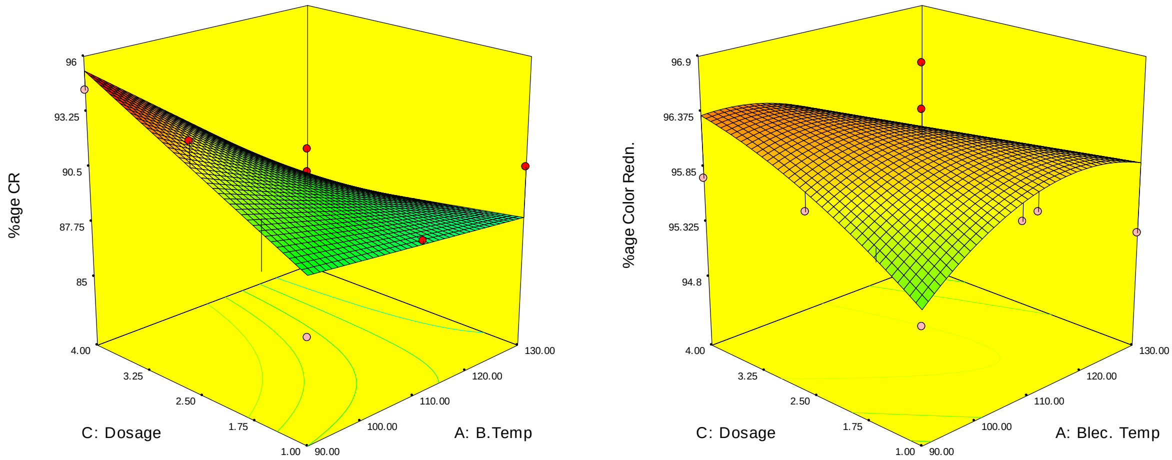


(A) **(B)**

Figure 4.10 3D response surface plot of temperature and time when clay dosage is 2.5% for bleaching of (A) Niger seed oil (B) Rapeseed oil

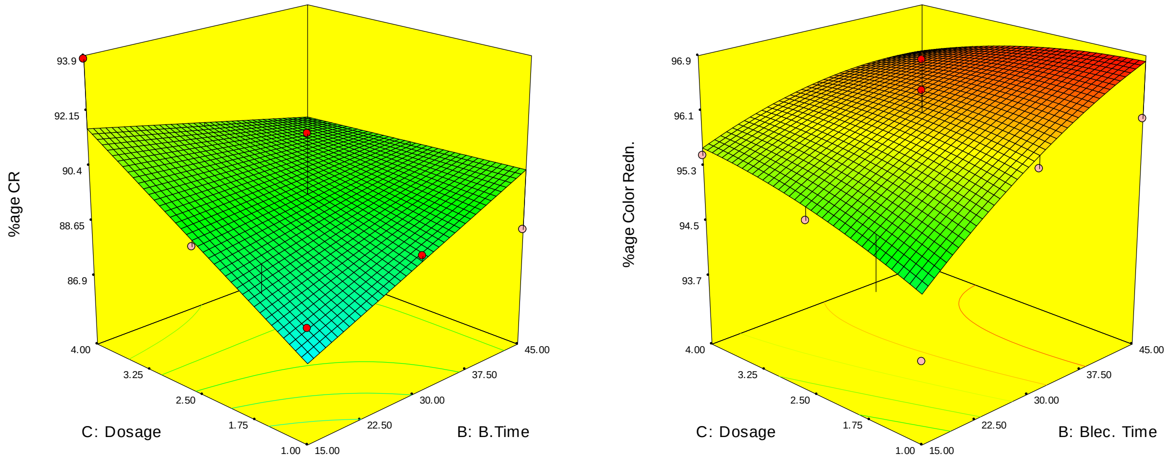
Figure 4.11 show the responses for the interaction of temperature and dosage on Niger seed and rapeseed oil. The 3D response plot Figure 4.11 (A) indicates that the percentage bleached increased when dosage increased. Increase in temperature showed decrease in the percentage bleached. Both factors have significant individual as well as interaction effect on bleaching performance for Niger seed oil. But for rapeseed oil, figure 4.11 (B) shows that maximum percentage color reduction occurs at center point of both factors. Further increase for this range leads decreasing of bleaching efficiency. This indicates that interaction of bleaching temperature and dosage has more significant from others.

Figure 4.12 shows the response variance (percentage color reduction) as a function of time and dosage under experimental conditions. From figure 4.12 (A), it can be seen that higher percentage bleached occurred at a higher dosage. Thus, dosage is the most important factor in improving the removal of undesired pigments in Niger seed oil bleaching. Increase in percentage bleached as a result of increase in dosage is because of the more surface area available, which will accommodate more undesired pigments. In this case time doesn’t has significant effect and at minimum time the bleaching process reaches equilibrium. For rape seed oil, bleaching efficiency occurs at the center point of clay dosage and time. Percentage color reduction becomes constant as shown in the figure 4.12 (B).



(A) **(B)**

Figure 4.11 3D response surface plot of temperature and clay dosage when time is 30min for bleaching of (A) Niger seed oil (B) Rapeseed oil



(A) **(B)**

Figure 4.12 3D response surface plots of time and clay dosage at temperature 110^{0}C for bleaching of (A) Niger seed oil (B) Rapeseed oil

4.4.6 Finding the optimal bleaching process parameters for Rape and Niger seed oil

The bleaching parameters were optimized subject to constraint shown in Table 4.12. The objective is to maximize percentage color reduction. Thirty (Niger seed oil) and twenty-one (Rapeseed oil) solutions were found and the solution with the highest desirability was chosen. In other to verify the optimization results, the selected parameters were validated in the laboratory with suggested values as shown in Table 4.13. The result from the experiments confirmed the selected solutions.

Table 4-12 Optimization constraints for bleaching performance

Name	Goal	Lower limit	Upper limit
Bleaching temperature (^{0}C)	**is in range**	**90**	**130**
Bleaching time (min)	**is in range**	**15**	**45**
Clay dosage (%)	**is in range**	**1**	**4**
Percentage color reduction (%) Niger seed oil	**maximize**	**84.37**	**94.71**
Rapeseed oil		**93.02**	**96.84**

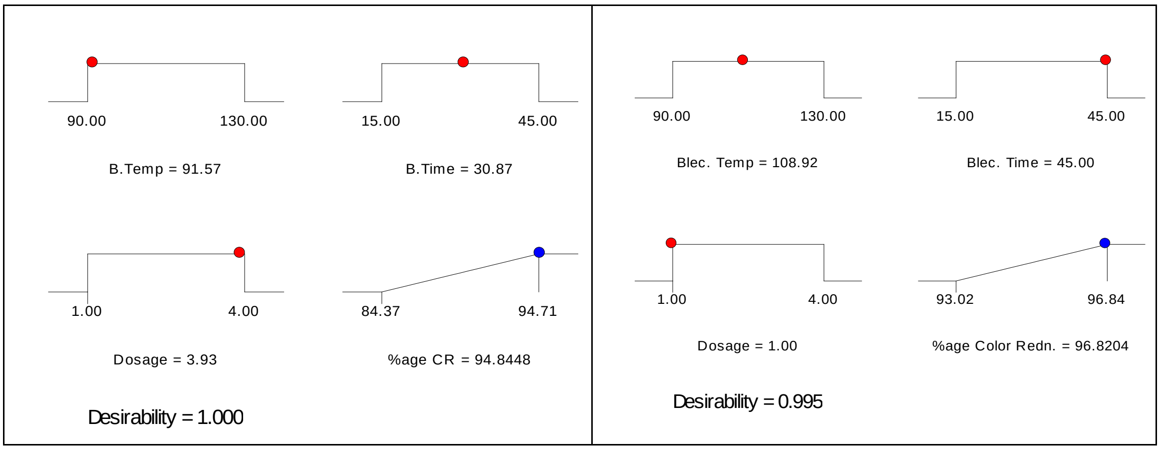


Figure 4.13 Optimum solution for (A) Niger seed and (B) Rapeseed oil

Table 4-13 Validation results

Parameters	Model predict		Experimental result	
	NS oil	**RS oil**	**NS oil**	**RS oil**
Bleaching temperature (^{0}C)	**91.57**	**108.92**	**90**	**110**
Bleaching time (min)	**30.87**	**45**	**30**	**45**
Clay dosage (%)	**3.93**	**1**	**4**	**1**
Percentage color reduction (%)	**94.8448**	**96.84**	**94.37**	**96.01**

NS = Niger seed and **RS** = Rapeseed

4.4.7 Comparison between the raw and activated bentonite

Natural/raw bentonite sample was then tested in order to verify its capacity to bleach Niger seed and rapeseed oil, and its performance was compared to that of activated bentonite. The bleaching ability of the natural bentonite was poor when compared with that of the activated adsorbent. Percentage color reduction are 33.56% and 39.44% for Niger seed and rapeseed oil bleaching, respectively, when raw bentonite used as adsorbent.

Figure 4.14 shows the color change of the bleached oils after bleaching process using the chosen activated bentonite. It shows that the color change can be seen even with simple eye observation. This indicates that the bleaching power of the acid activated bentonite is maximum and main objective of this study is achieved.

(A) **(B)**

Figure 4.14 Color change after bleaching of (A) Niger seed oil (B) Rapeseed oil

4.5 Acid Value and Percentage Free Fatty Acid Results

Acid value and free fatty acid was determined for unbleached Niger seed oil and rapeseed oil as well as for bleached oils which are processed by optimum bleaching parameters. From table 4.14, acid value and free fatty acid decrease after bleaching. This indicates the acid activated bentonite has power to remove not only pigments and also other impurities that reduce the percentage free fatty acid. discovered that in addition to producing a pale color, the adsorbent was also able to reduce levels of free fatty acid, peroxide value and phosphorus content in oil.

Table 4-14 Acid value and percentage free fatty results

Types of oil	Acid value (mg KOH/g oil)	Percentage free fatty acid
Unbleached NS oil	**5.5**	**2.77**
Bleached NS oil	**3.24**	**1.63**
Unbleached RS oil	**6.28**	**3.16**
Bleached RS oil	**3.30**	**1.66**

NS = Niger seed and **RS** = Rapeseed

CHAPTER 5 CONCLUSIONS AND RECCOMENDATIONS

5.1 Conclusion

The highest bleaching capacity and a model for acid activation of bentonite were investigated by means of full factorial design. The result presented herein provides clear evidence that activation temperature influence greatly the bleaching capacity of bentonite, while the acid concentration exerts no significant individual effect on the activation of bentonite. The investigated parameters also exert binary interactions that must not be neglected. The experimental data showed that 3M and 90^{o}C are the best parameters for activation of natural bentonite. A greater increase in acid concentration has a negligible role in the activation process and decrease the bleaching efficiency. The bleaching ability of the natural clay was poor when compared with that of activated adsorbent.

The effects of acid activation on clay structural properties were determined by XRD, FTIR, SEM and EDS. From the results, it can be concluded that, the acid treatment affected mainly the montmorillonite phases. Octahedral sheet was affected by acid activation resulting into the dissolution of cations (Mg^{2+}, Fe^{2+}, Al^{3+}) and consequent decomposition of montmorillonite structure. Therefore, it can be concluded that more active sites are generated on the clay surface.

The maximum bleaching parameters of the activated bentonites were investigated and models were developed by utilizing full factorial experimental design in order to bleach Niger seed and rapeseed oil. The bleaching performance of the activated bentonite were determined with respect to bleaching temperature, contact time and clay dosage. The results show that the best temperature, contact time and clay dosage for optimum bleaching of oil varied from one type of oil to the other. Optimum conditions are 90°C, 30min and 4% clay dosage for Niger seed oil and 110°C, 45min and 1% clay dosage and for rapeseed oil. The maximum percentage color reductions were obtained 94.37% and 96.01% for Niger seed and rapeseed oil, respectively.

The overall results lead to the conclusion that local bentonite clays can be converted into potent adsorbents by optimum acid activation for bleaching of local edible oils, and thus can permits a wider application area for the bentonite and represent a value-added to the economy of the country by avoiding foreign currency for importing activated bentonite clay.

5.2 Recommendation

If some further research work is carried out to explore the potential of these clays, recommended studies are listed below:

- Since effect of other parameters such as activation time, acid to clay ratio and agitation speed were not studied in the acid activation studies, it is recommended that these parameters get studied even though their effects as compared to the others is less as observed in literature reviews.
- It is also recommended to give the alternative method for activation procedure of bentonite clay and this method should be the safest method for both the labor and equipment used in vegetable oil industry.
- Sludge removal techniques were the sludge can be used for other applications should be studied or using fixed bed columns were regeneration techniques are incorporated.
- Determination of the bleaching capacity using adsorption isotherm models and kinetic adsorption in order to examine the controlling mechanism of the adsorption process were also suggested.
- It is recommended to perform preliminary design, economic feasibility study and establish economic scale for activated bentonite manufacturing unit.

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APPENDICES

Appendix A: Experimental Results

Table A-1 Moisture content of raw bentonite (After 4.5hr)

Clay sample	m_1 (g)	m_2 (g)	m_3 (g)	$m_2 - m_3$	Moisture content (%)	Average moisture content (%)
1	**2.0015**	**25.5302**	**25.3657**	**0.1645**	**8.219**	**8.209**
2	**2.0012**	**24.1855**	**24.0208**	**0.1647**	**8.23**	
3	**2.0008**	**24.7172**	**24.5537**	**0.1635**	**8.171**	

Table A-2 Bulk density of raw bentonite

Clay sample	m_1 (g)	m_2 (g)	$m_2 - m_1$	V_{cyl} (ml)	Bulk density (g/cm^3)	Average Bulk density (g/cm^3)
1	**20.2008**	**30.1886**	**9.9878**	**7.1**	**1.4067**	**1.4067**
2	**20.2007**	**30.1884**	**9.9877**	**7.1**	**1.4067**	

Table A-3 Apparent density of raw bentonite

Clay sample	m_1 (g)	m_2 (g)	$m_2 - m_1$	V_{pyc} (ml)	Bulk density (g/cm^3)	Average Bulk density (g/cm^3)
1	**30.0788**	**70.9753**	**40.8965**	**50**	**0.81793**	**0.8179**
2	**30.0788**	**70.9755**	**40.8987**	**50**	**0.81797**	

Table A-4 Swell index of raw bentonite

Clay sample	V_{int} (ml)	V_{fin} (ml)	T_{int} (^{0}C)	T_{fin} (^{0}C)	Swell index ($ml/2g$)	Average Swell index ($ml/2g$)
1	**12**	**14**	**22**	**22**	**14**	**13**
2	**11**	**13**	**21**	**22**	**13**	
3	**9**	**12**	**21**	**22**	**12**	

int = initial (at time=0)
fin = final (at time=24hr)

Table A-5 Acid value and Free fatty acid determination

Oil sample	Mass of oil sample (g)	Normality of KOH solution	Unbleached oil			Bleached oil		
			V KOH required (ml)	AV (mg KOH /g oil)	FFA	V KOH required	AV (mg KOH/g oil)	FFA
Niger seed oil	**5**	**0.1**	**4.9**	**5.5**	**2.77**	**2.9**	**3.24**	**1.63**
Rapeseed oil	**5**	**0.1**	**5.6**	**6.28**	**3.17**	**2.95**	**3.3**	**1.66**

Table A-6 Wave length vs. Absorbance on visible spectra of unbleached oil

Wave length (nm)	Absorbance 1	Absorbance 2	Average Absorbance
320	**0.252**	**0.252**	**0.252**
350	**0.271**	**0.273**	**0.272**
360	**0.278**	**0.280**	**0.279**
365	**0.286**	**0.282**	**0.283**
370	**0.287**	**0.287**	**0.287**
380	**0.293**	**0.294**	**0.294**
400	**0.311**	**0.312**	**0.312**
420	**0.325**	**0.326**	**0.326**
450	**0.354**	**0.350**	**0.352**
470	**0.345**	**0.345**	**0.345**
500	**0.339**	**0.336**	**0.338**
550	**0.310**	**0.307**	**0.308**
580	**0.268**	**0.267**	**0.268**
600	**0.229**	**0.233**	**0.231**
620	**0.212**	**0.212**	**0.212**
650	**0.199**	**0.197**	**0.198**
670	**0.178**	**0.178**	**0.178**

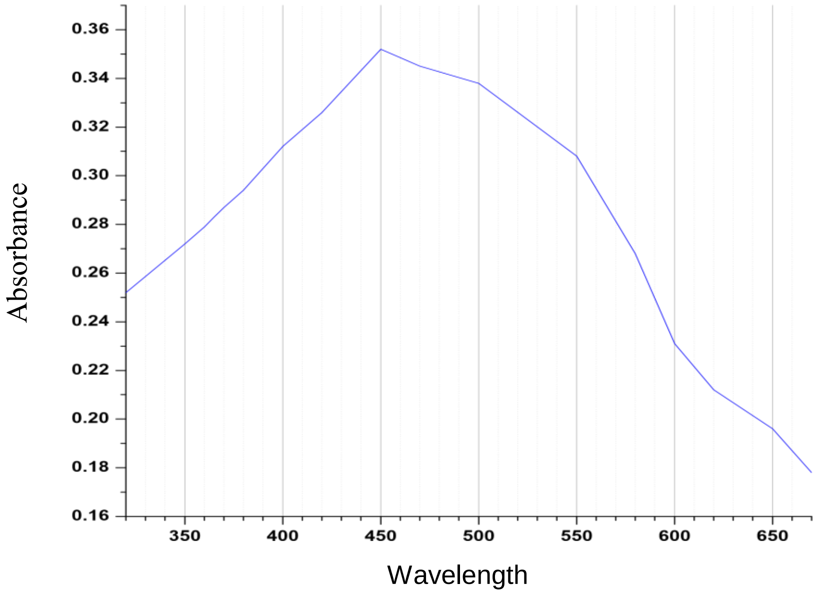


Figure A-1 Visible spectra of unbleached oil

Appendix B: Experimental Design Outputs

Table B-1 Experimental design data for activation process

Run No.	H_2SO_4 Concentration (M)	Activation Temperature (^0C)	Average Absorbance	Percentage Color Reduction	Final Mass (g)	Yield (%)
1	**5**	**90**	**0.044**	**74.19**	**20.17**	**67.23**
2	**3**	**90**	**0.0302**	**82.44**	**20.86**	**69.53**
3	**1**	**90**	**0.0372**	**78.38**	**21.37**	**71.23**
4	**5**	**60**	**0.0543**	**68.43**	**23.17**	**77.03**
5	**1**	**60**	**0.0629**	**63.45**	**26.48**	**88.27**
6	**5**	**75**	**0.0491**	**71.48**	**20.52**	**68.4**
7	**3**	**60**	**0.0535**	**68.88**	**25.72**	**85.73**
8	**1**	**75**	**0.0475**	**72.4**	**24.02**	**80.07**
9	**3**	**75**	**0.0425**	**75.32**	**23.19**	**77.3**

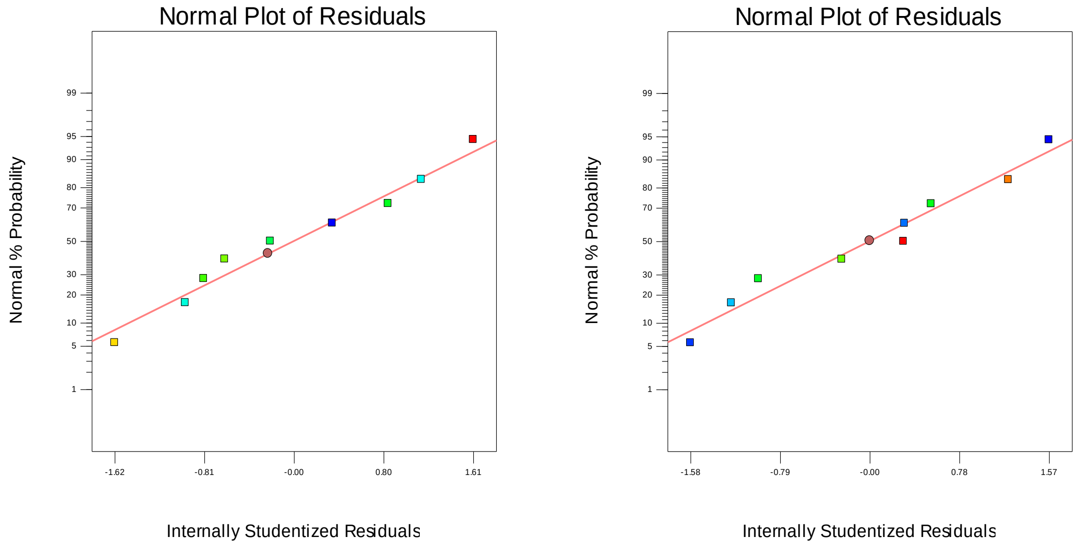
Absorbance of unbleached oil = 0.172
Initial mass of samples = 30g

Activation Time = 4hr
Agitation speed = 150rpm
Clay to acid ratio = 1:5

Table B-2 Design summary for activation process

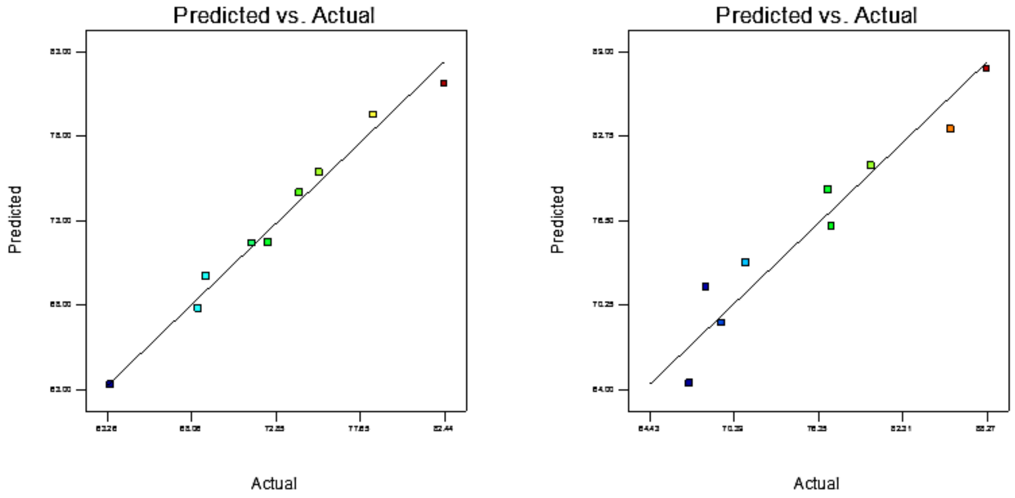
```
Study Type       Factorial        Runs     9
Initial Design   Full Factorial   Blocks   No Blocks
Design Model     2FI
                                           Low      High     Low     High
Factor       Name    Units       Type   Actual   Actual   Coded   Coded      Mean    Std. Dev.
     A  H2SO4 conc       M    Numeric        1        5      -1       1         3     1.632993
     B    Act.Temp      °C    Numeric       60       90      -1       1        75     12.24745

Resp      Name   Obs      Analysis     Min     Max        Mean   Std. Dev.       Ratio        Model
  Y1      % CR     9    Polynomial   63.45   82.44    72.77444    5.334696    1.299291    Quadratic
  Y2     yield     9    Polynomial   67.23   88.27    76.08778    7.178354    1.312956       Linear
```



(A) **(B)**

Figure B-1 Normal probability plots (A) Response: Percentage Color Reduction (B) Response: Yield



(A) **(B)**

Figure B-2 Predicted vs. Actual plots (A) Response: Percentage Color Reduction (B) Response: Yield

Table B-3 Experimental design data for bleaching of Niger seed oil

Run	Block	Bleaching Temperature (^{0}C)	Bleaching Time (min)	Clay Dosage (%)	Average Absorbance	Percentage Color Reduction
1	**Block 1**	**130**	**15**	**2.5**	**0.0385**	**87.07**
2	**Block 1**	**130**	**30**	**2.5**	**0.0438**	**85.31**
3	**Block 1**	**110**	**30**	**2.5**	**0.0388**	**86.99**
4	**Block 1**	**90**	**15**	**4**	**0.0211**	**92.93**
5	**Block 1**	**110**	**45**	**4**	**0.0332**	**88.87**
6	**Block 1**	**90**	**15**	**2.5**	**0.0247**	**91.72**
7	**Block 1**	**110**	**45**	**2.5**	**0.0321**	**89.23**
8	**Block 1**	**90**	**30**	**1**	**0.0403**	**86.48**
9	**Block 1**	**110**	**30**	**1**	**0.0332**	**88.86**
10	**Block 1**	**130**	**15**	**4**	**0.0423**	**85.81**
11	**Block 1**	**90**	**45**	**1**	**0.0222**	**92.56**
12	**Block 1**	**130**	**15**	**1**	**0.0441**	**85.21**
13	**Block 1**	**90**	**45**	**2.5**	**0.0158**	**94.71**
14	**Block 1**	**110**	**30**	**4**	**0.0327**	**89.03**
15	**Block 1**	**130**	**45**	**2.5**	**0.0410**	**86.23**
16	**Block 1**	**130**	**30**	**4**	**0.0393**	**86.81**
17	**Block 1**	**130**	**45**	**1**	**0.0395**	**86.75**
18	**Block 1**	**130**	**45**	**4**	**0.0453**	**84.81**
19	**Block 1**	**110**	**15**	**1**	**0.0355**	**88.08**
20	**Block 1**	**90**	**15**	**1**	**0.0466**	**84.37**
21	**Block 1**	**110**	**15**	**2.5**	**0.0324**	**89.14**
22	**Block 1**	**90**	**45**	**4**	**0.0177**	**94.06**
23	**Block 1**	**90**	**30**	**4**	**0.0168**	**94.37**
24	**Block 1**	**110**	**15**	**4**	**0.0185**	**93.79**
25	**Block 1**	**110**	**45**	**1**	**0.0345**	**88.41**
26	**Block 1**	**90**	**30**	**2.5**	**0.0192**	**93.55**
27	**Block 1**	**130**	**30**	**1**	**0.0280**	**90.6**
28	**Block 2**	**110**	**30**	**2.5**	**0.0317**	**89.35**
29	**Block 2**	**110**	**30**	**2.5**	**0.0254**	**91.49**

Absorbance of unbleached Niger seed oil = 0.298
Agitation speed = 150rpm

Table B-4 Experimental design data for bleaching of rapeseed oil

Run	Block	Bleaching Temperature (^0C)	Bleaching Time (min)	Clay Dosage (%)	Average Absorbance	Percentage Color Reduction
1	**Block 1**	**90**	**30**	**2.5**	**0.0146**	**95.8**
2	**Block 1**	**90**	**45**	**2.5**	**0.0124**	**96.42**
3	**Block 1**	**110**	**45**	**2.5**	**0.0131**	**96.24**
4	**Block 1**	**130**	**45**	**4**	**0.0185**	**94.68**
5	**Block 1**	**130**	**15**	**4**	**0.0211**	**93.95**
6	**Block 1**	**110**	**30**	**4**	**0.0225**	**95.53**
7	**Block 1**	**130**	**45**	**1**	**0.0133**	**96.17**
8	**Block 1**	**130**	**30**	**2.5**	**0.0175**	**94.97**
9	**Block 1**	**90**	**15**	**2.5**	**0.0203**	**94.17**
10	**Block 1**	**110**	**15**	**4**	**0.0157**	**95.48**
11	**Block 1**	**90**	**45**	**4**	**0.0142**	**95.91**
12	**Block 1**	**110**	**15**	**1**	**0.0216**	**93.79**
13	**Block 1**	**130**	**45**	**2.5**	**0.0171**	**95.09**
14	**Block 1**	**110**	**45**	**4**	**0.0137**	**96.06**
15	**Block 1**	**130**	**30**	**4**	**0.0178**	**94.89**
16	**Block 1**	**110**	**30**	**2.5**	**0.0156**	**95.52**
17	**Block 1**	**130**	**15**	**2.5**	**0.0179**	**94.86**
18	**Block 1**	**110**	**45**	**1**	**0.0139**	**96.01**
19	**Block 1**	**90**	**15**	**1**	**0.0243**	**93.02**
20	**Block 1**	**90**	**30**	**1**	**0.0168**	**95.18**
21	**Block 1**	**90**	**45**	**1**	**0.0133**	**96.18**
22	**Block 1**	**130**	**15**	**1**	**0.0175**	**94.98**
23	**Block 1**	**130**	**30**	**1**	**0.0166**	**95.23**
24	**Block 1**	**110**	**15**	**2.5**	**0.0171**	**95.09**
25	**Block 1**	**90**	**15**	**4**	**0.0166**	**95.24**
26	**Block 1**	**90**	**30**	**4**	**0.0148**	**95.76**
27	**Block 1**	**110**	**30**	**1**	**0.0146**	**95.8**
28	**Block 2**	**110**	**30**	**2.5**	**0.011**	**96.84**
29	**Block 2**	**110**	**30**	**2.5**	**0.0125**	**96.41**

Absorbance of unbleached Niger seed oil = 0.348
Agitation speed = 150rpm

Table B-5 Design summary for bleaching of Niger seed oil

Study Type	Factorial	**Runs**	29
Initial Design	Full Factorial	**Blocks**	2
Design Model	2FI		

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded	Mean	Std. Dev.
A	B.Temp	oC	Numeric	90	130	-1	1	110	15.75677
B	B.Time	min	Numeric	15	45	-1	1	30	11.81758
C	Dosage	%	Numeric	1	4	-1	1	2.5	1.181758

Resp	Name	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio	Model
Y1	%age CR	29	Polynomial	84.37	94.71	89.19276	3.13002	1.122555	2FI

Table B-6 Design summary for bleaching of rapeseed oil

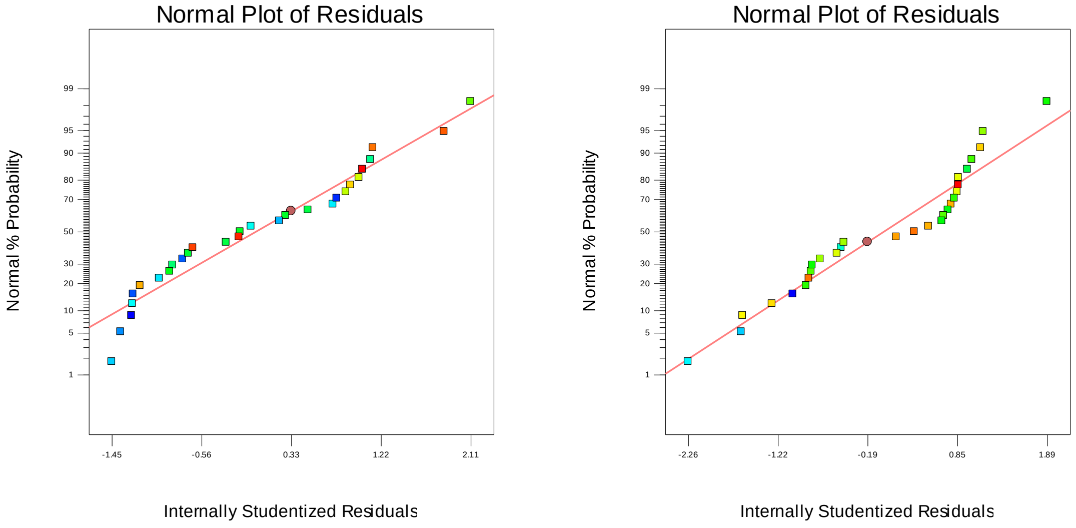
Study Type	Factorial	**Runs**	29
Initial Design	Full Factorial	**Blocks**	2
Design Model	2FI		

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded	Mean	Std. Dev.
A	B.Temp	oC	Numeric	90	130	-1	1	110	15.75677
B	B.Time	min	Numeric	15	45	-1	1	30	11.81758
C	Dosage	%	Numeric	1	4	-1	1	2.5	1.181758

Resp	Name	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio	Model
Y1	%age CR	29	Polynomial	93.02	96.84	95.35414	0.853664	1.041066	Quadratic

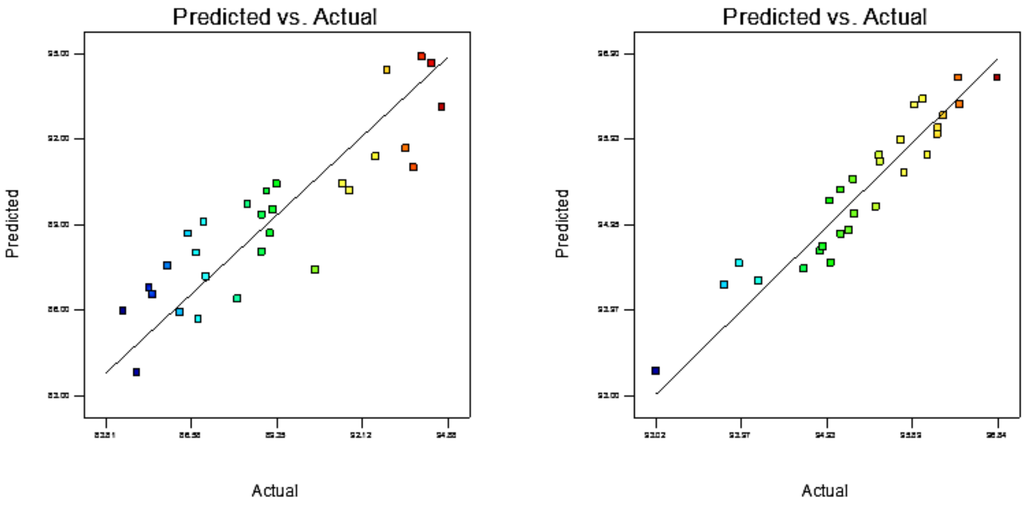
Table B-7 Measurement of significance using R^2 and adequate precision

Stat. tool	Niger seed oil	Rapeseed oil
R-Squared	**0.7757**	**0.8738**
Adjusted R-Squared	**0.7116**	**0.8108**
Predicted R-Squared	**0.5353**	**0.6152**
Adequate Precision	**12.175**	**15.442**



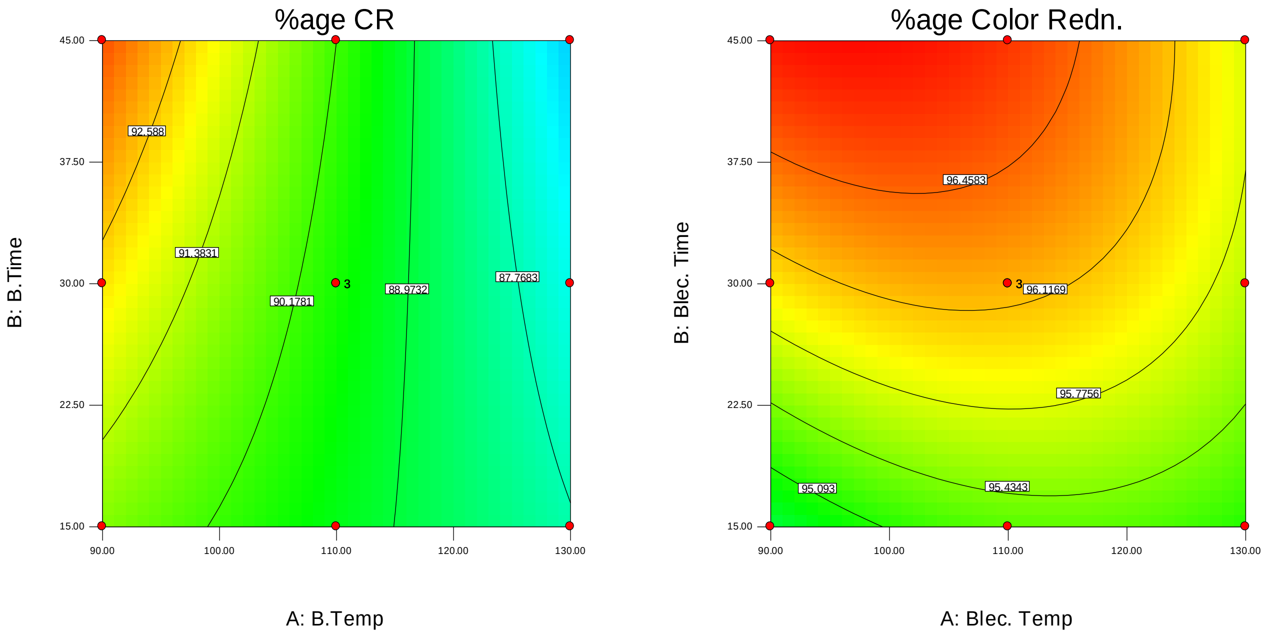
(A) **(B)**

Figure B-3 Normal probability plots for (A) Niger seed oil (B) Rapeseed oil



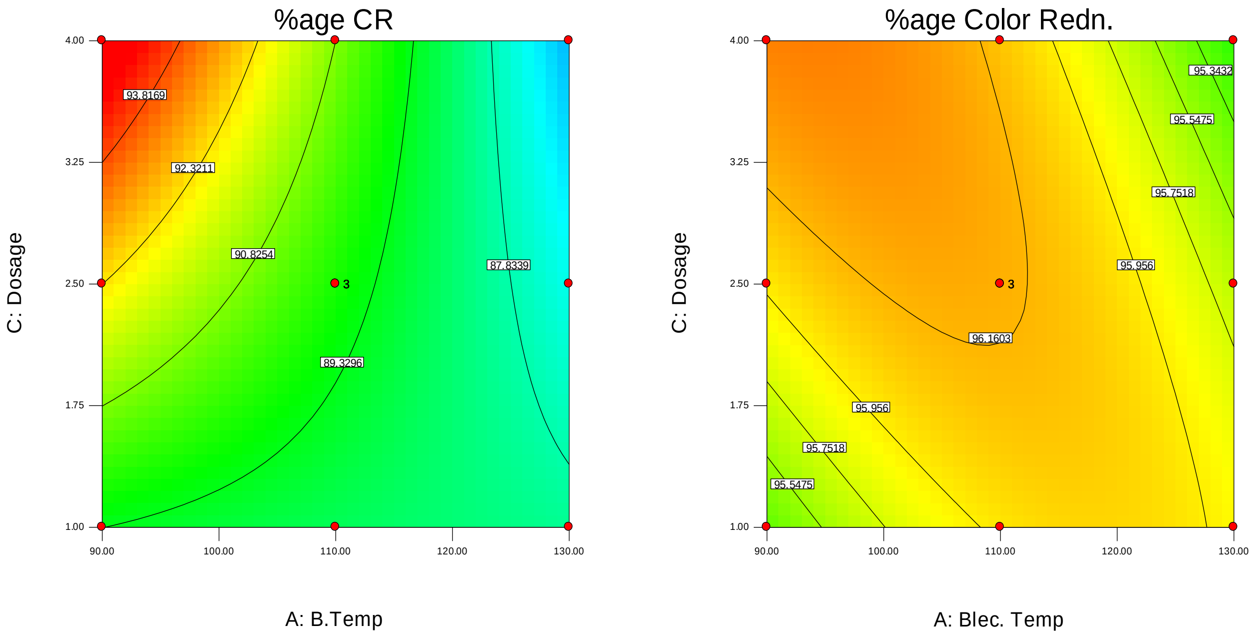
(A) **(B)**

Figure B-4 Predicted vs. Actual plots for (A) Niger seed oil (B) Rapeseed oil



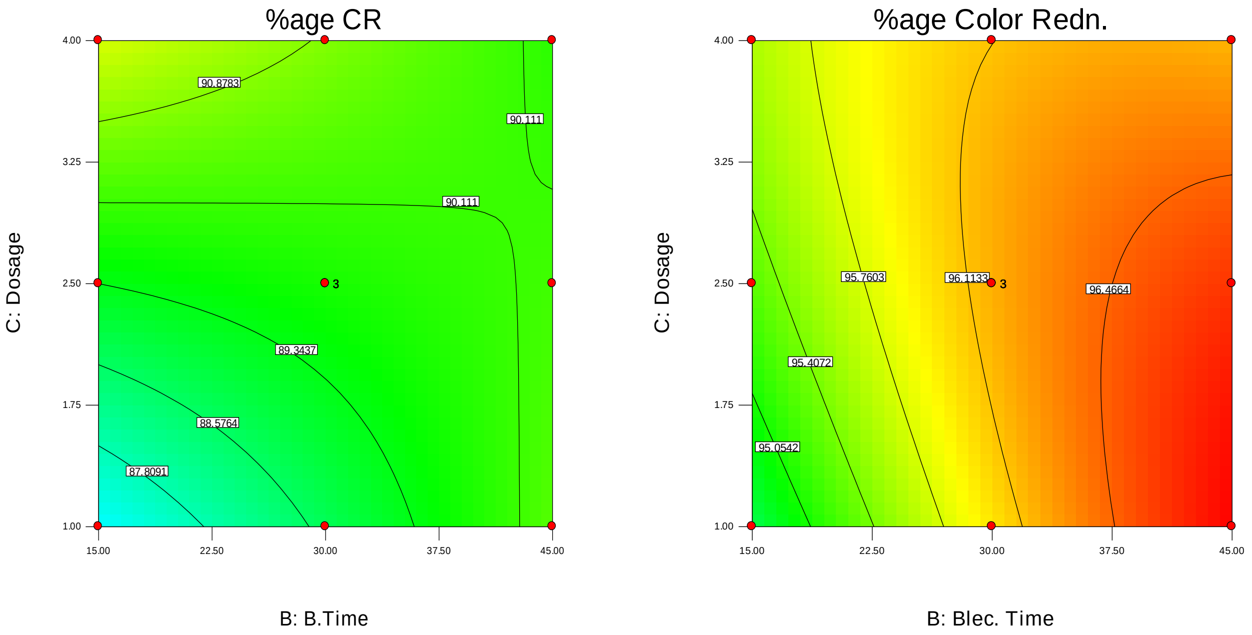
(A) **(B)**

Figure B-5 Contour plot of temperature and time when clay dosage is 2.5% for bleaching of (A) Niger seed oil (B) Rapeseed oil



(A) **(B)**

Figure B-6 Contour plots of temperature and clay dosage when time is 30min for bleaching of (A) Niger seed oil (B) Rapeseed oil



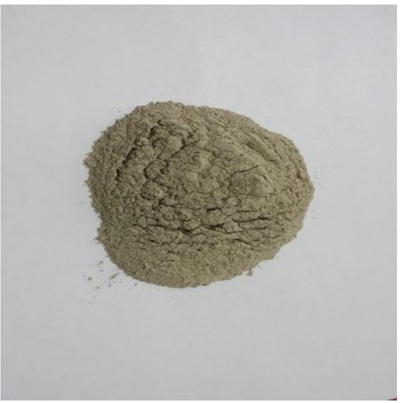
(A) **(B)**

Figure B-7 Contour plots of time and clay dosage at temperature 90^{0}C for bleaching of (A) Niger seed oil (B) Rapeseed oil

Appendix C: Experimental Pictures


Raw bentonite


1st size reduction


3rd size reduction


Acid Activation


Vacuum filter


Washing

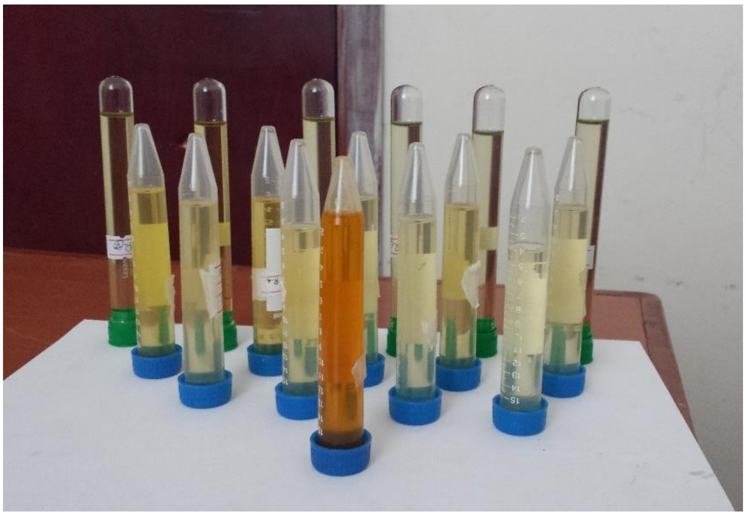

Before Drying


After Drying

Bleaching process

Before using centrifuge

After using centrifuge



Some of bleaching oil samples at different conditions