UNIVERSITY OF NAIROBI

OPTIMIZATION OF ACID ACTIVATION AND BLEACHING PERFORMANCE OF LOCAL BENTONITE CLAY

By

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2014

DECLARATION

This thesis is my original work and has not been submitted for examination to any other university.

……………………………………..

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This thesis has been submitted for examination with our approval as University supervisors.

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DEDICATION

This work is dedicated to the members of my family for inspiring me.

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I am sincerely grateful to the Almighty God for the unconditional love, mercy and above all his amazing grace throughout my academic life.

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May God Almighty bless all of you.

ABSTRACT

Bentonite clays from Athi River and Thika were activated using sulphuric acid at various concentrations under reflux, and investigated for their ability to bleach vegetable oil. Bleaching properties of acid-activated bentonite clays were studied to investigate their applicability as an alternative to the expensive imported bleaching earth. When the chemical composition and physical characteristics of the natural and activated clay samples were analyzed, Athi River bentonite clay was generally found to be more suitable for acid activation than Thika bentonite clay. For the Athi River bentonite clay, activation at 100 °C and 2.5 hours with constant stirring were found to be optimum conditions of temperature and contact time, respectively. Clay/acid ratio was found not to significantly affect the clay properties. Cation exchange capacity (CEC) was found to decrease with increase in concentration of acid used in the activation process. Palm oil was used to investigate the bleaching performance of the activated clay samples. When the oil was bleached at 90 °C for 30 minutes using 4% clay activated with 2 mol/L H_2SO_4, the bleaching performance increased up to 98%. The equilibrium data was analysed using Freundlich and Langmuir adsorption isotherms. Freundlich isotherm model (R^2 =0.9247) provided a better fit to the data than Langmuir isotherm (R^2 =0.04181). The heat of adsorption was determined to be -30.881 kJmol^{-1}. This revealed that bleaching of palm oil with activated Athi River bentonite clay was an exothermic reaction and a physico-chemical process. The kinetics was evaluated and the rate constant was found to be 0.148 min^{-1} for this clay which compared well with 0.127 min^{-1} for Commercial Bleaching Earth. The results from this study revealed that acid activation is an effective method of improving adsorption performance of Athi River bentonite clay. The activated clay can be used in oil industries for bleaching vegetable oils as it compared well with the commercial bleaching earth. Since bentonite is an abundant natural adsorbent, improving its properties by acid activation can make a cost effective adsorbent for bleaching vegetable oils.

Keywords: Acid activation, Bentonite clay, Palm oil, Bleaching oil

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LIST OF ABBREVIATIONS

A: Athi River

AAS: Atomic absorption spectrometer

ABD: Apparent bulk density

ABE: Activated bleaching earth

BP: bleaching performance

BPO: Bleached palm oil

CBE: Commercial Bleaching Earth

CCI: Cameron carbon incorporated

CEC: Cation exchange capacity

CaB: Calcium bentonite

CPO: Crude palm oil

D: Density

EPZA: Export processing zone authority

EUBA: European Bentonite Association

FAO: Food and Agriculture Organization

FFA: Free fatty acids

GOK: Government of Kenya

LOI: Loss on ignition

NaB: Sodium bentonite

OGA: Office of Global Analysis

OR: Oil retention

SD: Standard deviation

T: Thika

USA: United State of America

UV-Vis: Ultraviolet visible

WWF: World Wide Fund

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CHAPTER ONE

INTRODUCTION

1.1 Background

Bleaching is an adsorption process that utilizes clay as adsorbent. It serves both cosmetic and chemical purposes. It is used in refinery industries to stabilize the oil by removing coloured and colourless pigments which tend to destabilize vegetable oils [Didi *et al.*, 2009; Usman *et al.*, 2013].

Refining process comprises of several stages such as degumming, neutralization, bleaching and deodorization [Al-Zahrani *et al.*, 2000; Berbesi, 2006, CIWC, 2008, Farihahusnah *et al.*, 2011]. Bleaching is the most critical stage since it helps to improve the appearance, flavour, taste and stability of the final oil products [Farihahusnah *et al.*, 2011; Rohani *et al.*, 2006]. The bleaching process can be carried out after degumming and neutralizing the vegetable oil under specific conditions [Diaz and Santos, 2001].

Activated bleaching earth (ABE) is by far the most common adsorbent for oil purification. Other adsorbents that have been tested for removal of pigment and impurities from oil included activated carbon and silica based products [Ejikeme *et al.*, 2013]. Oil industries in Kenya use imported bleaching agents in spite of the fact that the raw material for ABE is the abundantly available bentonite clay.

Bentonite clays are used widely as binding agent in foundry sand and iron ore palleterization. Acid activated clays have been used as catalysts for a number of reactions of industrial interests [Foletto *et al.*, 2011; Didi *et al.*, 2009, EUBA, 2011]. Activated clays have also been utilized in paper industry, in sulphur production, for environment protection [Foletto *et al.*, 2011, EUBA, 2011], in food industries particularly in the bleaching of vegetable oils [Hassan and Abel-khalek, 1998; Makhoukhi *et al.*, 2009; Didi *et al.*, 2009].

Bentonite is a versatile natural mineral, in class of smectite clays formed from alteration of siliceous glass-rich volcanic rocks. It is primarily composed of montmorillonite. Industrial bentonites are generally either the sodium or calcium variety [Hassan and Abel-khalek, 1998; Nadežda *et al.*, 2011; Basim, 2011]. Calcium bentonite (CaB) is not a very good adsorbent and is, therefore, activated to develop a capacity to adsorb colouring matter and other impurities dissolved in oils (vegetables, animals and petroleum matter) [Diaz and Santos, 2001]. In this study, only acid activation of CaB has been optimized. It has been reported that clays which contain high proportions of montmorillonite and which are poor in natural bleaching potency are suitable for activation [Oboh *et al,* 1987, Usman *et al.,* 2013 and Makhoukhi *et al,* 2008]

Bentonites are found in nature abundantly. However, most of them need to undergo appropriate physical or chemical treatments such as acid activation, ion exchange and heating in order to increase surface properties, adsorption capacity, and range of applicability [Kariuki, 1996; Rossi *et al.*, 2003; Rožic *et al.*, 2010, Foletto *et al.*, 2011]. Ajemba and Onukwuli (2013) observed that activated clay adsorb colour pigments more than inactivated clay. Farihahusnah *et al.*, 2011 have reported that the high bleaching performance of bleaching earth depends on the activation treatment which results in structural modification. The modified clay minerals have a high potential of serving as an alternative to the most widely used high-cost activated carbon [Ajemba and Onukwuli, 2013].

During acid activation, initially interlayer cations are replaced with H^+ ions followed by partial destruction of aluminium octahedral sheets with subsequent dissolution of structural cations [Komadel *et al.*, 1990; Korichi *et al.*, 2009; Rossi *et al.*, 2003; Rožic *et al.*, 2010]. A study by Usman *et al.*, (2013) reported that acid activation depends considerably on the conditions of activation such as acid concentration, contact time and the temperature of the activation process.

Many studies have reported successful bleaching of oil using acid activated clays from across the World [Usman *et al.*, 2013; Makhoukhi *et al.*, 2008, Diaz and Santos, 2001] but few have been carried out using local Kenya clay [Kariuki, 2013].

The purpose of this study was to characterize the local bentonite clays and to investigate optimum conditions for acid activation. The bleaching performance was to be based on palm oil because it is the most widely used vegetable oil in Kenya.

1.2 Problem Statement

Bleaching is an important process in oil refining industries. It removes pigments and other impurities which negatively influence the taste of oils [Makhoukhi *et al.*, 2009]. Bleaching of oil is done by the use of adsorbents such as activated carbon and the less expensive activated bleaching earths. The latter is produced from clays which contain high proportions of montmorillonite through acid activation [Usman e*t al.*, 2013; Makhoukhi *et al.*, 2008].

Natural clays which are locally available in abundant quantities have potential to undergo modification to enhance the surface area, adsorption capacity for use in a range of applications including bleaching earth, catalyst beds, carbonless copy paper and medication [Usman e*t al.*, 2013]. In order to promote value addition of natural resources, for example bentonite clay, a number of physical and chemical methods have to be investigated in order to ameliorate the adsorption properties and increase its applicability.

In Kenya, few studies have been reported on the activation of bentonite clay [Omondi, 2012; Kariuki, 2013], and the results demonstrated that sulphuric acid was more efficient than hydrochloric acid. However, studies on physico-chemical characteristic of activated clay and adsorption power need more investigation. Therefore, the aim of this study was to activate local bentonite by acid treatment, and to evaluate the product for oil bleaching performance in comparison with commercial bleaching clay.

1.3 Justification

Acid activation for clay has been reported to be an effective process to improve adsorption property of clay [Foletto *et al.*, 2011]. Clays in their activated forms are extensively used in the fats and oil industries in the production of vegetable oil.

Kenya's national demand of edible oil is continuously increasing. Thus, the government of Kenya (GOK) together with the Food and Agriculture Organization (FAO), other government organizations and the private sector have initiated the development of raw material centre in the country [EPZA, 2005 and OGA, 2009]. The commercial bleaching earth used is for the most part imported by the refining industries. Therefore, it is important to investigate the use of natural clay deposits for their potential in making substitutes for this purpose. Besides developing a cost effective method for improving adsorbent properties of native clay, commercial exploitation of the clay will increase income and reduce imports thus contributing to the GOK's vision of food self sufficiency by 2030.

1.4 Objectives

1.4.1 Overall objective

The main objective of this study was to enhance and optimize the bleaching activity of selected native bentonite clays.

1.4.2 Specific objectives

1. To characterize various local clays with respect to acid activation
2. To monitor the variation of some physicochemical properties with respect to activation
3. To investigate the bleaching performance of activated bentonite clays
4. To carry out a comparative study of the activated clay *vis-a vis* commercial bleaching earths with respect to industrial application

1.4.3 Scope and limitation

The scope of this project was laboratory-scale investigation of activation potential of two bentonite clays obtained from Athi River and Thika respectively using sulphuric acid. Only 200-mesh clay particle size was used. After the initial activation studied, more work was to be carried on the clay that gave better performance than the other. Palm oil was used to test the performance of the activated clay with regard to pigment removal. Apart from degumming, no other oil refining processes were carried out on the oil before it was used for the bleaching tests. Also, the effects of such oil characteristics as viscosity on bleaching performance were not studied. The study did not include regeneration of the clay after bleaching.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background On Bentonite Clay

The term bentonite was first used to designate a particular, highly colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming, USA [Kutlic *et al.,* 2012]. Later the term was attributed to every plastic clay generated by the alteration of organic ash or glass emitted from volcanoes [Nadežda *et al.*, 2011; Basim 2011]. Bentonite is a part of smectite clay minerals, which is mainly composed of montmorillonite [Kutlic *et al.,* 2012]. They are generally classified as sodium (Na), calcium (Ca), potassium (K) and aluminium (Al) depending on the dominant element. Of these elements, Na and Ca bentonites possess some physical properties, which make them valuable to a great variety of industries [Olugbenga *et al.,* 2013; Nadežda *et al.*, 2011]. Na bentonite clays have extensive water absorption properties, accompanied by swelling and ability to remain suspended in water for long periods of time. Ca bentonite clays do not show swelling properties [Kutlic *et al.,* 2012] and forms colloidal suspensions very quickly [Basim, 2011]. Clays have been widely investigated because of their potential application in many fields such as adsorbents in the bleaching of edible oils, purification of discharge waters, medication and in the preparation of pillared clays and organoclays [Diaz and Santos, 2001; Usman *et al.,* 2013].

2.1.1 Bentonite Occurrence in Kenya

In Kenya, we find bentonite clays (CaB) in different parts of the country, such as Athi River, Amboselli, Timau, Nanyuki, Meru and Namanga among others [Mutisya *et al.,* 2011]. Mineralogical and X-ray diffraction tests that have been done on samples of different clays occurring in Kenya have shown a low swelling potency in water. Thus according to the particular usage, for example, when NaB is of interest (electrochemistry), these clays are converted to NaB by addition of soda ash before use [Kariuki, 1996]. The fact that CaB clays are available and inexpensive qualifies them as an important candidate in acid activation studies. By improving their properties, they could possibly satisfy local demand for bleaching oil and other uses as well as earn the government of Kenya (GOK) the much needed foreign exchange through cross border trade.

2.1.2 Composition and properties of Bentonite clay

Clay minerals are small fragments of hydrous layer silicates. The most important of these minerals are kaolinite, montmorillonite, illite vermiculite and chlorite, each having specific characteristics [Ejikeme *et al.,* 2013]. The bentonite clay consists essentially of montmorillonite. The swelling type or sodium bentonite (NaB) has a single water layer particles containing Na^+ as an exchangeable ion. Calcium bentonite (CaB), which is non-swelling type, has double layer particles with Ca^{2+} as an exchangeable ion [Kutlic *et al.,* 2012]. Therefore, a description and discussion of montmorillonite is applicable to bentonite [Basim, 2011].

Chemically, montmorillonite is described as a hydrous aluminium silicate and is classified under phyllosilicates; $(Al,Mg)_2(OH)_2(Si,Al)_4O_{10}Ca_x.nH_2O$. Its structure is made of two basic building blocks, an edge-linked octahedral sheet and a corner-linked tetrahedral sheet, with a 2:1 relationship between tetrahedral and octahedral sheets [Nadežda *et al.,* 2011; Basim, 2011]. Each tetrahedron consists of M^{x+} cation, coordinated to four oxygen atoms. The dominant M^{x+} cation in the tetrahedral sheet is Si^{4+}, but Al^{3+} substitutes Fe^{3+} occasionally (Figure 2.1).

Chemical analysis of the composition of bentonite shows considerable variation with SiO_2 ranging between 45 and 65%, Al_2O_3 from 17 to 25% and Fe_2O_3 up to 12%. It has been found that clays turn towards non-swelling type if CaO content is 1% or more, or if MgO content in form of exchangeable ions is above 2.5% [Kutlic, *et al*, 2012].

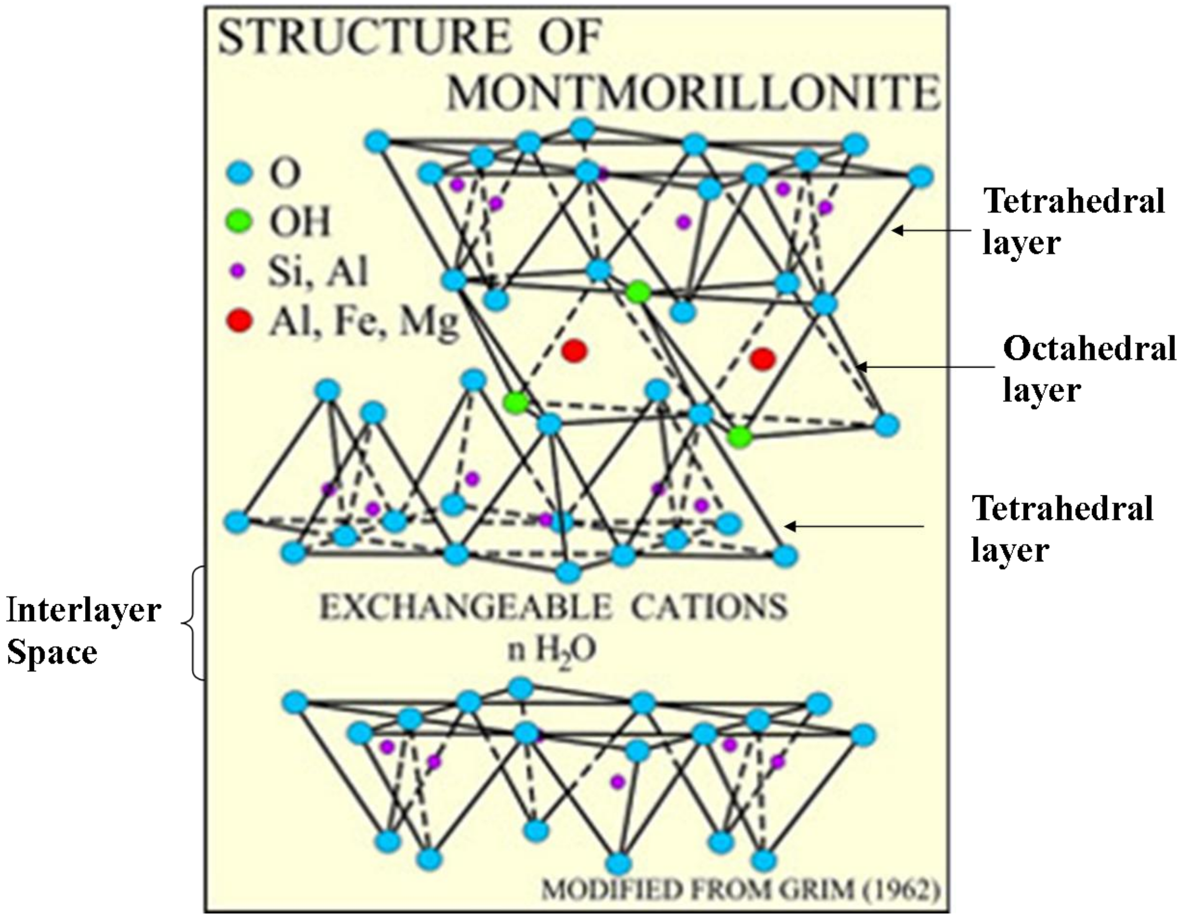


Figure 2.1: Illustration of 2:1 phyllosilicate minerals

[Sipag Bisalta, retrieved on 10th October 2014]

Bentonite clays are valued for their physical properties such as shape and size, thixotropy, adsorbent properties, cation exchange capacity (CEC), plasticity, high bonding strength, hydration and swelling capacity [Olugbenga *et al.*, 2013; Nadežda *et al.*, 2011; Rossi *et al.* 2003]. Some properties of these clays are improved commonly with mineral acid activation for applications in purification, decolourization and stabilization of vegetable oils with respect to market consumption [Nadežda *et al.,* 2011]. Therefore, it is important to examine the qualitative properties of bentonite and to determine the mineral composition and physicochemical parameters which control their behaviour. Europian Bentonite Assosiation (EUBA) qualitatively distinguishes five types of bentonite: Ca bentonite, activated bentonite, natural Na bentonite, organofilic bentonite and acid activated bentonite [Kutlic *et al.,* 2012].

2.2 Industrial Use of Activated Bentonite Clay

Natural CaB has some bleaching action useful in activities such as oil refining, pharmaceutical preparation, catalyst, and sugar refining. Its bleaching power can be increased manifold by treatment with strong mineral acid such as sulphuric or hydrochloric acid. There are many others uses but the major use for activated clay is for refining oils [Makhoukhi *et al.*, 2009].

Acid activated bentonites have been used as solid acid catalysts and catalyst supports of organic applications that require an extreme degree of reaction control of considerable industrial interest [Didi *et al.* 2009, Foletto, *et al.*, 2011].

2.2.1 Wastewater treatment

Wastewater treatment can be achieved by chemical precipitation, ion exchange, adsorption, membrane filtration, and electrodialysis. 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 *et al.*, 2012; Qingliang *et al.*, 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].

2.2.2 Catalyst

Activated montmorillonite is used to catalyse 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]. Vijayakumar *et al.*, (2009) have reported high efficient catalyst for esterification of various carboxylic acids with phenol alcohols made from acid activated Indian bentonite.

2.2.3 Edible Oils refining

In vegetable fats and oils industries, bentonite is utilized in the removal of impurities, where its adsorptive properties are crucial [EUBA, 2011].

Mineral oils such as lubricating oils and other hydrocarbons are refined by treatment with activated bleaching clays. The unburned fuel is stripped off by steam, and the oil-soluble impurities, which are corrosive and gum-forming, are removed by the bleaching earth [Hartwell, 1965]. 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]

Most of these oils are refined in vegetable oil refineries in Kenya using imported bleaching agent. This prompted the need to investigate the optimization of adsorption capacity of natural bentonite clays in this project.

2.2.4 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].

2.2.5 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].

2.2.6 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. In Kenya, it is mostly used as drilling mud [Mutisya *et al.*, 2011].

2.3 Activation Methods of Clay Mineral

Generally, activation is a chemical or physical treatment applied to certain types of clays to improve the capacity to adsorb colouring matter and other impurities in oils and solutions [Farihahusnah *et al.,* 2011].

2.3.1 Acid activation of bentonite clay

Bentonite clays are found abundantly in nature; however most of them can be modified in different ways such as acid activation, ion exchange and heating in order to promote their surface properties [Korichi *et al.,* 2009, Ejikeme *et al.,* 2013].

Acid activation of bentonite is an important process for modifying the physical and chemical properties of the clay [Diaz and Santos, 2001; Korichi *et al.*, 2009]. Acid activated bentonite is a bentonite whose structure has been dissolved by treatment mostly with inorganic acids. Depending on degree of activation, Ca^{2+}, Mg^{2+} and Na^{+} are mostly replaced by H^{+}, while Al, Fe, Mg and Si are dissolved from the lattice [Kutlic *et al.,* 2012].

The acid activation of clays is usually made on non-swelling types [Diaz and Santos, 2001]. In addition, it has been reported that natural bentonite clays are generally less efficient in the removal of impurities. However, the activated clays are more effective [Farihahusnah *et al.*, 2011]. Acid activation of CaB clay result in an important increase in the specific surface area, increase in acids centres and ion exchanges, and consequently makes it an excellent adsorbent [Makhoukhi *et al.*, 2009].

2.3.1.1 **Acid activation process**

Acid activation is complex and involves a series of chemical reactions, resulting in strongly protonated clay mineral surface and increased specific surface area. Activation proceeds with partial dissolution of bentonites and includes an initial replacement of exchangeable cations by protons (H^+); indeed Al^{3+}, $Mg^{2+}$and Fe^{2+} cations are extracted from octahedral and tetrahedral sheets and are also replaced by H^+, with subsequent release of the structural cations as salts of the mineral acid, as shown in Figure 2.2 which indicates the site of substitution. This attack alters the structure, chemical and physical properties of the clay while increasing the adsorption capacity **[**Korichi *et al.*, 2009; Rossi *et al.*, 2003; Rožic *et al.* 2010]. Didi *et al.*, 2009 examined the bleaching capacity and optimized acid activation of bentonites from Algeria and found that acid concentration and activation time influence greatly the bleaching capacity of bentonite. Despite numerous studies, no definite relationship exists between the performance of the acid activated clay and the composition or properties of the original clay. Hence, each clay has to be specifically activated and tested for its performance [Foletto, *et al.*, 2011].

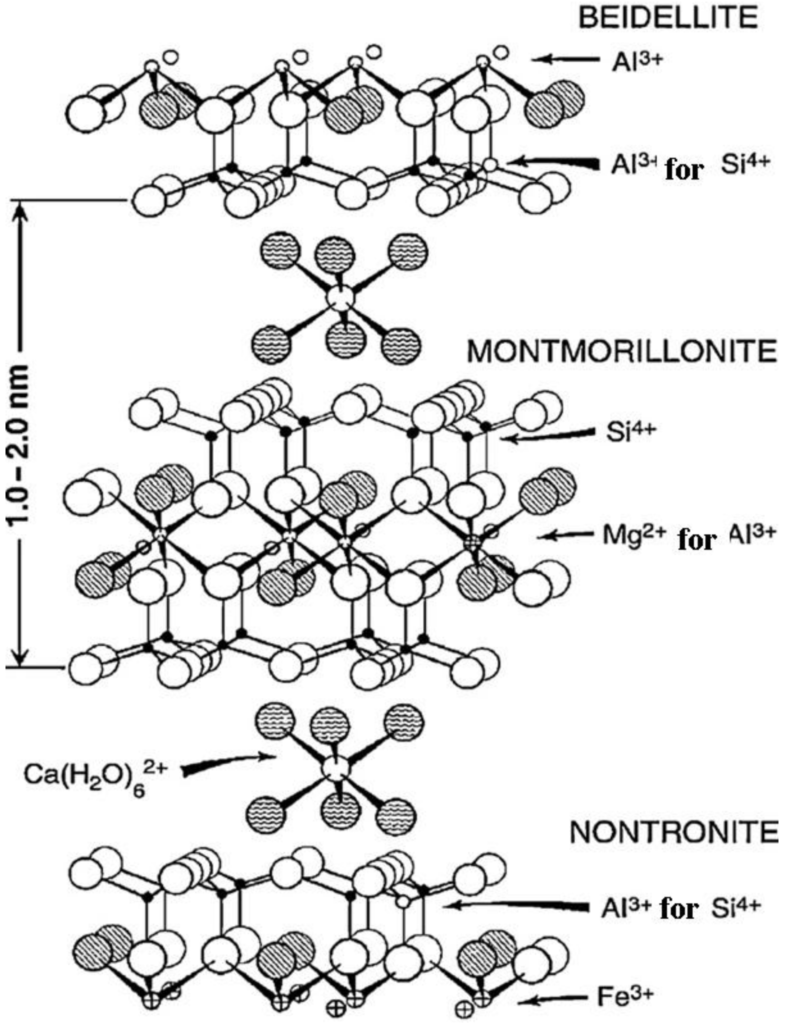


Figure 2.2: Structure of 2:1 phyllosilicate minerals indicating charge sites and different locations of substitutions

[Farihahusnah *et al.*, 2011].

The acid attack plays an important role to enhance the adsorption capacity of bentonite clay. Generally, raw bentonite sample is washed and crushed before treatment with a mineral acid at fixed temperature and contact time with constant stirring. When activation is completed, the mixture is filtered, washed several times with distilled water and then dried. The dried clay is sized and kept for future applications [Ajemba and Onukwuli, 2013 and Usman *et al.,* 2013]. The simplified flow diagram of the process for the production of acid activated bleaching earth is illustrated in Figure 2.3 below.

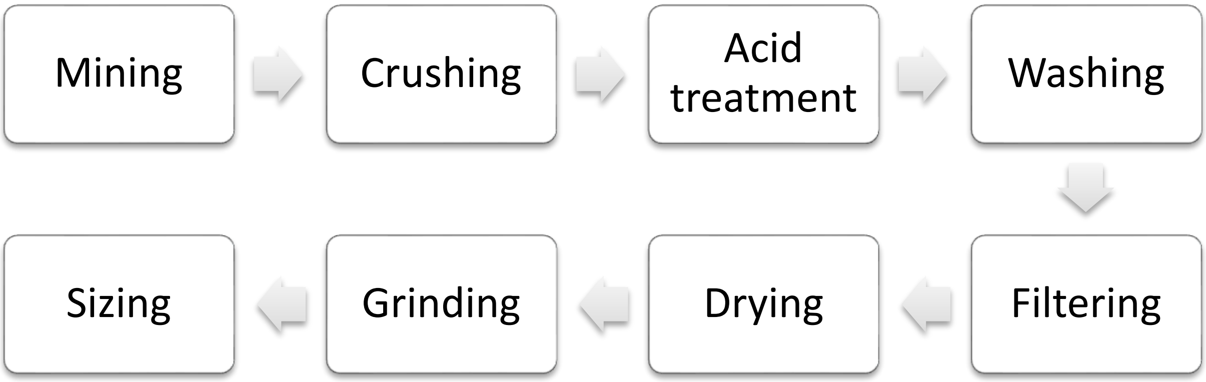


Figure 2.3: Industrial process of acid activation [Farihahusnah *et al.*, 2011]

2.3.1.2 **Factors affecting acid activation process**

Acid activation is mostly affected by the following factors [Farihahusnah *et al.*, 2011]:

- Nature of the natural clay
- Contact time
- Temperature
- Acid concentration and
- Type of acid used for activation.

2.3.2 Pillaring treatment

Pillaring is a method which alters the properties of bleaching earth by using combination of chemical and physical treatment. Pillared clays are produced by calcinations of the exchangeable oxacations (for example Al, Cr, Ga, Si, Ce,) for use as adsorbents or catalysts, especially in production of fuel by cracking vegetable oils [Kloprogge *et al.*, 2005].

2.3.3 Cationic surfactant treatment

Organic surfactants are adsorbed by montmorillonite to form 'organo-montmorillonite complex'. These hydrophobic complexes are used as adsorbents of organic pollutant and as components in the synthesis of clay-polymer nanocomposites as low cost organoclays [Hongping *et al.,* 2010].

2.3.4 Thermal activation

Thermal activation of clay mineral is a physical treatment process which involves calcination of clays at high temperatures. It removes impurities and moisture content in clay particles [Ajemba, 2012].

2.3.5 Polymer modified clays

Polymer modified clays are generally formed by physical adsorption, chemical grafting or ion exchange with surfactants. It enhances the physical and chemical properties, but does not affect the structure [Peng, 2007].

2.4 Vegetable Oil

Oils are usually obtained from animal tissues. Most vegetable oils are from seeds and fruits. Vegetable oils and fats contain the highest source of energy per unit mass than any other nutrient and are carriers of fat-soluble vitamins [Fortification basics, 2014]. They are used in the production of shortening, margarines, frying oils, and other edible products, as well as in food manufacturing. Besides the food industry, they also have applications in oleo-chemical, leather, paint, rubber, textile and pharmaceutical industries [Gunstone, 2002].

Edible oils in Kenya represent the second important import after petroleum oils [EPZA, 2005]. The increase in consumption of vegetable is considerable, and therefore, the government of Kenya (GOK) has invested in both plantation of oilseeds and in the importation of crude vegetable oils [OGA, 2009]. Malaysia is the main supplier as it sells at a lower price than other world markets [OGA, 2009]. Kenya has considerable opportunities for boosting local production in terms of conducive climate and a range of annual and perennial oil seed crops. Hence, GOK and Food and Agriculture Organization (FAO) have promoted traditional crops in western Kenya such as coconut, groundnuts, sunflower, soybeans, palm oil, cotton seed and maize. Figure 2.4 shows the production, consumption and trade of vegetable oil in Kenya [EPZA, 2005; OGA, 2009]. Kenya embassy in Brussels has reported that services that enhance the production of industrial crop such as oil seeds are among the main stay of Kenya's economy with abundant opportunities [www.kenyabrussels.com/Investment_Opportunities, retrieved on 17th September 2013].

Office of global analysis (OGA) in 2009 has reported that about 30 Kenyan companies refine vegetable oilseeds with the largest of them crushing about 100 tons of oilseeds per day, while refining another 800 tons of oils per day. The five largest companies process over 550 000 tons of oilseeds and crude oils per year. Therefore, using activated clay from locally available bleaching earth is an advantage to the country's economy and the entire society.

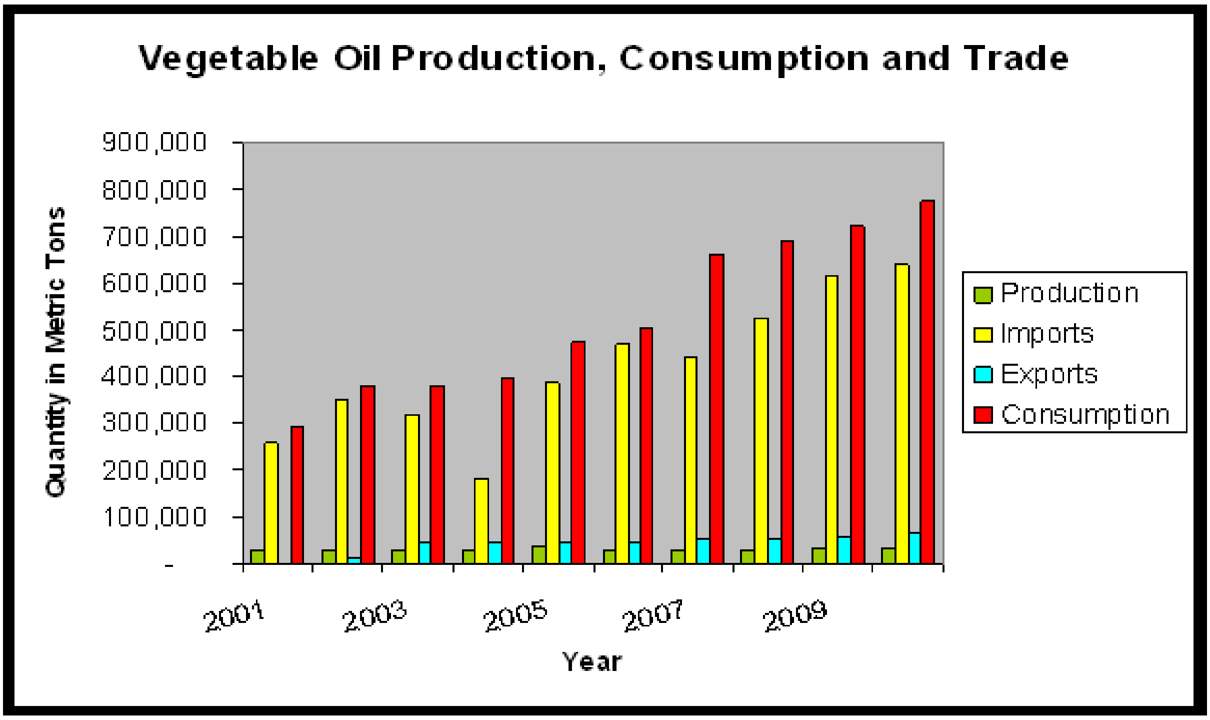


Figure 2.4: Vegetable oil production, consumption and trade in Kenya

[OGA, 2009]

2.4.1 Palm oil

Palm oil (*Elaeis guineesis*), one of the most important oil producing plants originated from West Africa. In 2012, The World Wide Fund for nature (WWF) reported that, among 17 oils and fats on the global market, palm oil has emerged as the leader, accounting for approximately a third of the world’s edible oil production. The main areas of palm oil production are Malaysia, Indonesia, Africa and Latin America [WWF, 2012].

Oil extracted from palm nut is termed crude palm oil (CPO). It is a raw material for products such as cooking oil, margarine and shortening but also has non-food applications in soap, detergent, and cosmetics production [Rohani *et al.,* 2006].

Table 2.1 shows the composition of crude palm oil which has 5 main chemical groups [Ejikeme *et al.*, 2013].

Table 2.1: Chemical composition of CPO

Group	**Components in the group**
Oil	-Triglycerides, diglyceride , monoglyceride - Phospholipids, glycolipid and lipoprotein - Free fatty acids
Oxidized Products	- Peroxides, aldehydes, ketones, furfurals (from sugars)
Non-oil (but oil soluble)	- Carotene - Tocopherols - Squalene - Sterols
Impurities	- Metal particles - Metal ions - Metal complexes
Water Soluble	- Water (moisture) - Glycerol - Chlorophyll pigments - Phenols - Sugars (soluble carbohydrates)

The pigmentation of fruits is related to their stage of maturity. The ripe palm is extracted and the resulting oil has a rich orange-red colour due to its high content of carotene. The major saturated fatty acids that compose CPO is palmitic acid (C_{16}) 44.3% which is balanced by almost 38.7% monosaturated oleic acid (C_{18}) and 10.5% polyunsaturated linoleic acid (C_{18}). The reminder is largely stearic (C_{18}) 4.6% and myristic (C_{14}) 1% acids [Mukherjee and Mitra, 2009].

CPO contains impurities such as organic pigments, soaps, oxidation metals and trace metals. These impurities have negative impacts on the taste and smell of the oil as well as on its appearance and shelf life stability which reduces consumer acceptance and marketability, hence the need for removal through refining [Usman *et al.*, 2013, Ejikeme *et al.*, 2013]. In addition, CPO has a very low smoke point, which can be removed if the oil can be bleached to remove impurities [Ajemba and Onukwuli, 2013].

2.4.2 Methods of refining vegetable oils

Refining process is a necessary step for production of edible oil and fats products. The aim of this process is to remove coloured material, impurities such as gums (phosphatides), traces of metal and free fatty acids which may produce oxidation products leading to degeneration and short life of the finished product [Barbesi, 2006, Usman *et al.*, 2013].

It is important to have proper refining process in order to produce high quality finished product with specified quality range that meet user’s requirements. There are basically two types of refining processes available in the vegetable oils industries, namely, chemical and physical refining [Farihahusnah *et al.*, 2011; Rossi *et al.*, 2003]. These processes differ in the type of chemicals used and the mode of removing the free fatty acid. These processes comprise of several stages such as degumming, neutralization, bleaching and deodorization [Farihahusnah *et al.*, 2011, Berbesi, 2006]. The processing routes for chemical and physical refining are as illustrated in Figure 2.5 below.

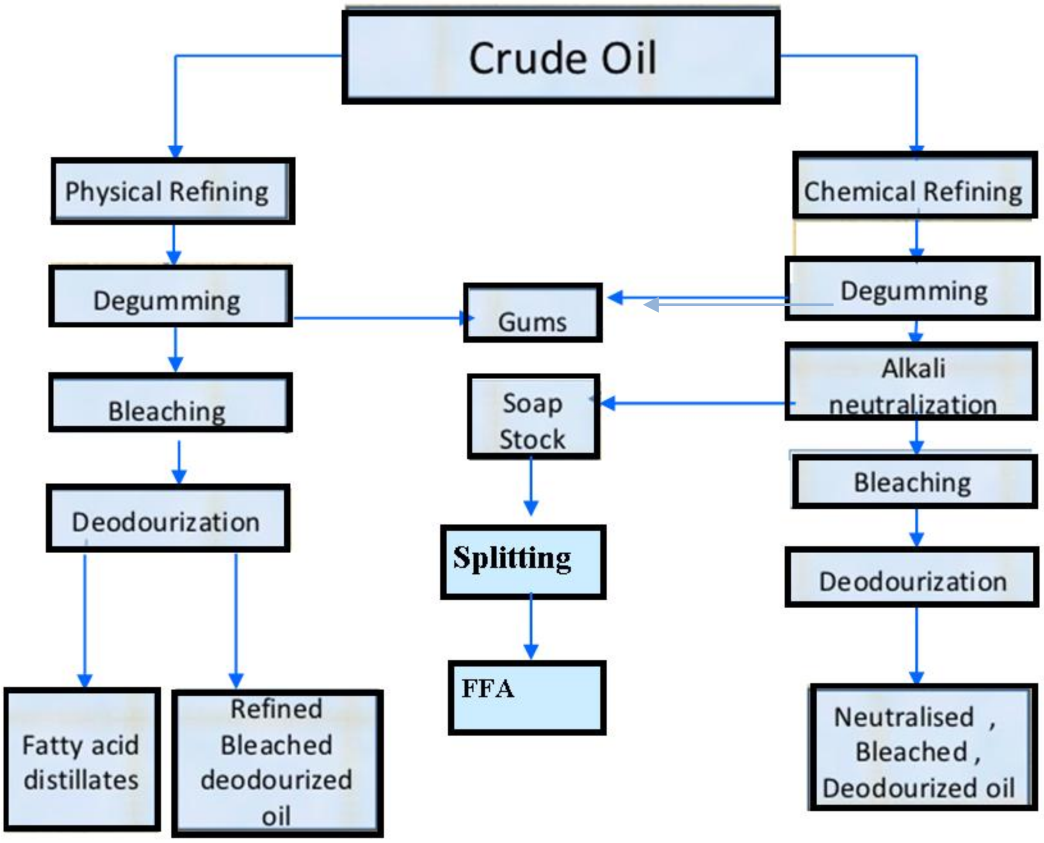


Figure 2.5: Chemical and physical refining routes

Among these stages, bleaching is the most critical phase since it helps to improve the appearance, flavour, taste and stability of the final oil products [Rossi *et al.*, 2003].

2.5 Bleaching of vegetable oil

Bleaching stage of the refining process is regarded as the most important step in fats and oil refining, as it is designed to remove not only pigments (colour-producing substances), but also a wide range of other impurities; it guarantees an excellent quality of the final products [Langmaack and Eggers, 2002] and it is also a cost intensive process for refining vegetable oils attributed to use of bleaching agent. Bleaching basically consist of impurities and colouring matter adsorption by means of bleaching agents. This consists of bringing the oil into contact with adsorbent mineral clay. In vegetable oil industry, they usually use acid activated bleaching earth (bentonite), natural bleaching earth, activated carbon and synthetic silicates [Rohani *et al.*, 2006].

During the bleaching process, the oil is brought into contact with surface active substances that adsorb undesired particles. The adsorbent and the adsorbed are filtered off, and the oil leaves the plant with the desired colour. As a consequence, the quality of the oil is stabilised, since precursors and catalysts of autoxidation are removed [Langmaack and Eggers, 2002]. Activated clay may act as a catalyst for oxidation in the presence of oxygen at elevated temperatures. The oxidation products lead to degeneration and short shelf life of the final product [Usman *et al.*, 2012]. Therefore the bleaching process is carried out either under steam/ nitrogen blanket or vacuum.

Figure 2.6 shows annual imports of bleaching earth in Kenya. Between 1997 and 2007, the importation cost increased about five times. The amount imported rose from 76 tons to 740 tons during the same period as shown in Fig. 2.7 [World Integrated Trade Solutions, 2014]. Information from Kapa Oil Refineries, one of the vegetable refiners in Kenya indicated the cost of activated bleaching in 2013 was 46 Kenya shillings exclusive of value added tax.

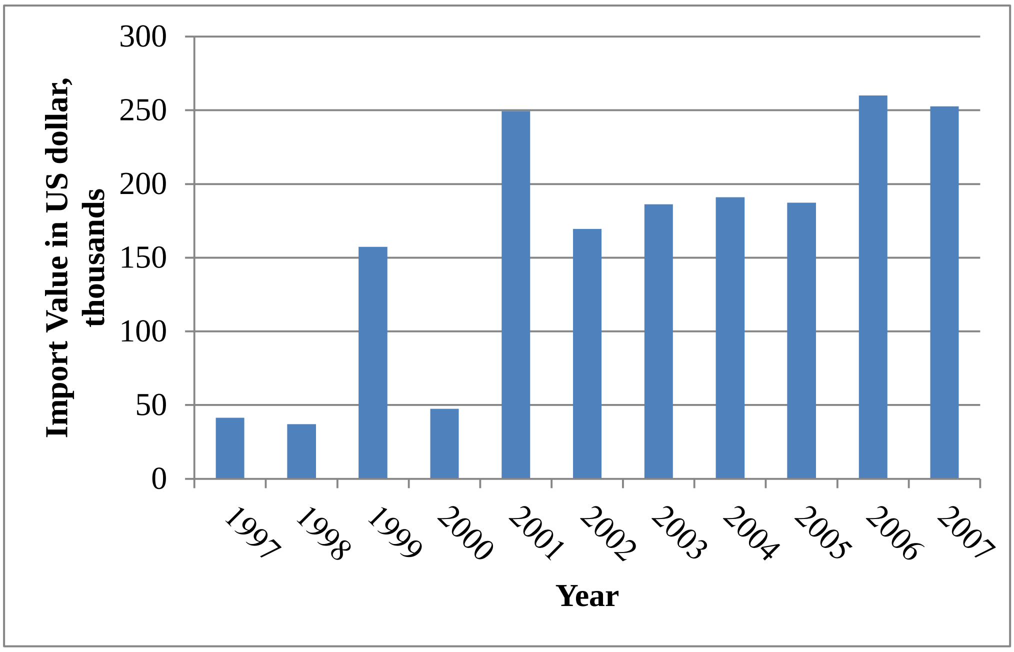


Figure 2.6: Kenya's imports for decolorizing earth and fuller's earth, 1997-2007 (World Integrated Trade Solutions, 2014)

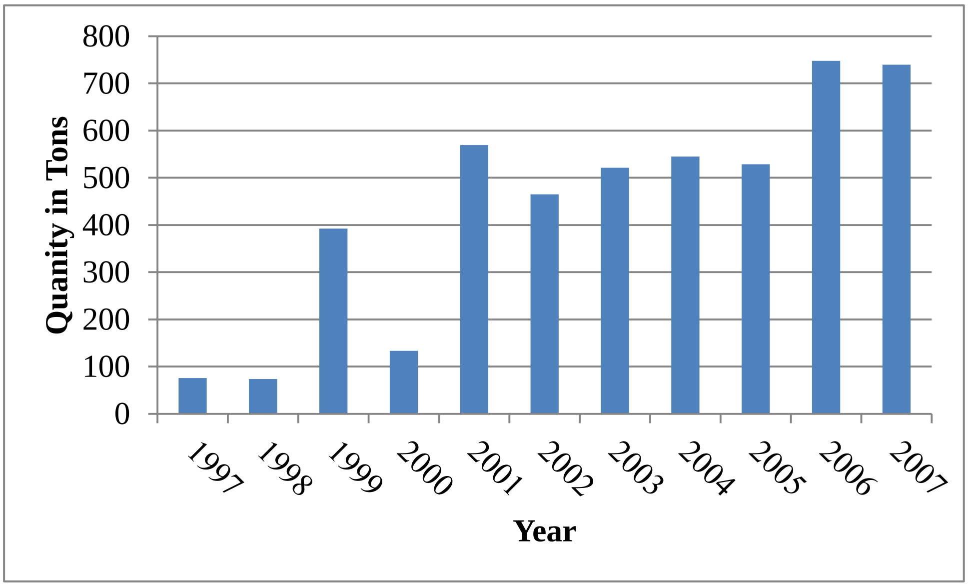


Figure 2.7: Quantity of Kenya's imports for decolorizing earth and fuller's earth, 1997-2007 (World Integrated Trade Solutions, 2014)

2.5.1 Types of Bleaching Methods

Generally, there are three types of bleaching methods that can be used in edible oil industry [Morad *et al.*, 2001; Farihahusnah *et al.*, 2011, Ejikeme *et al.*, 2013].

2.5.1.1 **Heat Bleaching**

During heat bleaching, oil must be heated at high temperature to more than 175° C. The oil is heated until the carotenes become colourless. However this will leave the pigments molecules in the oil and may have adverse effect on it. Moreover, if this oil comes into contact with air, degradation of coloured products present may be formed and these products are very difficult to remove.

2.5.1.2 **Chemical Oxidation**

In chemical oxidation, carotenes are made colourless or less coloured by oxidation. But such oxidation invariably affects the glycerides and destroys natural antioxidants. Consequently, it is never used for edible oils but it is restricted to oils for technical purposes, such as soap-making.

2.5.1.3 **Adsorption**

Adsorption is the common method usually used for bleaching edible oil using bleaching agents. Examples of bleaching agents are acid activated bleaching earths, activated carbon and silica gel. Bleaching agents normally posses a large surface that has a more or less specific affinity for pigment-type molecules, thus removing them from oil without damaging the oil.

2.5.2 Freundlich isotherm

Mathematically, the bleaching process follows Freundlich adsorption isotherm [Rohani *et al.*, 2006]. Adsorption is the equilibrium relationships between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature [Rossi *et al.*, 2003]. The mathematical expression relating adsorption to residual solute concentration is illustrated as per the equation below:

$$\mathbf{\frac{x}{m} = Kc^{n}} \qquad \textbf{Equation (2.1)}$$

By linearization the Freundlich equation becomes,

$$\boldsymbol{\log\frac{x}{m} = \log K + n\log c} \qquad \textbf{Equation (2.2)}$$

Where x = amount of substance adsorbed

m = quantity of adsorbent

c =quantity of residual substance dissolved

K and n = constants unrelated to the amount of solute and adsorbent.

As demonstrated by Topallar, (1998), by measuring the absorbance, the relative amount of pigment adsorbed (X) and the relative residual amount at equilibrium (X_e) are obtained from Equations 2.3 and 2.4:

$$\boldsymbol{X = \frac{A_0 - A_t}{A_0}} \qquad \textbf{Equation (2.3)}$$

$$\boldsymbol{X_e = \frac{A_t}{A_0}} \qquad \textbf{Equation (2.4)}$$

Where A_0 is the absorbance of unbleached (crude) oil and A_t is the absorbance of bleached oil at time t. Thus, by replacing the residual substance C with X_e, Equations 2.1 and 2.2 become:

$$\frac{x}{m} = K{X_e}^n$$ **Equation (2.5)**

$$\log\frac{x}{m} = \log K + n\log X_e$$ **Equation (2.6)**

The value of K determines the adsorption capacity of the adsorbent for a specific solute, whereas the value of n determines the ranges of bleaching in which the adsorbent shows its greatest effect. According to Rossi *et al.* (2003), if n is high, the adsorbent will be effective for removing the first portions of colour but less efficient for reaching highest bleaching degree. The value of K and n depend on the kind of adsorbent and oil and also the operating conditions of the bleaching process.

2.5.3 Langmuir isotherm

Langmuir isotherms are also used to describe adsorption processes. Langmuir demonstrated the dynamic equilibrium between adsorbed and free molecules and suggested the following relation [Topallar, 1998]

$$\frac{X_e}{x_{\ m}} = \frac{1}{a} + \frac{b}{a}X_e$$ **Equation (2.7)**

Where a and b are Langmuir constants, and are evaluated by plotting Xe/(x/m) against Xe.

2.5.4 Bleaching Agents

2.5.4.1 **Acid –Activated Bleaching Earth**

Acid-activated bleaching earths (Figure 2.8) are normally used in the refining of minerals and in the bleaching of vegetable oils for removing all kind of impurities. Acid activated bleaching earths are in general produced from naturally occurring high montmorillonite clays. The structural features of the clay are modified by treatment with mineral acids. Bleaching earth works based on adsorption and ion exchange [Rohani *et al.*, 2006].

Figure 2.8: Acid activated bentonite clay

[Rohani *et al.*, 2006]

The adsorption process is influenced by some factors such as:

- Adsorbent polarity
- Particle size
- Surface area
- Pore volume

- Pore size

2.5.4.2 **Natural Bleaching Earth**

Natural/neutral bleaching earths are used with limited colour-reducing effect but are particularly useful in treating animal fats. According to Rossi *et al.*, (2003), they are excellent metal adsorbents.

2.5.4.3 **Activated Carbon**

Activated carbon is derived from all materials containing high fixed carbon content. The most used are coal, coconut shell, wood, peat and petroleum based residues. Depending upon the raw material and the production procedures, activated carbons contain different pore diameters ranging from micropores (40 Angstrom) to macropores (>5000Angstrom) structures. Adsorption process is due to the large adsorbent surface and small volume of carbon and therefore the micropores structure is more suitable for bleaching action [CCI, 2006].

Activated carbon has been used in bleaching oil, but its use is limited due to the high operation costs, which is a major economic consideration in any production process [Qingliang *et al.*, 2013; Usman *et al.*, 2013].

2.5.4.4 **Synthetic Silicates**

Synthetic silicates are used in edible oil bleaching, largely in wet bleaching with a focus on selectively removing phosphatides, trace metals and soaps. Although they have a moderate capacity for pigment removal, they are used in combination with bleaching clay and due to the synergic action the amount of bleaching clays is reduced [Rossi *et al.*, 2003].

2.5.5 Bleaching process

The general bleaching process is carried out at temperature in the range of 80-120°C and contact time ranging from 20 to 40 minutes under vacuum or nitrogen. The dosage of bleaching earth can vary depending on both the process and oil type. Chemical refining uses 0.5-2% on a weight basis while physical refining uses 0.25-2%. However for darker oils, 2-4% bleaching earth may be used to meet final colour requirements [Diaz and Santos, 2001, Usman *et al.,* 2012]. After bleaching, the bleaching agent is removed through vacuum filtration. The filter cake still contains oil and this parameter is referred to as ‘oil retention’.

Excessive oil retention increases the cost of running the bleaching process. In general, oil loss results from oil lost to filter cake and this oil retention can go up to 40% [Usman *et al.*, 2012]. This value can be reduced to 20-30%, either by the use of steam or nitrogen at the end of filtration. Smaller particle size of clays produce better bleaching performance however, filtration rate and oil retention can be affected adversely. Therefore for efficient filtration, short filtration time and low oil retention are desired.

Bleaching can be carried out as either batch or as continuous process.

2.5.5.1 **Batch bleaching**

Batch bleaching is the simple operation, where the bleaching vessel is fed with a set amount of oil and heated by steam to remove the moisture while the apparatus is maintained under vacuum by the barometric condenser and vacuum pump. During this stage the bleacher acts as dryer. After drying, a metered amount of bleaching earth is added to the mass and the adsorbent is pulled into the vessel by the vacuum existing therein. Upon completion of bleaching, the oil-bleaching earth suspension is pumped to filtration section where components are separated [Rohani *et al.*, 2006].

2.5.5.2 **Continuous bleaching**

In a continuous bleaching plant, the crude oil is heated by means of steam in the exchanger and is sucked as very small drops in the lower part of the vacuumed bleacher which operation is ensured by the presence of barometric condenser and ejectors. Dry steam is injected to the oil mass in order to facilitate the operation and also to keep the mass in agitation. The oil is then taken by a pump through a series of heat exchangers to raise its temperature to a desired level and is then sent to the upper part of the bleaching vessel. The oil remains in contact with the earth for a specified period of time and then the suspension is sent to filtration [Rohani *et al.,* 2006].

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials

The grey and brownish coloured bentonite clays were obtained locally from Thika (Silverstone Masters Ltd) and Athi River, Kenya respectively at 1 m from the surface. Bentonite clays were used after washing with distilled water, ground and sieved through 200 mesh size (75 µm). The crude palm oil was obtained from Kapa Oil Refineries Ltd. (K). All chemicals used were of analytical grade.

3.2 Physical Characterization

3.2.1 Moisture Content

Moisture content of both raw and acid activated bentonite clays were determined by drying approximately 1.00g of bentonite clay at 110 °C in an oven (E 28# 04-71528) until the mass became constant. Then after cooling in desiccator the moisture content was determined using equation below. Each sample was analyzed twice and the average percentage was reported.

$$W\% = \frac{A-B}{A} * 100 \qquad \text{Equation (3.1)}$$

Where W%: percentage of moisture in the sample

A: weight of wet sample (grams)

B: weight of dry sample (grams)

3.2.2 pH determination

pH of both activated and natural bentonite clays were determined by soaking 5g±0.025g of clay in 25 ml of distilled water for twelve hours before pH was tested using pH-meter (HANNA instruments, pH 211).

3.2.3 Apparent bulk density determination

The sieved clay (whether raw or activated) was put into a graduated cylinder of known weight and avoiding compression. The cylinder was tapped vigorously on the horizontal surface to constant clay volume. The volume of the packed clay was taken and apparent bulk density (ABD) was calculated [Rich, 1960] as follows:

$$ABD = \frac{W_x - W_y}{V} g/cm^3 \qquad \textbf{Equation (3.2)}$$

Where W_x is the weight of the cylinder plus clay; W_y is the weight of the empty cylinder; V is the total weight of clay used after compression.

3.2.4 Cation exchange capacity (CEC)

CEC of bentonite clay was determined by the $BaCl_2$ compulsive exchange method. 1mg of sample clay was put in a centrifuge tube, followed by 10 ml of 0.1 M $BaCl_2.2H_2O$. (LOBA chemie PVT Ltd India). After the mixture was shaken for 2 hours, the slurry was separated by centrifuging at 10000 rpm and was then decanted. The CEC was determined by measuring Ca, Mg, K and Al in the extract using AAS (SpectrAA-10, Varlan) and then applying the following equation:

CEC (cmol/kg of clay) = Ca/20 + Mg/12 + K/39 +Al/9 Equation (3.3)

3.3 Chemical characterization of bentonite clay

Chemical composition of bentonite clay was determined using atomic absorption spectroscopy (AAS). Approximately 0.100 g of clay sample was digested by adding 3 ml of 48% hydrofluoric acid and 1ml of aqua regia and the mixture was left overnight. 50 ml of boric acid was added and after one hour, 46 ml of distilled water was added to make 100 ml solution which was then diluted to 10% with 50% v/v boric acid.

At least 1g of clay sample was ignited at 1000°C for loss of ignition (LOI) determination.

3.4 Acid activation of bentonite clay

Acid activation was done according to the method described by Foletto, (2011), with slight modifications. Figure 3.1 shows the image of the activation process used in this study.

Figure 3.1: Set up of acid activation process

3.4.1 Effect of acid concentration

The samples of clay were initially washed thoroughly with distilled water. They were then dried in the oven at 105 °C for 3 hours and sieved through a 200 mesh sieve. Five concentrations of sulphuric acid (BDH Chemicals Ltd, Poole England) were prepared (1.0 M, 2.0 M, 3.0 M, 4.0 M and 5.0 M). 5g ± 0.025g of the dry 200 mesh clay sample was mixed with 50 ml 1.0 M acid concentrations and the mixture heated at 100 °C under reflux for 3 hours. The procedure was repeated with the other acid concentrations.

The obtained samples were then cooled, filtered under vacuum and washed repeatedly with distilled water until the filtrate was free of SO_4^{2-} ions. The filtered samples were dried at 105 °C for 3 hours. All bentonite clay samples were again crushed to a particle size that would pass through a 200 mesh size and labeled A0, A1, A2, A3, A4, A5, T0, T1, T2, T3, T4, and T5, where numbers indicate the molar acid concentration used in activation steps, while A and T stands for Athi River and Thika bentonite clays respectively. Then they were stored in polyethylene bags for bleaching and other studies.

3.4.2 Effect of activation contact time

5g ± 0.025g of the dry 200 mesh clay sample was treated with 50 ml of 2.0 M H_2SO_4. The mixture was heated at 100 °C under reflux. The experiment was carried out for various contact times ranging from 30 minutes to 180minutes. The obtained samples were then cooled, filtered under vacuum and washed repeatedly with distilled water until the filtrate was free of SO_4^{2-} ions. The filtered samples were dried at 105 °C for 3 hours. Then dried activated bentonite clays were again crushed to a particle size that would pass through a 200 mesh sieve and were stored in polyethylene bags for bleaching studies.

3.4.3 Effect of temperature on activation

5 g ± 0.025g of the dry 200 mesh clay sample was treated with 50 ml of 2.0 M H_2SO_4. The mixture was heated under reflux at 100 °C and 120 °C for 3 hours. The obtained samples were then cooled, filtered under vacuum and washed repeatedly with distilled water until the filtrate was free of SO_4^{2-} ions. The filtered samples were dried at 105 °C for 3 hours. Then dried activated bentonite clays were again crushed to a particle size that would pass through a 200 mesh sieve and were then stored in polyethylene bags for bleaching studies.

3.4.4 Effect of clay acid ratio

5 g ± 0.025g of the dried 200 mesh clay sample was activated with 5.0 M H_2SO_4 the mixture was heated under reflux at 100 °C for 3 hours with a constant stirring. The procedure was repeated for 15 g, 25 g, and 35 g of bentonite clays. The obtained samples were then cooled, filtered under vacuum and washed repeatedly with distilled water until the filtrate was free of SO_4^{2-} ions. The filtered samples were dried at 105 °C for 3 hours. Then dried activated bentonite clays were again crushed to a particle size that would pass through a 200 mesh sieve and were then stored in polyethylene bags for bleaching studies.

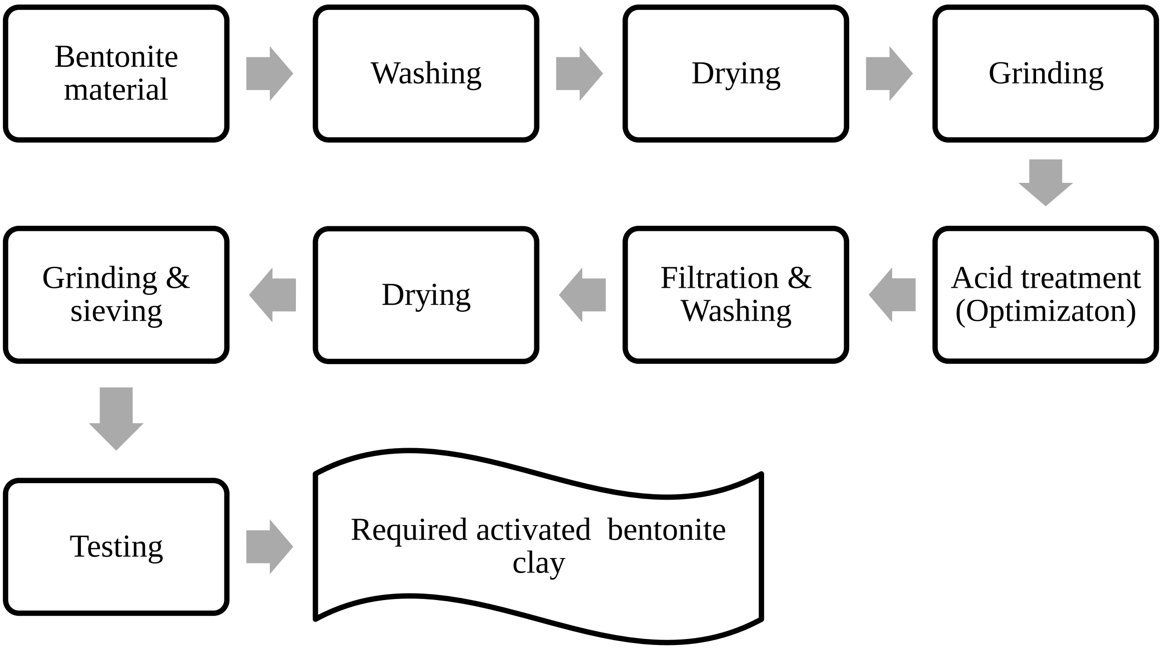


Figure 3.2: Flow schematic diagram for acid activation of bentonite clay

3.5 Evaluation of bleaching performance of bentonite clay

The crude palm oil was first degummed by adding 0.1 % of concentrated phosphoric acid to oil at 80 ºC, stirred for 15 min and then washed with hot distilled water. The mixture was centrifuged into two layers. The oil phase was vacuum-dried and used in bleaching process, while the aqueous phase which contained the phosphatides was discarded. Bleaching process was carried out by adding 0.1 g ± 0.005g of activated clay to 10 ml of the degummed oil (1 % w/v) initially at 70°C and was then raised to 90°C for 30 minutes with constant stirring. During the process, a stream of nitrogen (N_2) was maintained above the oil surface (Figure 3.3). The bleached oil was cooled to 70°C and filtered under vacuum. This process was repeated with dosage of 0.05 g ± 0.005g, 0.2 g ± 0.001g, 0.3 g± 0.001g and 0.4 ± 0.002 g ; temperature between 70 and 120°C and contact time ranging from 5 to 60 minutes. Each adsorption experiment was repeated twice, and the mean of the results was reported.

The absorbance of the palm oil was measured using UV-Vis spectrometer (UV-1700). Palm oil was first diluted in acetone solution (LOBA Chemie PVT ltd India,) and the maximum absorbance was read at 450 nm wavelength using acetone as reference. The percentage bleaching performance of the clays was determined as:

$$BP\% = \frac{A_0 - A}{A_0} * 100 \qquad \textbf{Equation (3.4)}$$

Where; A_o and A, are the absorbances of the unbleached and bleached palm oil respectively [Foletto *et al.*, 2011, Usman, *et al.*, 2013].

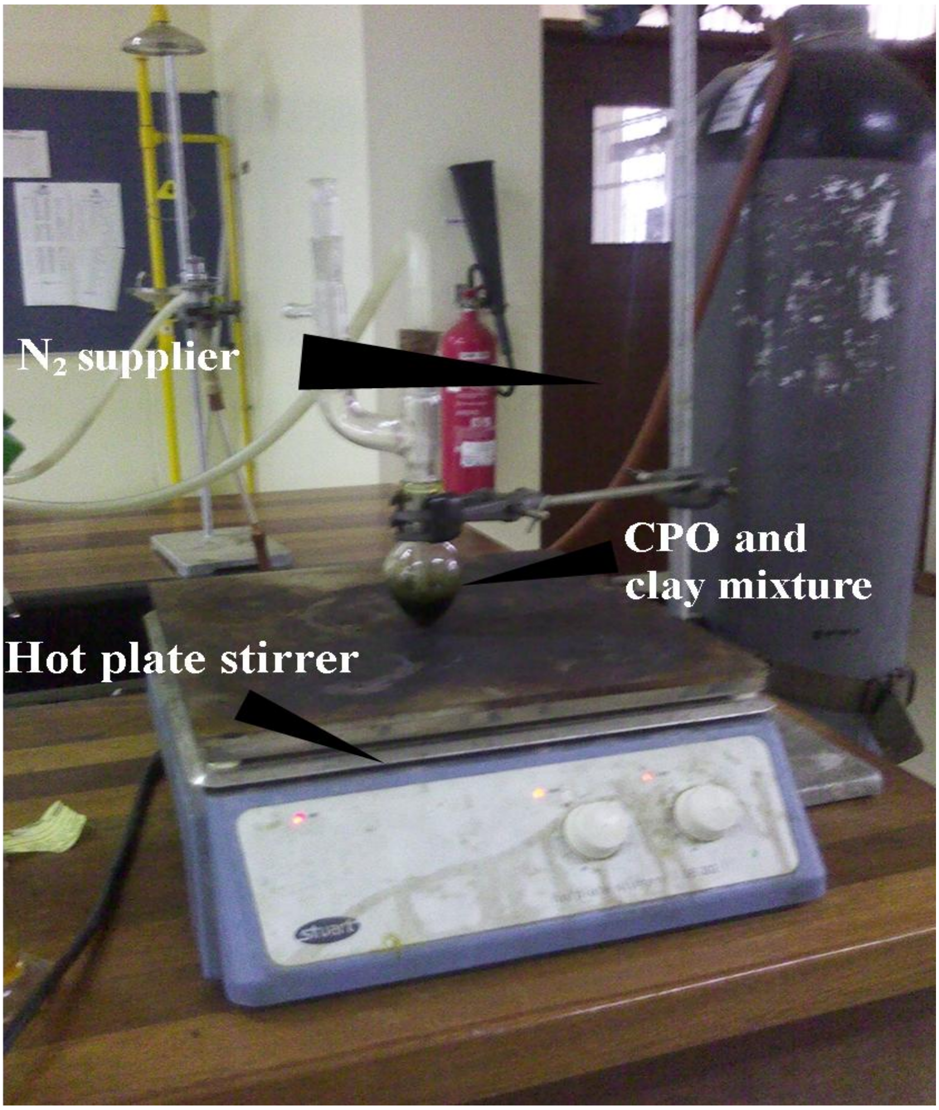


Figure 3.3: Bleaching process unit

3.6 Analysis of the final product

3.6.1 Oil retention (OR)

The bleached palm oil (BPO) was filtered using vacuum for 10 minutes, after which the filter cake was weighed ($W_{\text{filter cake}}$), dried at 105 °C until the weight was constant (W_{H_2O}). The oil retention (OR %) was calculated using the equation below [Usman *et al.*, 2012].

$$OR\ \% = \frac{W_{filter\ cake} - W_{BE} - W_{H_2O}}{W_{filter\ cake}} * 100 \qquad \textbf{Equation (3.5)}$$

Where W_{BE}: weight of bleaching earth

3.6.2 Free fatty acid (FFA) determination

FFA content in the crude and bleached palm oils were determined using titration method [Worthen, 1938, Rohani *et al.*, 2006, Lubrizol test procedure, 2010]. The following procedure was used

The oil was melted at 60 °C and thoroughly homogenized before sampling. 10 ml of neutralized isopropyl alcohol (ET Monks & Co.Ltd) was put in an Erlenmeyer flask and 5 drops of phenolphthalein indicator were added and the flask placed on the hot plate stirrer. The solution was homogenised and 1ml of oil was added. The slurry was stirred while titrating with 0.1 M sodium hydroxide (Uni-Chem Chemical Reagents, AR) to the first permanent pink colour after at least 30 seconds.

The results were expressed as:

$$FFA\ \%\ as\ palmitic\ acid = \frac{25.6\ x\ N\ x\ V}{W} \qquad \textbf{Equation (2.6)}$$

Where N: normality of NaOH solution

V: volume of NaOH solution used in ml

W: weight of oil sample

3.6.3 Oil density (D)

Density of both crude palm oil and bleached palm oil were determined using a pycnometer. First the weight of empty pycnometer was determined, and then it was filled with oil. The density of oil was calculated as follow:

$$\mathrm{D} = \frac{M_{oil}}{V}\left(\frac{g}{ml}\right)$$ **Equation (3.7)**

Where M_{oil} was weight of oil and V was the volume of the pycnometer.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Chemical properties of the clay

The chemical composition and loss of ignition (LOI) of Athi River (A) and Thika (T) clay samples of both raw and activated bentonite clay minerals activated at different acid concentration are shown in Tables 4.1 and 4.2.

Acid treatment was observed to modify the structure of bentonite as indicated by the change in the chemical composition. Except for SiO_2 which recorded a consistent increase in amount from 46.71 % to 78.52 % for A bentonite and 63.88 % to 76.81 % for T bentonite as acid concentration was increased, the composition of other components decreased after activation. The increase in SiO_2 content and a decrease of others was in conformity with the results reported by Usman *et al.,* (2012) and Arfaoui *et al.,* (2008) which indicated a partial destruction of the octahedral sheet by dissolution of the exchangeable cations.

Table 4.1: Chemical composition (% oxide content) of raw and acid activated Athi River bentonite clay and Commercial bleaching earth (CBE)

Chemical composition % Oxide content	Athi River bentonite clay						CBE
	Untreated	Treated with different concentration of H_2SO_4					
		1M	2M	3M	4M	5M	
SiO_2	46.71	60.03	69.45	74.8	78.52	78.34	62.89
Al_2O_3	15.96	13.75	9	6.8	5.31	4.13	12.68
CaO	4.09	0.57	0.58	0.6	0.83	0.63	0.457
MgO	1.53	0.4	0.33	2.7	0.5	3.6	1.212
Na_2O	3.8	0.98	1	1.09	1.12	1.17	0.397
K_2O	1.35	1.16	1.23	1.3	1.2	1.17	0.778
TiO_2	0.65	0.49	0.12	LD	LD	0.82	0.492
MnO	0.6	0.4	0.2	0.2	0.3	0.2	LD
Fe_2O_3	7.86	4.09	1.37	0.71	0.36	0.22	3.742
LOI	14.56	17.58	16.58	11.26	10.42	9.39	17.25

Note: LD: Means the oxide content was below the limit of detection.

The change observed for CaO, Al_2O_3 and Fe_2O_3 composition with increase in acid concentration (Table 4.1) is related to the progressive dissolution of the clay mineral. According to Diaz and Santos (2001), the octahedral sheet destruction passes the cations into the solution, while the silica generated by the tetrahedral sheet remains in the solid phase due to its insolubility.

Table 4.2: Chemical composition (% oxide content) of raw and acid activated T bentonite clay

Chemical composition % Oxide content	Thika bentonite clay					
	Untreated	Treated with different concentration of H_2SO_4				
		1.0M	2.0M	3.0M	4.0M	5.0M
SiO_2	63.88	67.87	70.54	70.62	74.79	76.81
Al_2O_3	9.96	10.92	9.79	9.22	9.73	9.28
CaO	1.44	0.63	0.78	0.77	0.58	0.64
MgO	0.56	3.36	0.31	0.33	0.29	0.29
Na_2O	4.7	6.04	5.63	5.78	5.05	5.31
K_2O	4	2.4	3	3.4	3	0.3
TiO_2	0.45	0.08	LD	LD	LD	LD
MnO	0.2	0.4	0.3	0.3	0.09	0.14
Fe_2O_3	8.41	4.66	6.2	6.12	4.25	4.99
LOI	1.68	2.83	2.05	1.63	1.62	1.68

Note: LD: means the oxide content was below the limit of detection

It is expected that both interlayer and exchangeable cations were removed during acid activation of bentonite. However, considerable amounts of these elements remains in the activated samples (Table 4.2), implying that, the acid treatment slightly affect this type of bentonite. It was reported elsewhere, that the swelling types of bentonite are not recommended to acid activation for improvement of their adsorption properties [Diaz and Santos, 2001].

It can be seen in Figure 4.1 and 4.2 that acid treatment had insignificant effect on Na_2O for Thika bentonite, which is among the exchangeable cations. This could be attributed to the fact that T bentonite has a high capacity to hold Na^+ ions [Quirine, *et al.*, 2007]. In addition, it could be attributed to the high viscosity of the dispersions, which made it difficult for mass transport necessary for acid activation [Diaz and Santos, 2001].

The MgO content in the Athi River and Thika samples were 1.53 and 0.56 respectively (Figure 4.1). It has been reported that bentonite with high MgO content in their structure are more acid activated than those with low MgO content [Foletto *et al.*, 2011], hence, the higher activation of Athi River clay samples. In addition, the results presented in Table 4.1 showed that for A bentonite, the ratio of Na_2O to CaO was 0.92, a value less than 1 which is indicative of the absence of swelling bentonite. For Thika bentonite the ratio of Na_2O to CaO was 3.26, which indicated the presence of swelling bentonite [Basim, 2011, Usman *et al*, 2012]. Therefore, the two clays can be classified as calcium bentonite and sodium bentonite respectively.

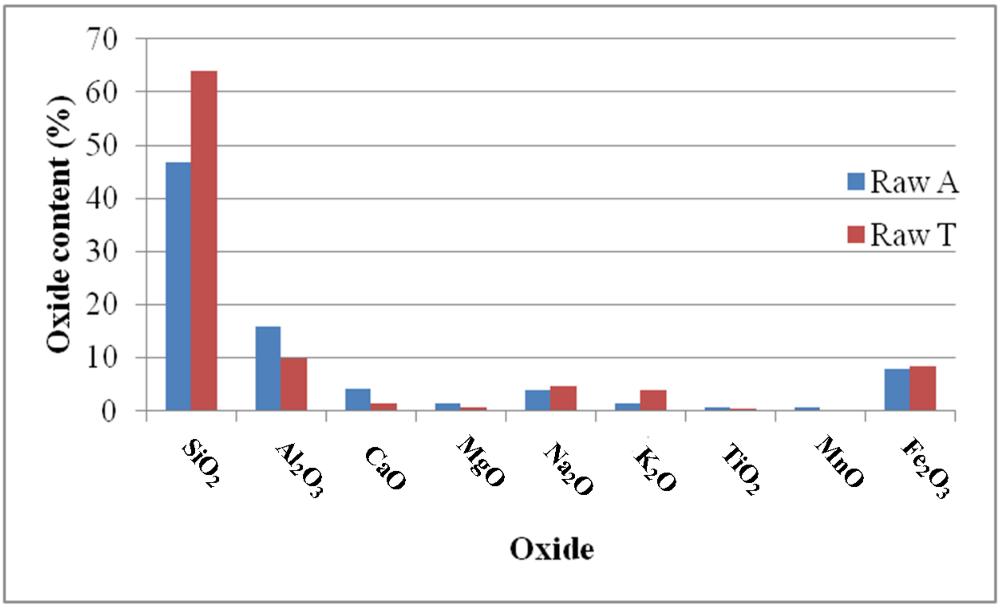


Figure 4.1: Chemical composition of raw Athi River (A) and Thika (T) bentonite clay

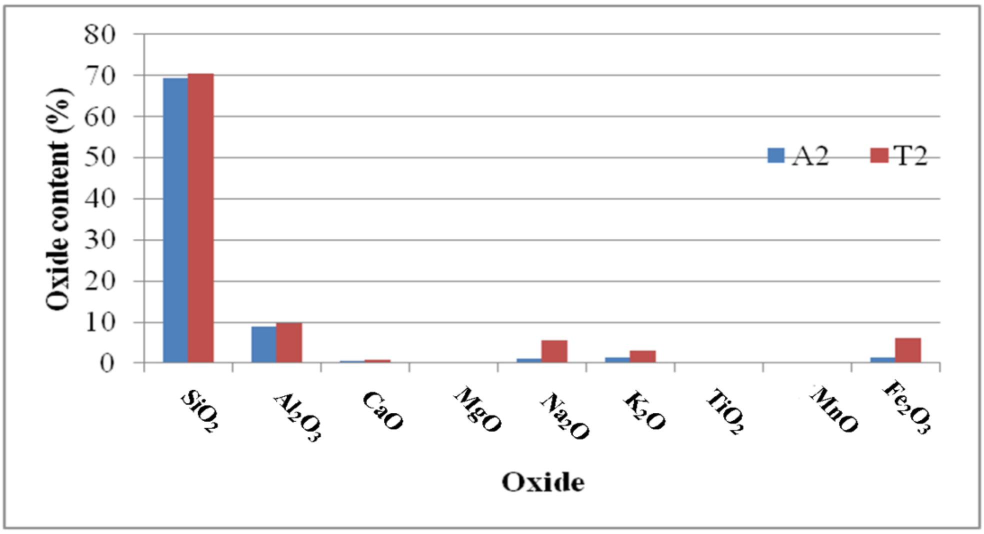


Figure 4.2: Chemical composition of Athi River (A) and Thika (T) bentonite clay activated with 2M H_2SO_4

4.2 Physical characteristics

4.2.1 Moisture content determination

After oven-drying, the free moisture remaining in samples was determined and this varied from 5.69 to 2.38 for A bentonite and 10.07 to 9.54 for T bentonite, as shown in Table 4.3 below.

Table 4.3: Variation of moisture content with acid concentration

Sulphuric Acid Concentration used		0M	1M	2M	3M	4M	5M
Moisture content (%)	Athi River clay	5.69	7.58	7.18	3.45	3.21	2.38
	Thika clay	10.07	10.03	10.03	9.76	10.95	9.54
	Commercial bleaching earth	8.83					

The results presented in Table 4.3 for A bentonite, revealed that at first, the acid attack increased the capacity of the clay to hold water. Subsequently, the moisture content decreased as the acid concentration was further increased. This could be attributed to the increase in void space as created as the exchangeable metal ions were displaced by hydrogen ions which have smaller volumes than metal ions. However, T bentonite showed only 1 % moisture difference, which could be attributed to less change in the T clay structure.

4.2.2 Cation exchange capacity (CEC)

Figure 4.3 shows the CEC of the two bentonite clays before and after acid activation. The CEC of Athi River bentonite decreased as the acid concentration increased. A similar trend was observed by Ajemba and Onukwuli (2013) during acid activation of Nteje clay. This could be attributed to the removal of the exchangeable ions from the lattice of the clay samples and replacement by hydrogen ion [Rossi *et al.,* 2003]. However, Thika bentonite showed an increase followed by a slight decrease in CEC with the increase in acid concentration. The same trend was observed for Al_2O_3, MgO and Na_2O in Thika samples. This small change could be attributed to the change in CaO content during activation process (Table 4.2). Quirine *et al.,* (2007), pointed out that the higher the CEC the higher the number of cations held by the soil, and the higher the swelling capacity.

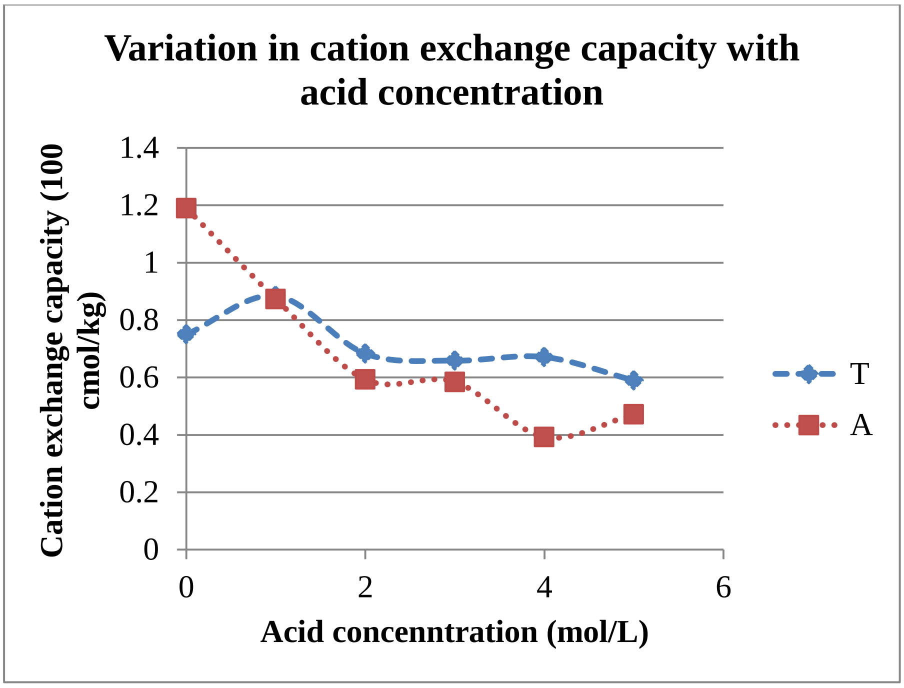


Figure 4.3: Variation in cation exchange capacity of Athi River and Thika bentonite clays with acid concentration

4.2.3 Density

The bulk density of both A and T bentonite clays were determined for various acid concentrations and acid/clay ratio (% w/v). The results are shown in the Figures 4.4, 4.5, 4.6 and 4.7 below.

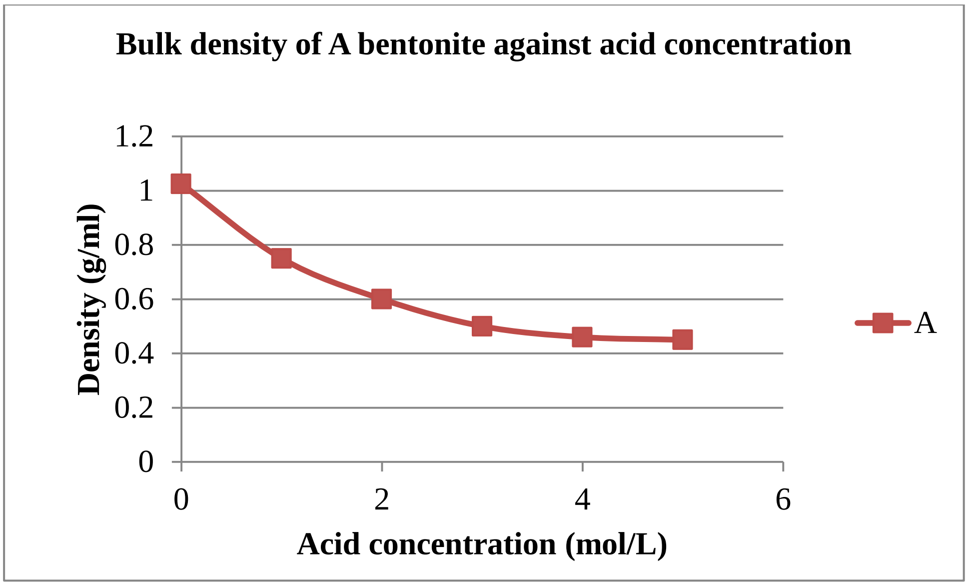


Figure 4.4: **Bulk density of Athi River bentonite against acid concentration**

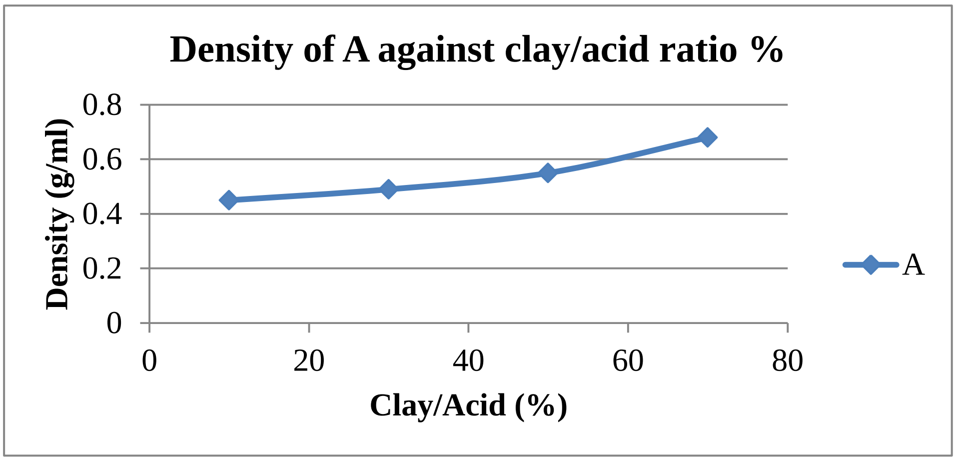


Figure 4.5: **Bulk density of Athi River bentonite against clay/acid %**

The exhibited results for A bentonite show a decrease in density as acid concentration was increased. After 4M acid concentration, the density did not decrease further. According to this variation, clay mineral properties are changed as the acid activation progresses. However, the opposite trend was observed for clay/acid ratio where the density increased with increasing clay/acid ratio (Figure 4.5). This could be attributed to the decreased contact of the clay surface by acid.

The density of T bentonite clay increased as the acid concentration used for clay activation increased from 1.11g/ml to a maximum of 1.22g/ml at about 2M and then decreased to 1.18g/ml at 5M. This indicates that the density of T bentonite was only slightly altered by acid treatment.

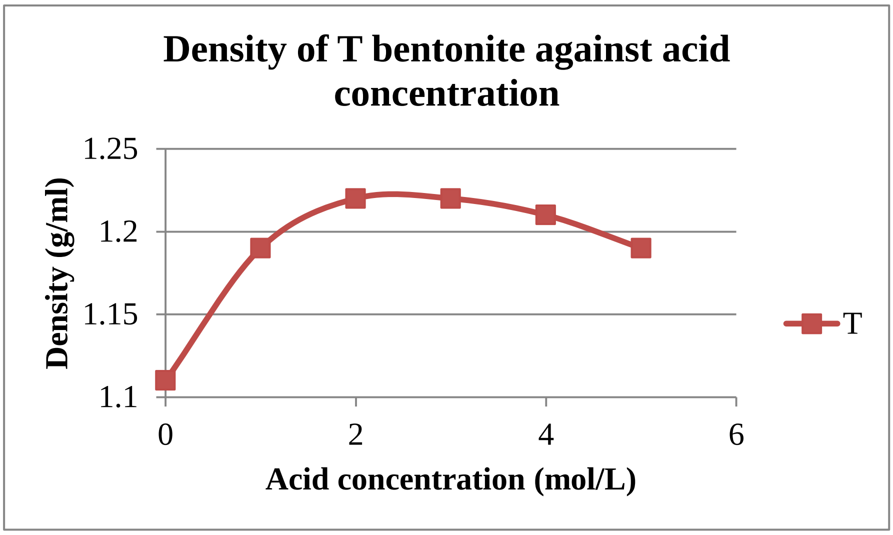


Figure 4.6: Bulk density of Thika bentonite against acid concentration

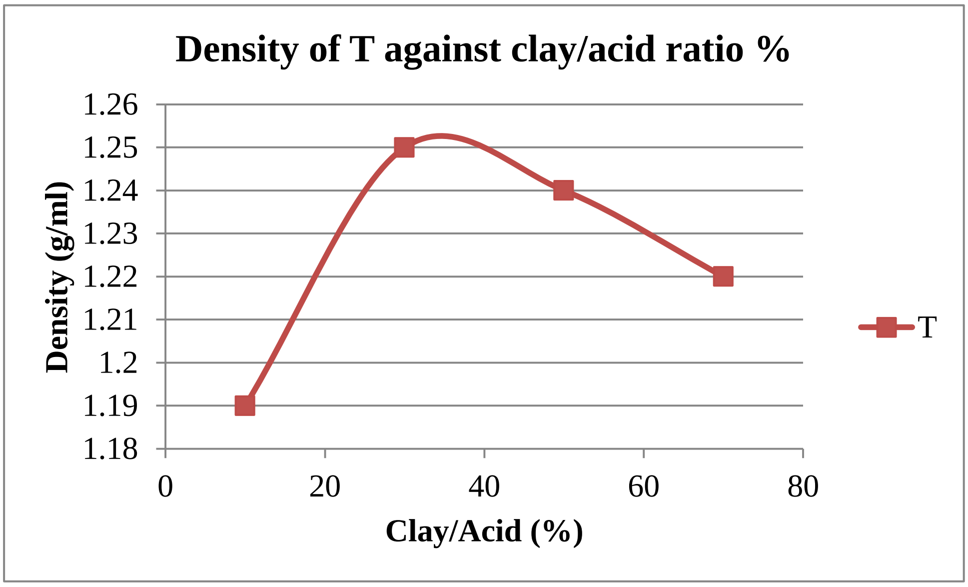


Figure 4.7: Bulk density of Thika against clay/acid ratio

4.3 Maximum absorption wavelength (λmax)

Maximum absorption wavelength of pigments in palm oil samples was determined by scanning from 400 nm to 700 nm using UV-Vis spectrophotometer (UV-1700, SHIMADZU). The λ_{max} was found to be 450 nm, as shown in Figure 4.8 below. A similar λ_{max} value was obtained by Ejikeme *et al.*, (2013) and Usman *et al.*, (2013) during adsorption studies of palm oil.

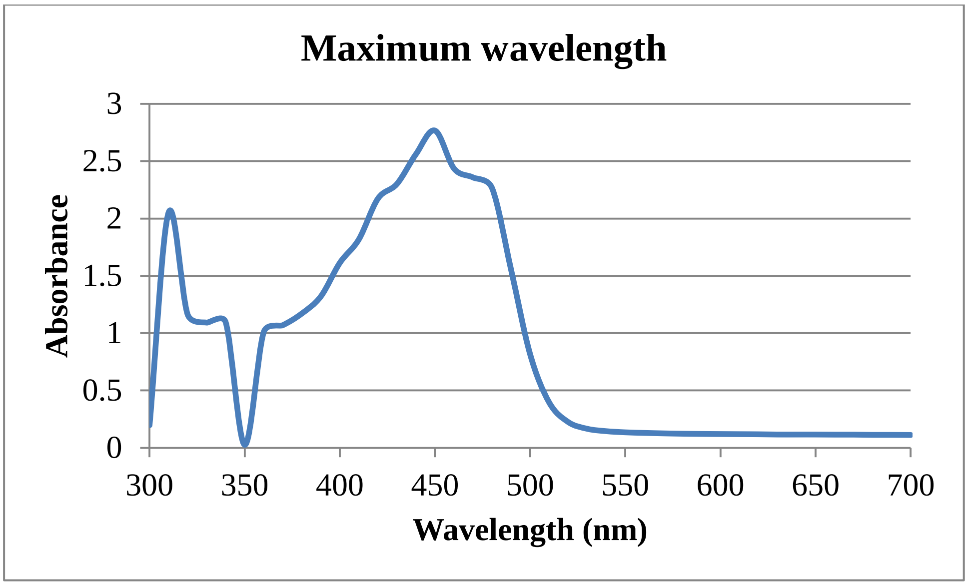


Figure 4.8: A plot of absorbance versus wavelength of palm oil

4.4 Acid activation of bentonite clay

After chemical and physical characterization of both A and T bentonite clays, it was observed that A bentonite was more affected by acid attack during the activation process, whereas T bentonite clay was not changed as much by activation. Consequently, the optimization experimental conditions of acid treatment were focused on A bentonite clay. After acid treatment, A bentonite changed from brown to whitish colour as shown in Figure 4.9. This could be due to the replacement of metal ions such as Al^{3+}, Fe^{3+} and Ca^{2+} in the clay structure with H^+. The T bentonite remained grey in colour and this could be due to the relatively high amount of cations such as Al^{3+} and Fe^{3+} which still remained after the activation. Moreover, the higher the content of Na^+ (4.7%) and K^+ (4%), the more the clay structure resist acid attack (Figure 4.10).

Figure 4.9: Raw (inactivated-left) and activated (right) A bentonite clays

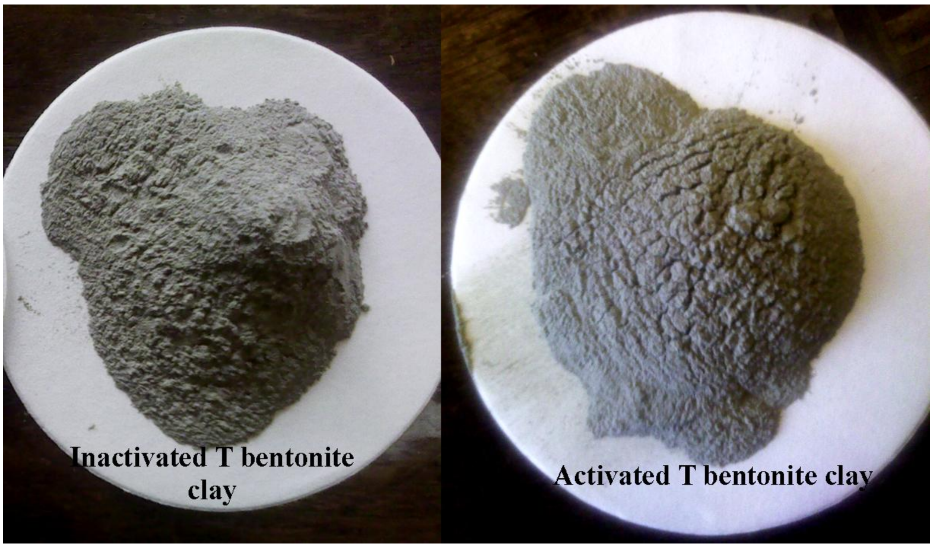


Figure 4.10: Raw (inactivated-left) and activated (right) T bentonite clays

4.4.1 Effect of acid concentration

The effect of acid concentration on bleaching of palm oil was studied at 90°C with 1% (w/v) clay dosage for 30 minutes.

The effect of acid concentration for A bentonite on the bleaching performance of palm oil is shown in the Figure 4.11 below;

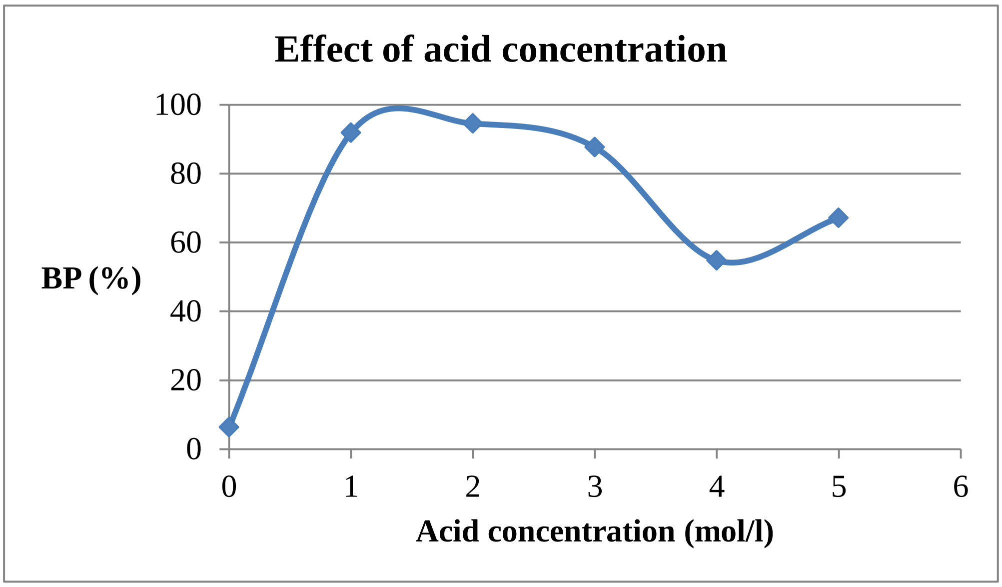


Figure 4.11: A plot of percent bleaching performance versus acid concentration

It can be seen that the activated clay samples adsorbed colour pigments from the palm oil more than the raw clay sample, raising the bleaching performance from 6.3 % to 91.86 %. The bleaching performance first increased with the concentration of acid used up to 2 M H_2SO_4 Above this concentration, the performance dropped. These results indicate that the maximum value of bleaching performance (94.54 %) was attained at 2 M acid concentration. Subsequent decline in bleaching performance could be due to passivation of the rest of the clay which protects the clay layers from further acid attack [Christidis *et al.*, 1997]. The initial increase in bleaching performance with increasing sulphuric acid concentration was probably due to the formation of active sites on bentonite surface.

4.4.2 Effect of activation time

The effect of activation contact time was investigated with 2 M H_2SO_4 concentration, at 100 °C and 10 % clay acid ratio (w/v). The samples obtained were used in bleaching performance experiments carried out at 90 °C for a duration of 30 minutes. The results are shown in the Figure 4.12 below.

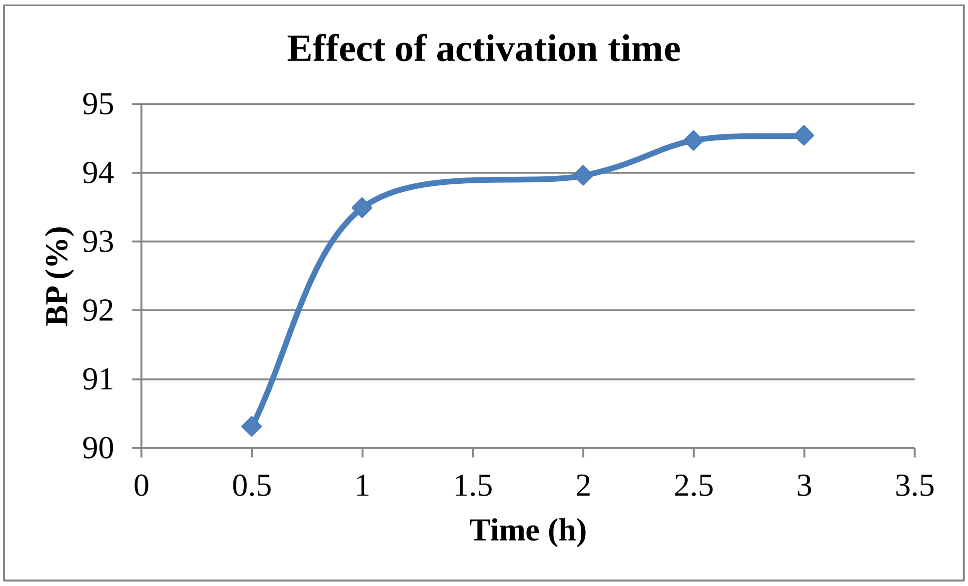


Figure 4.12: Effect of activation contact time on the bleaching of palm oil

The variation of bleaching performance showed an increase in the first one hour, and slight increase up to two and half hours when the increase of time had no significant effect on the clay modification and thus the bleaching performance. Monolayer adsorption was observed after the first hour, after which the bleaching power increased until about 94.5 % when saturation took place. This may point at physisorption in that amount of time, whereby the molecules were adsorbed on the available active sites, after which adsorption continued until saturation. Thus, the optimum activation time was about 2.5 hours for A2 bentonite clay.

4.4.3 Effect of activation on temperature

The effect of temperature on activation of A bentonite was investigated with 2 M H_2SO_4, 10 % clay acid ratio (w/v). The results of bleaching performance at 90 °C within 30 minute using 1 % clay from samples activated at 100 °C and 120 °C are shown in Figure 4.13.

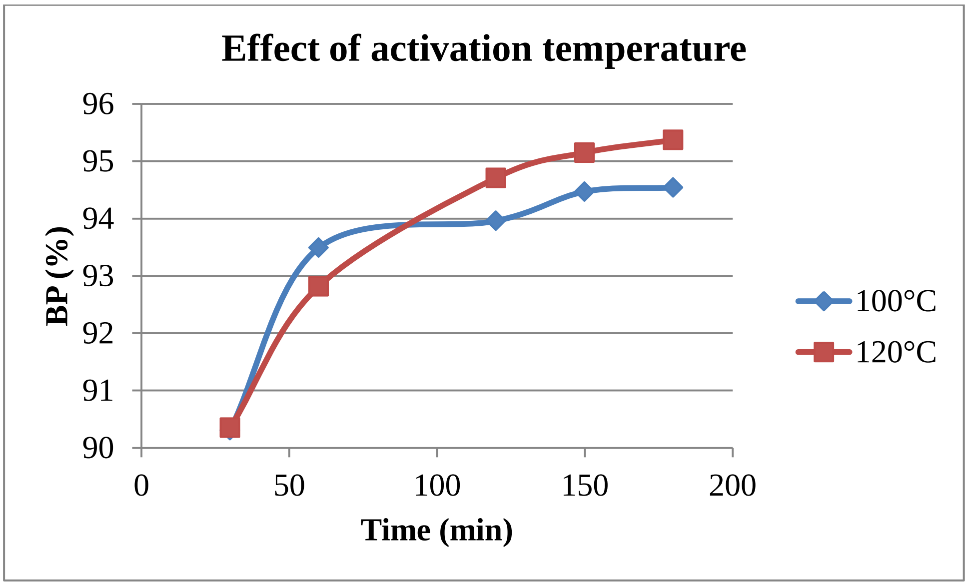


Figure 4.13: Variation of bleaching performance with time at different temperature

The above figure shows that temperature influences the activation. Increasing temperature increased activation of A bentonite clay. This is probably due to the increase of the velocity of molecules in solutions which increase contact between clay surface and acid ions as the temperature was increased.

4.4.4 Effect of clay acid ratio

The effect of clay acid ratio was studied at 100 °C, with 5 M H_2SO_4, for 3 hours; the results are shown in Figure 4.14

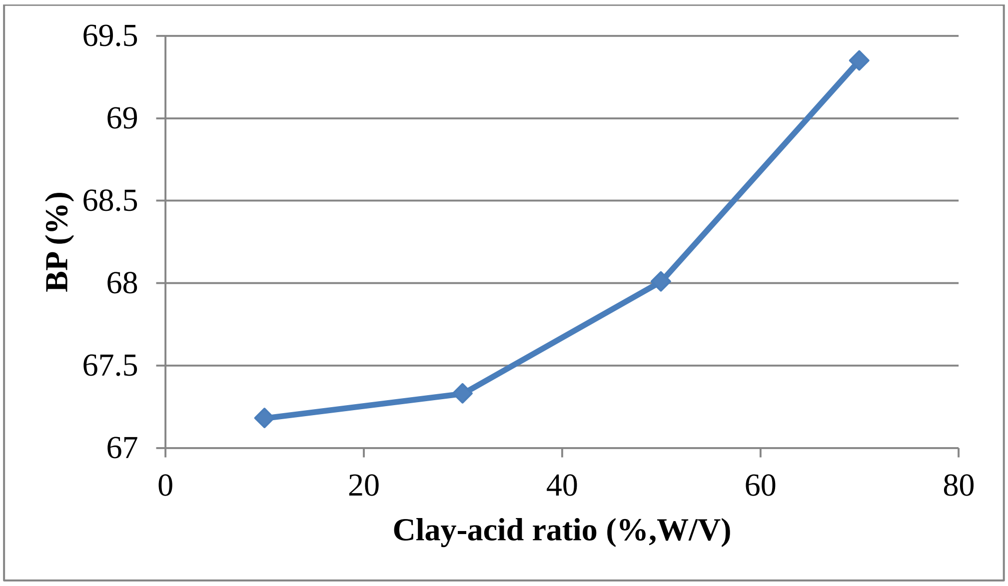


Figure 4.14: Effect of clay/ acid ratio on bleaching performance of Athi River bentonite

The bleaching performance is observed to increase with increase in clay-acid ratio for the range assessed. The above figure shows that the bleaching performance of clay acid ratio of 10-70 % w/v varied between 67.18 and 69.35 which is an increase of 2 % bleaching performance only. Thus, increasing clay acid ratio from 10 % to 70 % had only a small effect on beneficiation of bentonite clay.

4.5 Bleaching studies

Optimization of bleaching performance of bentonite clay was investigated on the raw and activated clays with clay acid ratio of 10 % weight by volume (w/v), activated at 100 °C for 3 hours. It was observed that after bleaching, the oil became brighter and less coloured due to the removal of colour-producing material like the carotenoids (Figure 4.15)

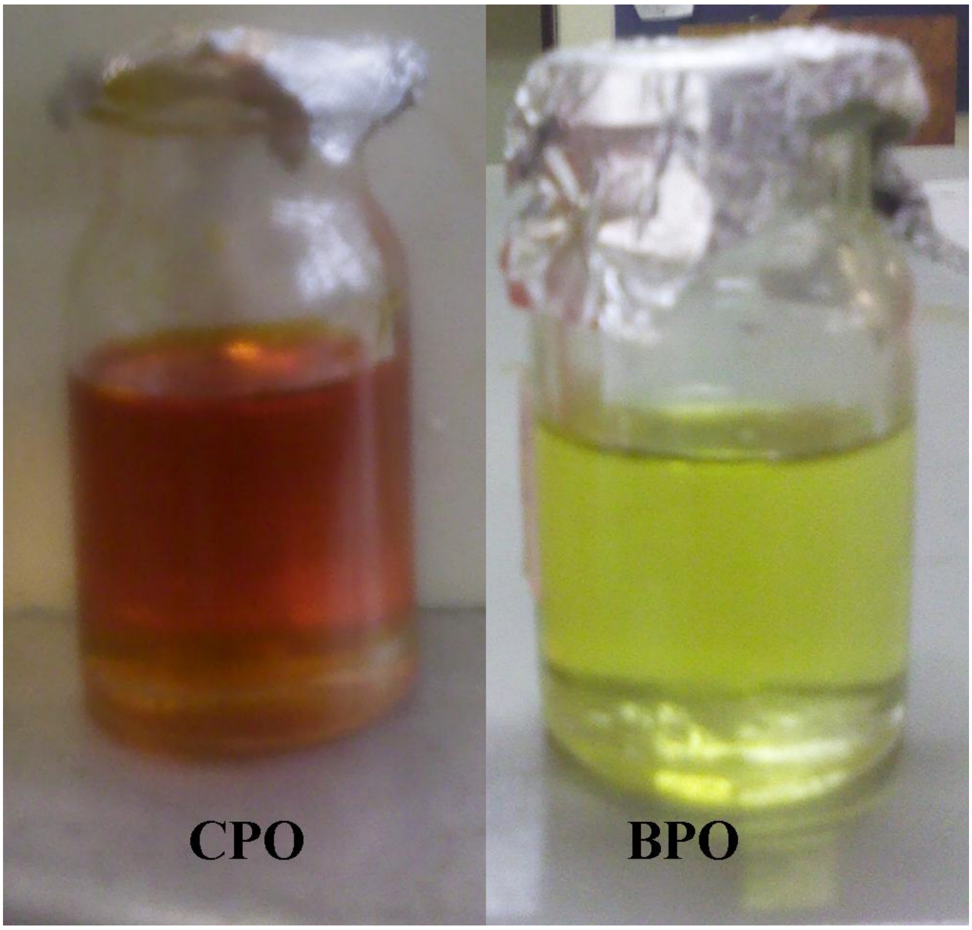


Figure 4.15: Crude palm oil (left) and bleached palm oil (right)

4.5.1 Effect of bleaching contact time and acid concentration

To study the effect of contact time on bleaching performance of the activated bentonite clay, the bleaching process was performed at different times ranging from 5 to 60 minutes, with 1 % clay. The results are shown in Figures, 4.16, 4.17 and 4.18.

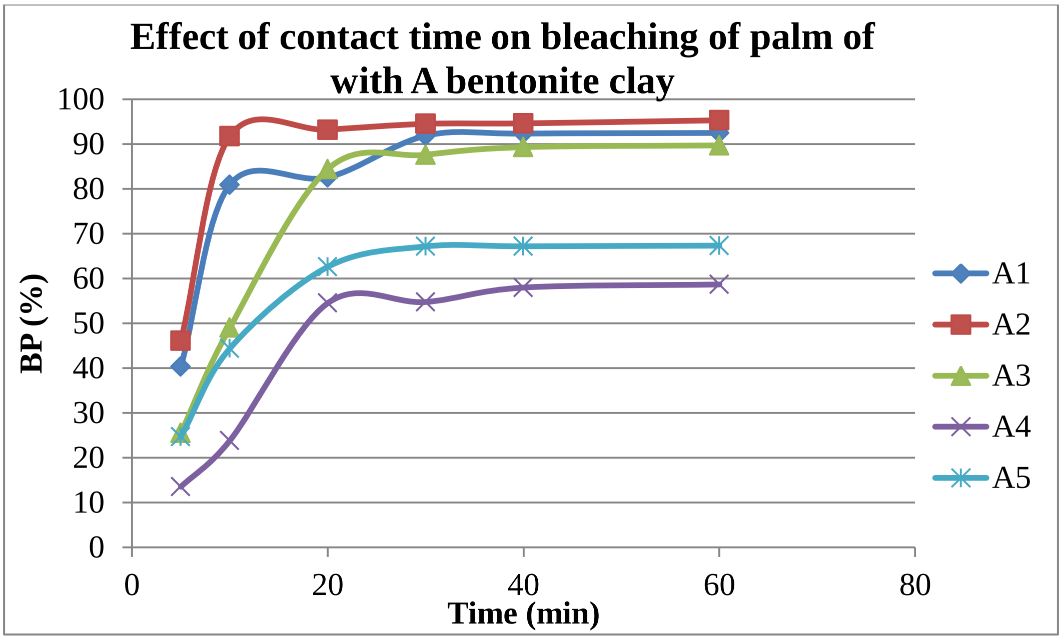


Figure 4.16: Effect of contact time and acid concentration on bleaching of palm oil with 1% A bentonite clay.

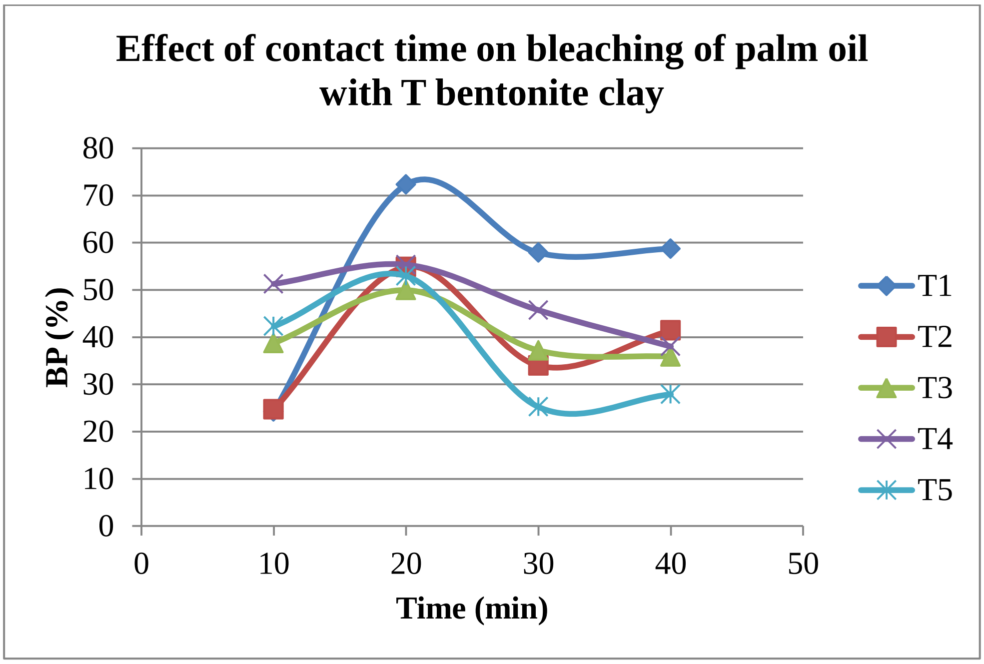


Figure 4.17: Effect of bleaching time and acid concentration on bleaching of palm oil with 1% T bentonite

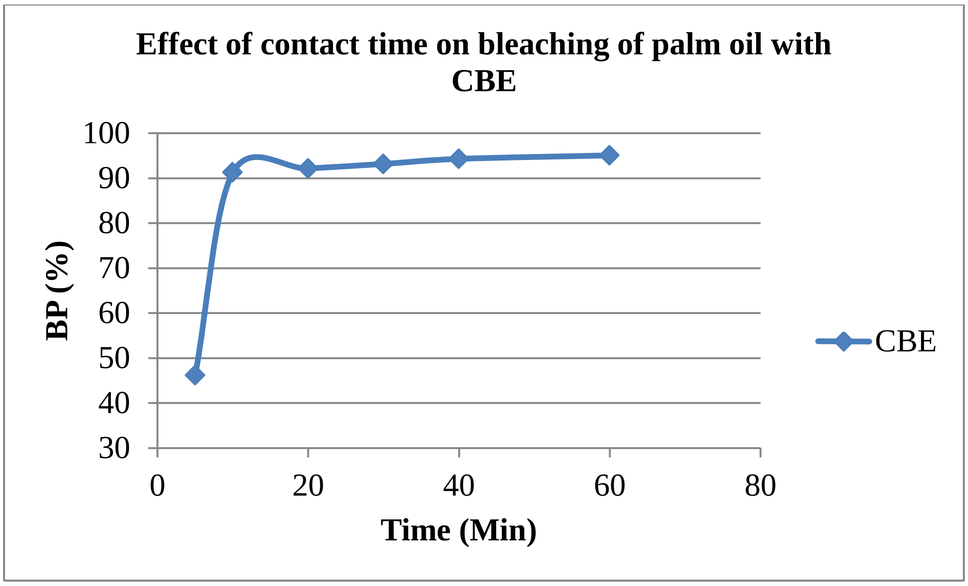


Figure 4.18: Effect of contact time on bleaching of palm oil by 1% CBE

Figure 4.16 shows the effect of bleaching performance by A bentonite. It is clear from the curves that bleaching performance increased rapidly with contact time up to an optimum contact time of 30 minutes for all acid concentrations apart from A2 whose optimal contact time was 10 minutes. It is also the concentration that had the highest bleach performance of all the 5 concentrations, which indicates that it is the optimal concentration for bleaching performance of Athi River bentonite clay. Nwabanne and Ekwu (2013) also observed an increase of colour removal from palm oil with increase in contact time. Similar observations have also been reported by Usman *et al.*, (2013). The rapid pigment adsorption by the adsorbent in the first 5 to 20 minutes can be attributed to the increased availability of vacant surface sites at the initial stages.

The fact that optimal contact time is a maximum of 30 minutes for the various acid concentrations is in agreement with the report of Berbesi (2006) who concluded that the contact time for effective bleaching normally ranges from 15 to 45 minutes, with 20 to 30 minutes being the most common. After 30 minutes the adsorption was slow, implying equilibrium conditions had been attained.

It is clear from Figure 4.16 that acid concentration used during activation process had a significant effect on palm oil bleaching.

In Figure 4.17 the effect of contact time and sulphuric acid concentration on bleaching performance of activated T bentonite clays is shown. Performance rose to a maximum at 20 minutes for all the samples. Thereafter the bleaching performance decreased. A concentration of 1 M H_2SO_4 was found to be the optimum.

The effect of contact time on bleaching of palm oil with commercial bleaching earth (CBE) was studied for comparison with the activated local bentonite clay. From Figure 4.18, it is seen that the bleaching curve of CBE is similar to that of activated Athi River bentonite sample A2. Thus, it is clear that activated bentonite from Athi River can be used to bleach crude vegetable oil in place of commercially obtained bentonite.

4.5.2 Effect of temperature on bleaching of palm oil

The percentage pigment removal increases with increase in temperature as observed in Fig. 4.19. This is most probably because increase in temperature activates the molecules, and increases their kinetic energy, thereby promoting access to more adsorption.

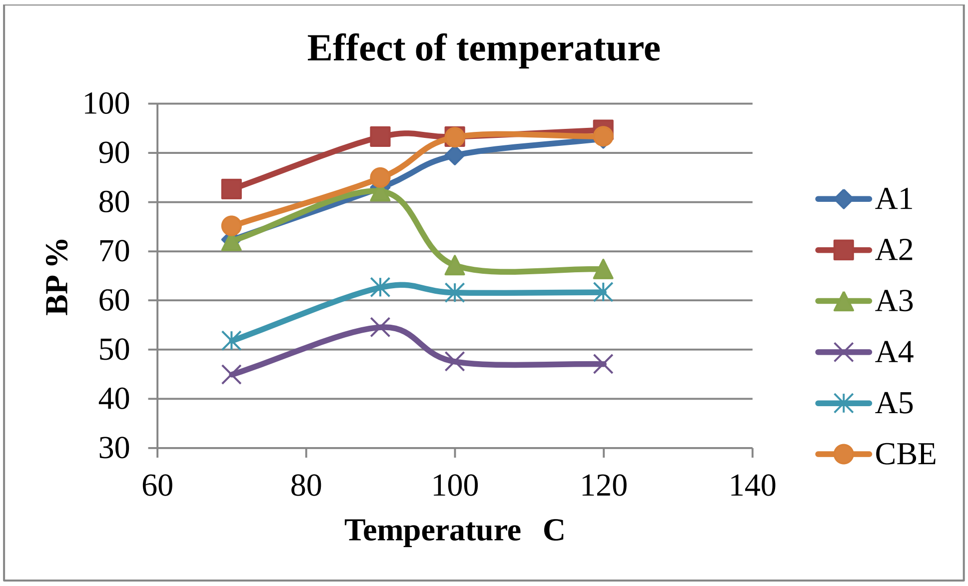


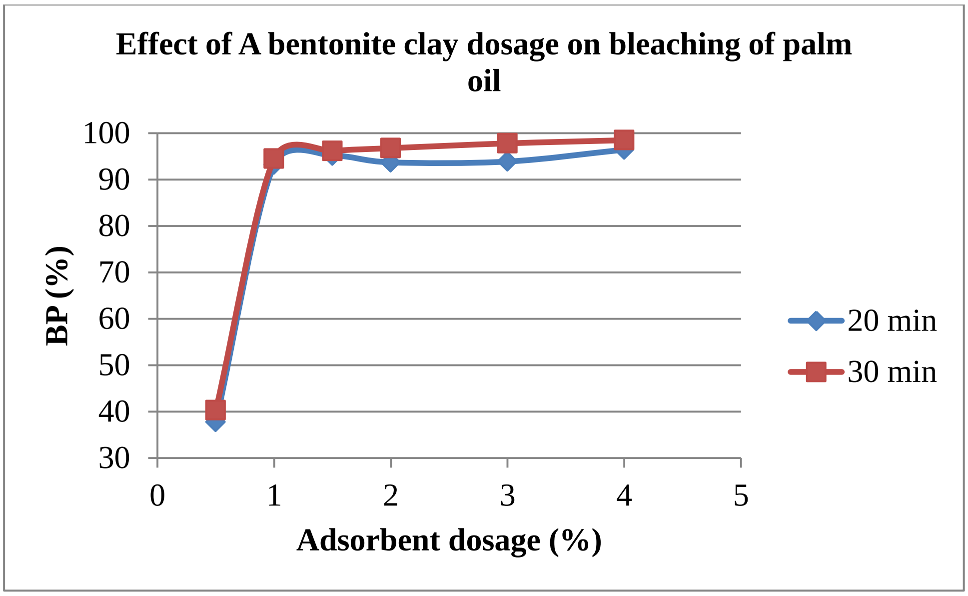
Figure 4.19: Effect of temperature on bleaching of palm oil by A bentonite and CBE

The BP % increased with temperature to a maximum and then remained constant for all the A- species studied except A3, which attained a maximum value at 90 ^{o}C before dropping drastically until equilibration was reached at bleaching performance value of 65 %. It can be deduced that the highest bleaching performance was obtained at 90 °C, which agrees with the observation by Berbesi (2006), who noted that bleaching temperature typically ranges from 90-125 °C. He also noted that oil viscosity decreases with increasing temperature resulting in better dispersion of bentonite clay particles, improved clay oil interactions and less resistance to flow.

The maximum bleaching performance for bleaching palm oil with CBE was attained at 100 °C after which temperature, it remained constant. This is in agreement with results obtained by Berbesi (2006).

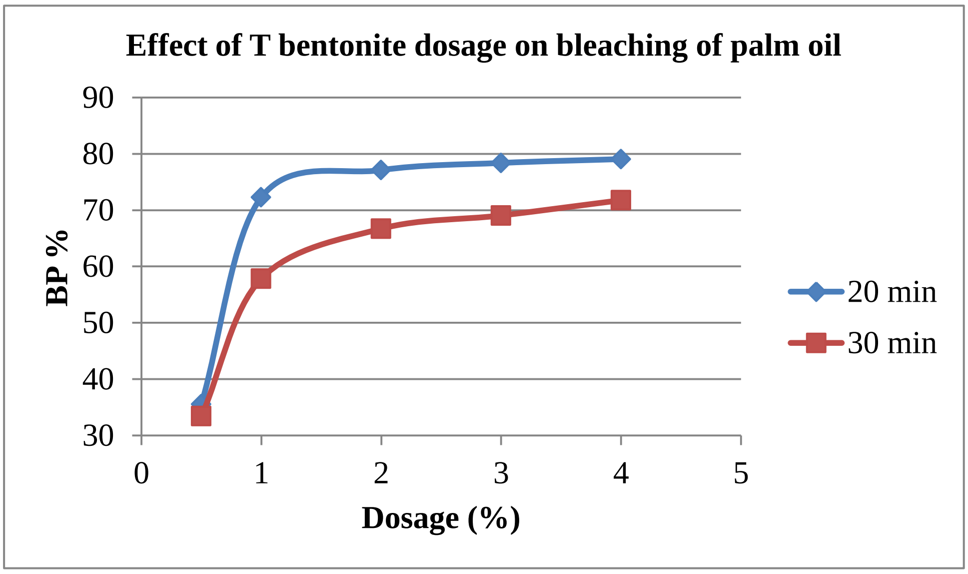
4.5.3 Effect of clay dosage on bleaching of palm oil

The clay dosage was varied from 0.05 g to 0.4 g in 10 ml of palm oil.



% dosage: mass of clay/ volume of oil * 100%

Figure 4.20: Effect of A bentonite clay dosage on bleaching of palm oil



% dosage: mass of clay/ volume of oil * 100 %

Figure 4.21: Effect of T bentonite clay dosage on bleaching of palm oil

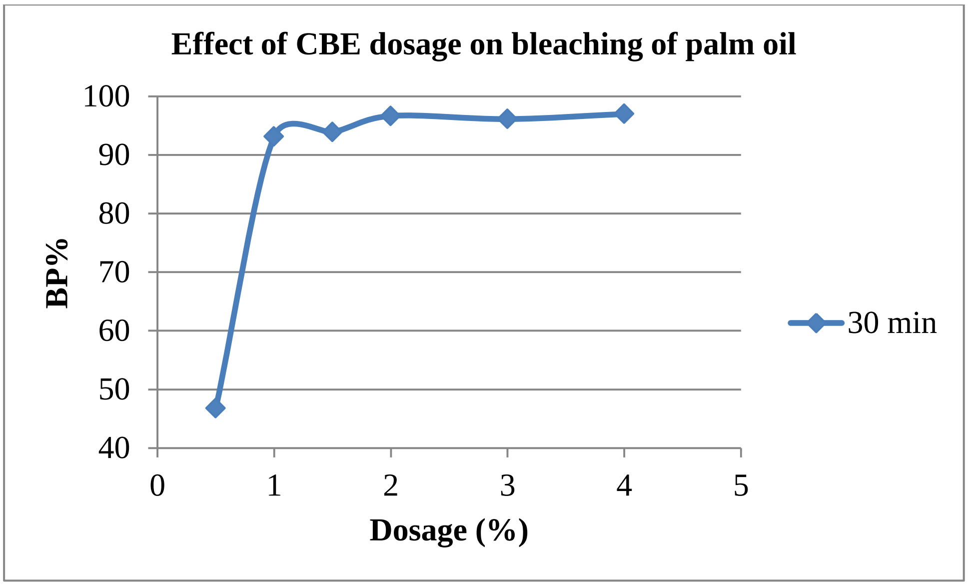


Figure 4.22: Effect of CBE dosage on bleaching of palm oil

Figure 4.20, 4.21 and 4.22 show that the bleaching performance increased to a maximum with increasing clay dosage. This can be attributed to the increase in active sites available for adsorption. Bleaching clay dosage was varied between 0.5 and 4 %. The bleaching performance of A2, T1 and CBE increased from 40 %, 35 % and 46.8 % to 98.49 %, 71 % and 97 % respectively.

The results show that the bleaching performance increased to an optimum value of 1-2% the adsorbent dosage after which further increase in adsorbent dosage had little effect on performance. Diaz and Santos (2001) stated that darker oils like palm oil require as much as 2 %- 4 % or more to meet the colour requirements. Nwabanne and Ekwu (2013) have reported the increase of BP % with the increase in clay dosage for decolourization of palm oil using local Nigerian clay.

4.6 Adsorption isotherms

In this study, it was observed that as temperature increased, the amount of pigments adsorbed on clay surface increased. According to Ajemba *et al.,* (2012), this change occurs as a result of increase in kinetic energy of the colour pigment particles, which increases the frequency of collisions between the adsorbent and pigment particles and hence enhancement of adsorption on the surface of the adsorbent.

Adsorption isotherm describes the equilibrium of the adsorption of pigments and oil impurities at constant temperature. To evaluate the nature of adsorption, Freundlich and Langmuir isotherm models were used.

4.6.1 Sample A2 isotherms

Figure 4.23 shows the Freundlich isotherm for the bleaching of palm oil using activated A bentonite clay. According to equation 2.6, n equals 0.8959 and k is 119.89 while the regression coefficient R^2 is 0.9247.

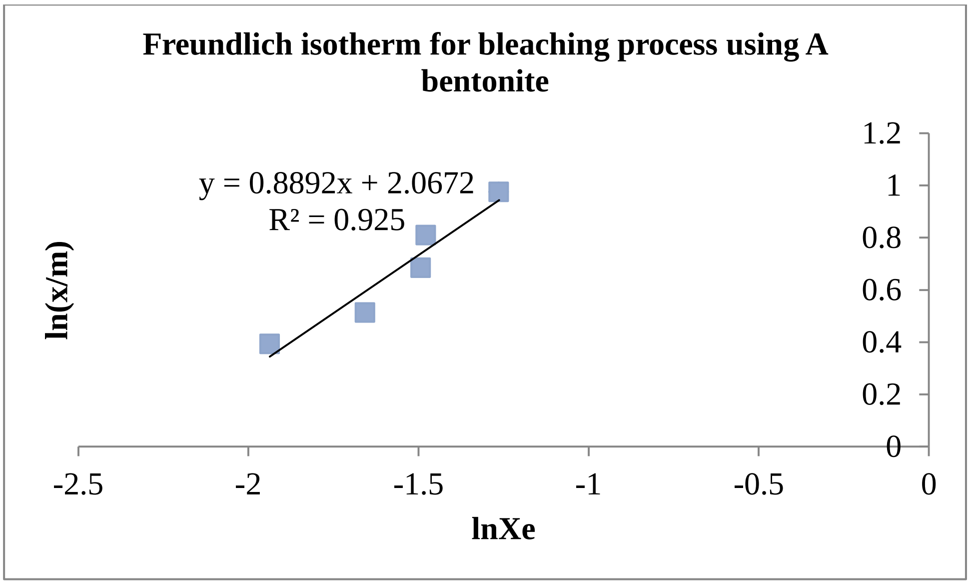


Figure 4.23: Freundlich isotherm for bleaching process using A2

Using equation 2.7, Langmuir constants were determined as shown in Table 4.4. It is clear that the Langmuir isotherm does not accurately represent the A2 data, based on the small R^2 value.

On the other hand, Freundlich isotherm is more appropriate for this process. Thus, the resulting isotherm equation to predict A2 adsorption becomes:

$$\log\frac{x}{m} = \log 119.89 + 0.8959 \log X_e \qquad \text{Equation 4.1}$$

The same conclusion was made by Ajemba *et al.*, (2012) during the study of colour pigment removal from palm oil using activated Ukpor clay.

4.6.2 Sample T1 isotherms

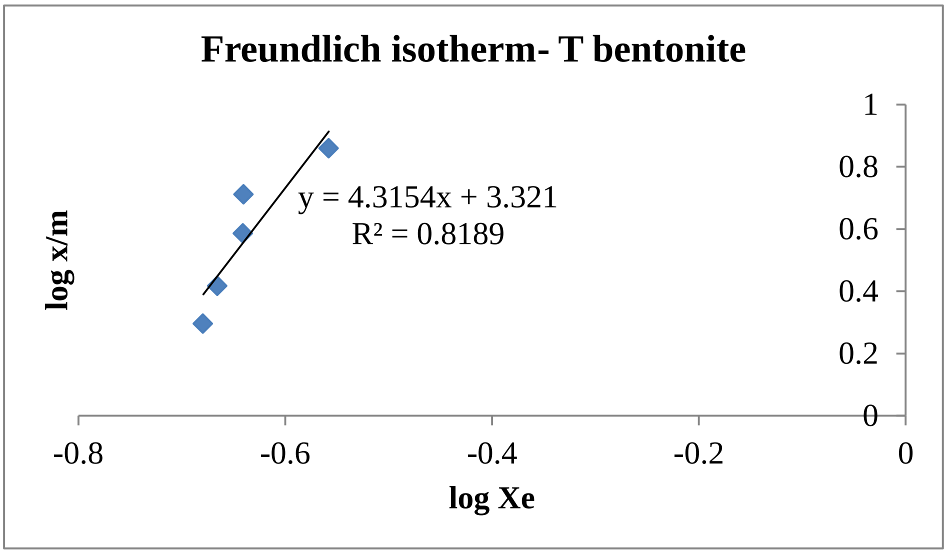


Figure 4.24: Freundlich isotherm for bleaching process on T

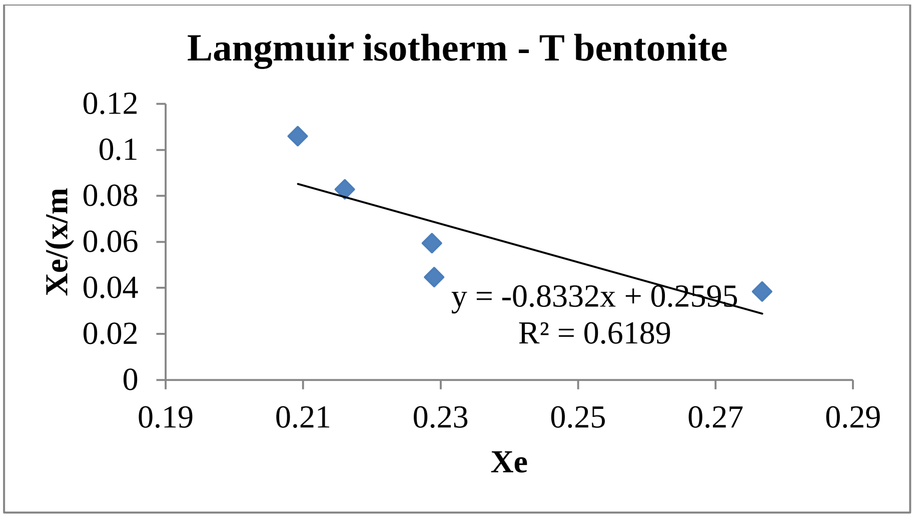


Figure 4.25: Langmuir isotherm for bleaching process on T

It can be seen from Figures 4.24 and 4.25 that the points of the Langmuir isotherm plot are presented randomly on the trend line, whereas a better fit was obtained using the Freundlich isotherm. As Freundlich isotherm model fits the T bentonite data more than Langmuir isotherm model, the bleaching equation takes the following form:

$$\log \frac{x}{m} = \log 2094 + 4.31 \log X_e$$ **Equation 4.2**

4.6.3 CBE isotherms

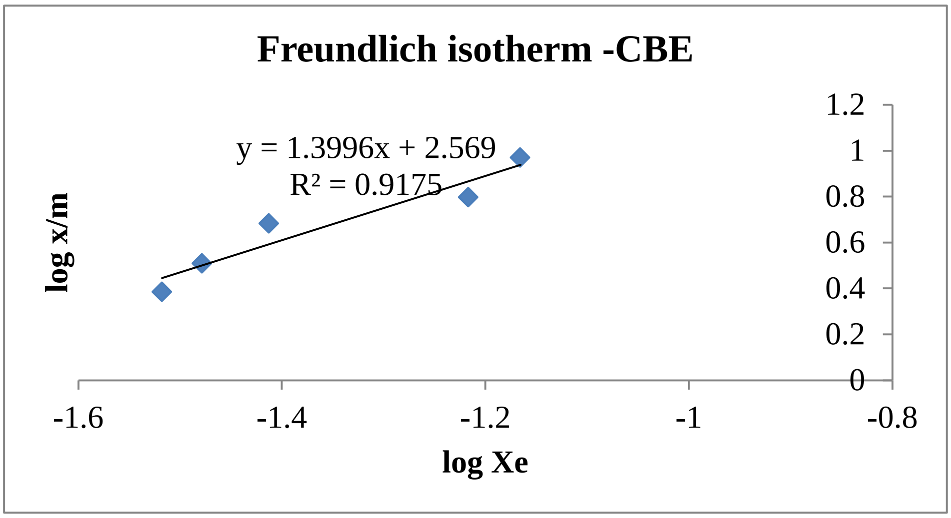


Figure 4.26: Freundlich isotherm for bleaching process on A2

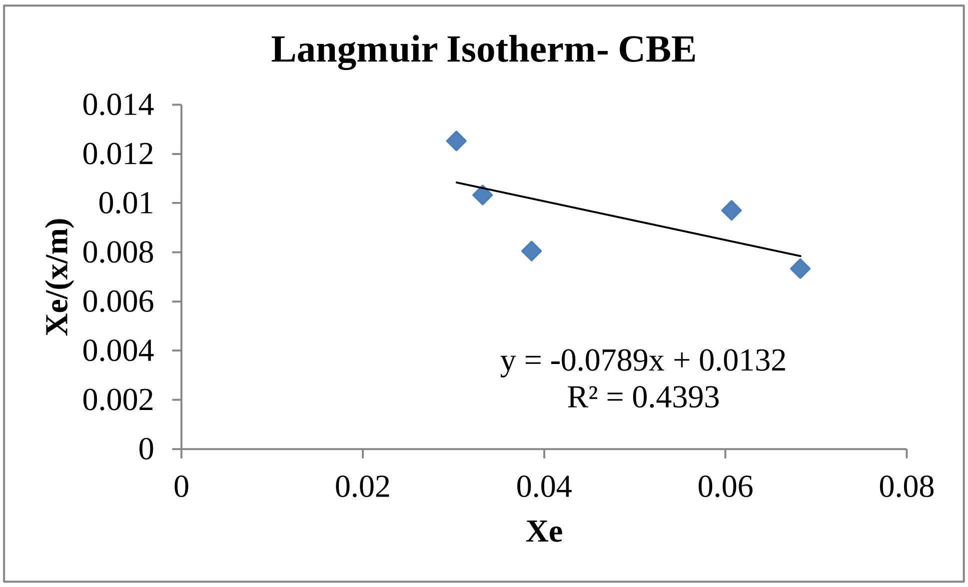


Figure 4.27: Langmuir isotherm for bleaching process on CBE

Figure 4.26 and 4.27 show that bleaching of palm oil with CBE follows the Freundlich isotherm model and the regression value (R^2) is greater than that for the Langmuir isotherm (R^2: 0.9175>0.4393). Thus for the three clay species observed, the adsorption process seems to favour the Freundlich isotherm more than the Langmuir isotherm as summarized in Table 4.4 below.

Table 4.4: Freundlich and Langmuir isotherm constants for the bleaching of palm oil with A , T bentonite clay and CBE

Isotherm model	Parameter	Athi River (A) bentonite clay	Thika (T) bentonite clay	Commercial bleaching earth (CBE)
Freundlich	k	119.89	2094	370.68
	n	0.8959	4.31	1.399
	R^2	0.9247	0.8189	0.9175
Langmuir	a.	185.18	3.85	75.75
	b	2.35	-3.21	-5.97
	R^2	0.0481	0.6189	0.4393

4.7 Heat evolved during the bleaching process

The heat evolved during the adsorption process was calculated using the following equation (Topallar, 1998).

$$Ln\ X_e = \frac{-\Delta H_a}{RT} + C$$ **Equation 4.3**

Where X_e: the residual amount of pigment at equilibrium

ΔH_a: Heat of adsorption (kJ/mol)

R: Gas constant (8.314 J/mol K)

T: Temperature (K)

C: integration constant from the plot of ln X_e against 1/T

4.7.1 Heat evolved during the bleaching of palm oil with A2

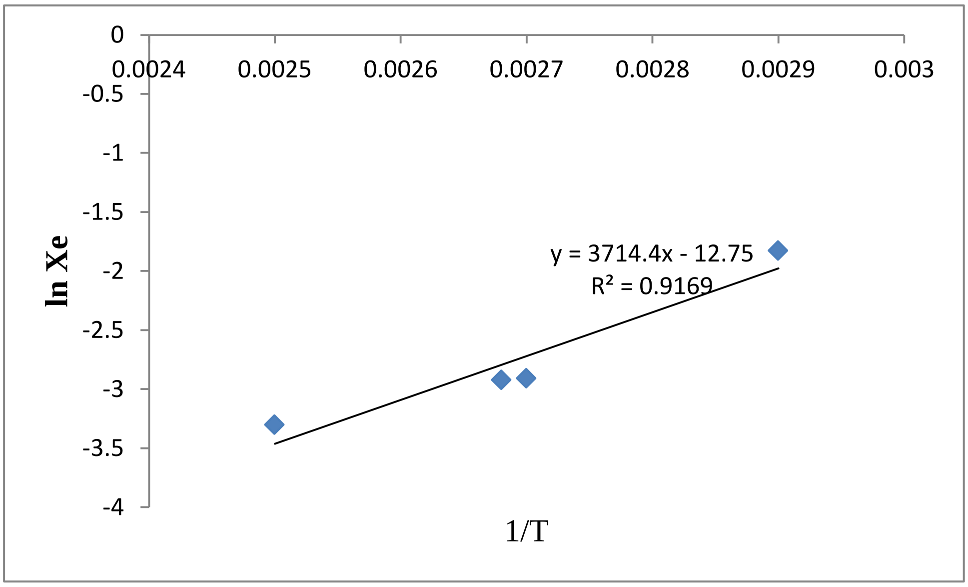


Figure 4.28: Plot ln X_e against 1/T for sample A2

The heat evolved was evaluated from Equation 4.3 and Fig. 4-28 to be -30.881 kJ/ mol, the negative value indicating that the adsorption of pigments from palm oil onto A bentonite clay is an exothermic process.

ΔH_a value also indicates the type of sorption. The heat evolved during physical adsorption falls in the range of 2.1 to 20.9 kJ/mol while that evolved during chemical adsorption is in the range of 80 to 200 kJ/mol [Ajemba *et al.*, 2012]. Therefore, since the value evaluated (-30.881 kJ/mol) lies between the upper value for physical and the lower value for chemical adsorption, the bleaching of palm oil by Athi River acid activated clay can be attributed to physico-chemical adsorption process.

4.7.2 Heat evolved during bleaching of palm oil with CBE

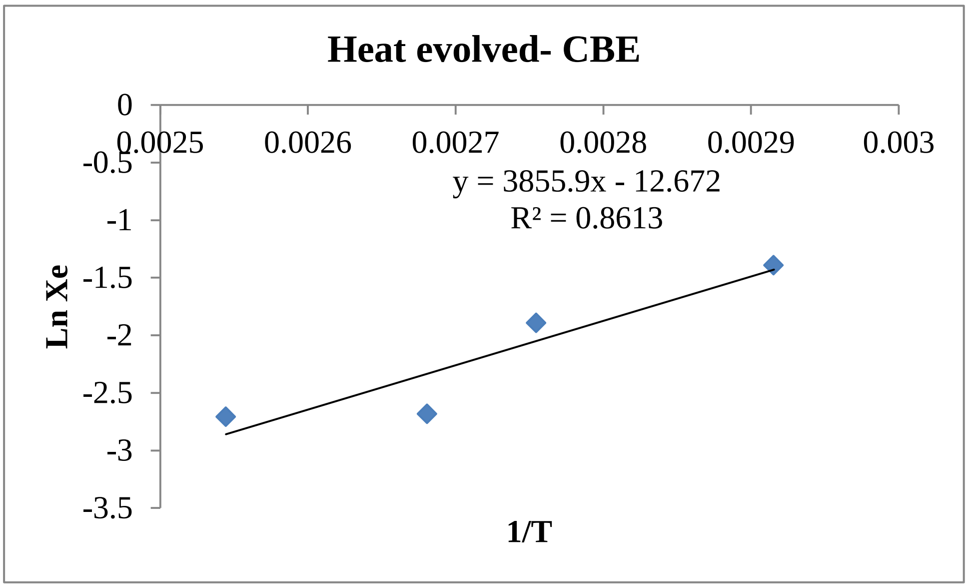


Figure 4.29: The plot of ln X_e against 1/T of CBE

From Figure 4.29, the heat evolved during the bleaching of palm oil using CBE was found to be -32.05 kJ/mol. The negative value indicates that it is an exothermic process which is the same observation made for Athi River activated clay (-30.881 kJ/mol).

ΔH_a values obtained from Figures 4.28 and 4.29 show that the bleaching process with Athi River bentonite is comparable to that with CBE.

4.8 Rate constant

The rate constant determines the speed of decolourization of vegetable oil. According to Brimberg (1982), the rate constant is determined from equation 4.4, which is based on the fact that absorbance is proportional to the concentration of the pigments in the oil; according to Beer Lambert law. Therefore, equation 4.2 has taken the form of equation 4.4:

$$Ln\ {}^{C}/{}_{C_0} = -k(t)^{0.5}$$ **Equation 4.4**

$$Ln\ {}^{A}/{}_{A_0} = -k(t)^{0.5}$$ **Equation 4.5**

where t is the bleaching contact time, C_0 is the initial concentration of the pigments and C is the concentration of pigments at time t, A_0 and A are the absorbances of the crude and bleached oils at time t respectively and k is the rate constant. From equation 4.5, the linear regression between ln A/A_0 and $t^{0.5}$ is a straight line whose slope is equal to –k.

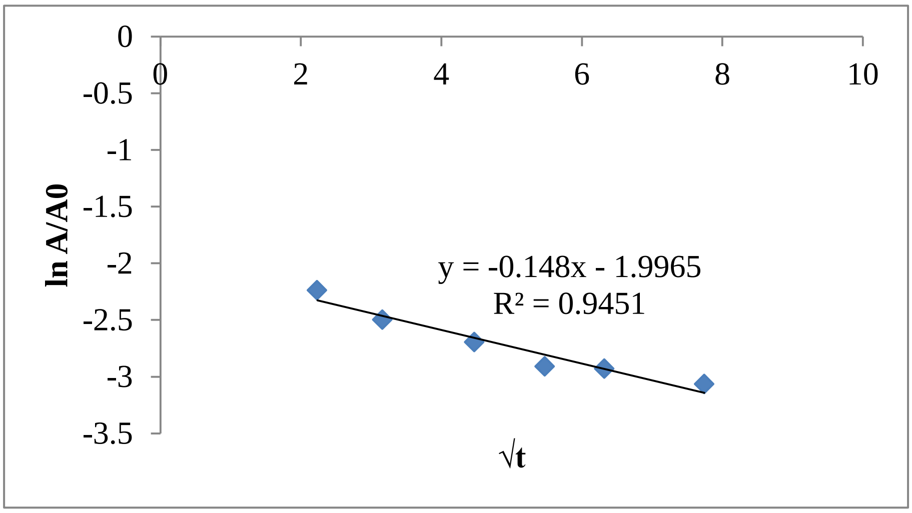


Figure 4.30: A plot of ln (A/A_0) against $t^{0.5}$ for the bleaching of palm oil with 1% of clay (A2)

It can be deduced from the linear equation in the Fig. 4.30 above that the rate constant k is 0.148 with the correlation coefficient R^2 of 0.945.

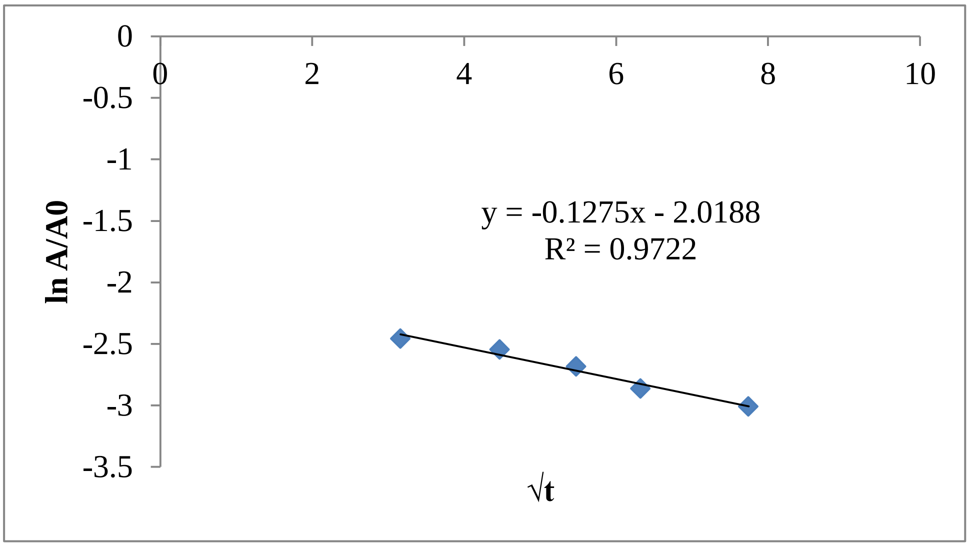


Figure 4.31: A plot of ln (A/A_0) against $t^{0.5}$ for bleaching of palm oil with 1 % of CBE

It can be seen from Figure 4.31 that the rate constant k is 0.1275, which indicates that the rate constant for the removal of pigments from palm oil by CBE is 0.1275 min^{-1} which is lower than the value 0.148 obtained for Athi River activated clay.

4.9 Analysis of final product

4.9.1 Oil retention (OR)

$$OR\% = \frac{W\ filter\ cake\ -(W_{(BE)} - W\ \ H_2O\ )}{W(filter\ cake)} * 100 \qquad \textbf{Equation 4.6}$$

The oil retention of oil for Athi River bentonite clay activated at 100°C with 2 M H_2SO_4 and for CBE was determined, and found to be 27.73 % and 27.04 % respectively. This is in agreement with the observation made by Rich (1960), who found that clay with higher apparent bulk density (ABD) value retain less amount of oil. In addition, according to Usman *et al.*, (2012), this OR % meets commercial standards. Once more the ABD values of A bentonite and CBE were seen to be comparable which concurs with the earlier observation that activated A bentonite meets the standards of CBE.

4.9.2 Free fatty acid (FFA) determination

Free fatty acids are included amongst compounds naturally present in low amounts in vegetable oil; however, they can be produced during storage or processing the edible oils. Therefore the quantity of FFA is a good measure of the quality of oil.

The FFA content in both crude palm oil (CPO) and bleached palm oil (BPO) was determined and the results are shown in the Table 4.5 below;

Table 4.5: FFA content in CPO and BPO

Clay samples	FFA content % in CPO	FFA % content in BPO
A2	6.68	0.268
T1	6.68	4.9
CBE	6.68	6.68

From the results obtained, the FFA content was observed to be more significantly decreased by A2 than T1. However CBE, showed no effect on FFA content. This implies that A2 has capacity to only reduce pigment from oil but also reduce FFA.

4.9.3 Oil density

Density of oil was determined and found to be 0.9357, a value less than that of water. This indicates that BPO produced cannot make a solution with water.

The specifications of the optimized activated bentonite clay and that of commercial bleaching earth are shown in Table 4.6 below:

Table 4.6: Characteristics and performance of the optimized Athi River (A) bentonite clay and commercial bleaching earth (CBE).

Parameter	Raw A bentonite	A bentonite activated with 2 M H_2SO_4	CBE
Colour	Brown	White	White
Particle size	200 mesh	200 mesh	200 mesh
pH (10% in water)	10.7	4.35	3.8
Apparent bulk density g/l	1024.97	600.68	715.81
CEC 10^2 cmol/kg	ND	0.5926	ND
Tested oil	Palm oil	Palm oil	Palm oil
FFA content %	6.68	0.268	6.68
Oil retention %	ND	27.73	27.04
Moisture content %	5.69	7.18	8.3
Cu	ND	0.047	0.0465
Pb	ND	0.001	0.0014

ND: not determined

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

In this project, the potential of activated Kenyan bentonite clay in palm oil bleaching was investigated.

Chemical composition of both bentonite clays allowed classification of Athi River bentonite as ‘Calcium bentonite’ and Thika bentonite as ‘Sodium bentonite’ clays’. Moreover, physical properties determination showed that Athi River bentonite responded well to acid attack more than the Thika bentonite as the properties of activated Athi River bentonite were significantly different from those of the inactivated clay, unlike for the Thika bentonite clay, whose physical properties did not change as much on activation. Therefore optimization conditions were focused on Athi River bentonite.

The acid clay ratio, the increase of temperature, time and acid concentration were found to significantly alter the clay structure and consequently improve bleaching performance. The results showed increase of bleaching performance up to the optimum concentration of 2M H_2SO_4.

Activation was found to decrease the cation exchange capacity (CEC), which implied an increase in surface area, and hence of the adsorption capacity. Also clay density showed a decrease with increased acid concentration.

On the investigation of the effect of various operating parameters on bleaching of palm oil, such as, contact time, adsorbent dosage and temperature, it was found that the optimal contact time, adsorbent dosage and temperature were 30 minutes, 4 % and 90 °C respectively.

Upon activation, the bleaching performance of the activated clay was observed to increase from 37.73 to 98.49 % for A bentonite and from 33.4 to 79 % for T bentonite indicating the importance of acid treatment in improving adsorption performance of local clay.

The bleaching data showed that the adsorption followed the Freundlich adsorption model. The heat evolved during bleaching process was determined and found to indicate an exothermic physico-chemical adsorption (-30.881 kJ/mol) Bleaching performance of Athi River bentonite was compared with that of commercial bleaching earth. Activated clay made under optimized conditions compared well in terms of bleaching performance with commercial bleaching earth. Furthermore, activated Athi River bentonite was found to reduce FFA content more than CBE.

This study has shown that Athi River bentonite clay is a viable source of adsorbent for palm oil bleaching when it is activated with sulphuric acid as it removes 98% of pigment from palm oil. The results can be applied in the local establishment of an activated clay manufacturing plant.

5.2. RECOMMENDATIONS

1. More work should be done to understand the science behind the change of bentonite structure by acid attack.
2. A pilot study should be undertaken as part of a feasibility study for the manufacture of activated Athi River bentonite clay in Kenya. In this study the stirring rate during

activation was kept constant. However stirring rate is expected to affect the dispersion of molecules into solution, therefore, it can be varied to find optimum speed.

3. Removal or reduction of peroxide value and phosphorous present in palm oil by activated Athi River bentonite clay can be investigated
4. Studies on other industrial uses of activated Athi River bentonite clay should be undertaken, for example in wastewater treatment or sugar refining.
5. More study should be done on Thika bentonite clay to evaluate the best method to optimise its bleaching performance or alternatively, its use as a drilling mud.

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APPENDICES

Appendix A: Wavelength, detection limits and optimum conditions of chemical composition analysis of clay samples by AAS

Oxides	Wavelength (nm)	Flame	Silt (nm)	Flow (/min)
TiO_2	364.0	Acetylene gas	0.5	4.5
SiO_2	251.6	Acetylene gas	0.2	4.5
Al_2O_3	309.3	N_2O-Acetylene gas	0.5	4.5
Fe_2O_3	248.3	Air-Acetylene gas	0.2	1.5
MnO	279.5	Air-Acetylene gas	0.2	1.5
MgO	285.2	Air-Acetylene gas	0.5	1.5
Na_2O	589.0	Air-Acetylene gas	0.5	1.5
CaO	422.7	N_2O-Acetylene gas	0.5	4.5
K_2O	766.5	Air-Acetylene gas	1.0	1.5

Appendix B: Apparent bulk density of Athi River bentonite clay

	Run 1					Run 2						
Clay sample	VF (g)	VF+S (g)	V (ml)	S (g)	D (g/ml)$_1$	VF (g)	VF+S (g)	V (ml)	S (g)	D (g/ml)$_2$	Average (g/ml)	SD
A0	21.9378	25.1012	3.1	3.1634	1.02045	21.9378	25.0263	3	3.0885	1.0295	1.02498	0.0064
A1	21.9437	24.1904	3.1	2.2467	0.72474	21.9411	24.0556	2.7	2.1145	0.78315	0.75395	0.0413
A2	21.9417	23.5039	2.8	1.5622	0.55793	21.939	23.6119	2.6	1.6729	0.64342	0.60068	0.06045
A3	21.94	23.3601	2.8	1.4201	0.50718	21.9377	23.3207	2.8	1.383	0.49393	0.50055	0.00937
A4	21.939	23.1176	2.6	1.1786	0.45331	21.94	23.2021	2.7	1.2621	0.46744	0.46038	0.01
A5	21.939	23.1755	2.7	1.2365	0.45796	21.9378	23.2085	2.8	1.2707	0.45382	0.45589	0.00293
A5-30	21.9408	23.3262	2.8	1.3854	0.49479	21.9055	23.2629	2.8	1.3574	0.48479	0.48979	0.00707
A5-50	21.9393	23.4243	2.7	1.485	0.55	21.941	23.4328	2.7	1.4918	0.55252	0.55126	0.00178
A5-70	21.941	24.0601	3	2.1191	0.70637	21.9393	24.0104	3.1	2.0711	0.6681	0.68723	0.02706
CBE	21.9055	23.7629	2.6	1.8574	0.71438	21.9378	23.8026	2.6	1.8648	0.71723	0.71581	0.00201

Appendix C: Apparent bulk density of Thika bentonite clay

	Run 1					Run 2						
Clay sample	VF(g)	VF + S (g)	V(ml)	S(g)	D(g/ml)	VF(g)	VF + S(g)	V(ml)	S(g)	D(g/ml)	AVRG(g/ml)	Sd
T0	21.94	25.6193	3.3	3.6793	1.11494	21.941	25.5017	3.2	3.5607	1.11272	1.11383	0.00157
T1	21.9437	25.8869	3.4	3.9432	1.15976	21.9386	26.0112	3.3	4.0726	1.23412	1.19694	0.05258
T2	21.9408	25.7683	3.2	3.8275	1.19609	21.9398	25.8027	3.1	3.8629	1.2461	1.2211	0.03536
T3	21.9417	25.8125	3.2	3.8708	1.20963	21.9408	25.7317	3.1	3.7909	1.22287	1.21625	0.00937
T4	21.9398	25.7119	3.1	3.7721	1.21681	21.9418	25.5521	3	3.6103	1.20343	1.21012	0.00946
T5	21.941	25.6109	3.1	3.6699	1.18384	21.9408	25.5307	3	3.5899	1.19663	1.19024	0.00905
T5-30	21.9437	25.9817	3.2	4.038	1.26188	21.9428	26.0698	3.3	4.127	1.25061	1.25624	0.00797
T5-50	21.9408	25.9797	3.2	4.0389	1.26216	21.9398	25.9891	3.3	4.0493	1.22706	1.24461	0.02482
T5-70	21.9399	25.5912	3.1	3.6513	1.17784	21.94	25.9677	3.2	4.0277	1.25866	1.21825	0.05715

Where A and T are Athi River and Thika bentonite clay, numbers represent the acid concentration used during activation.

Appendix D: Moisture content of Athi River bentonite clay

Clay sample	Empty vial (g)	Vial + Wet Sample (g)	Vial + Dry sample (g)	Wt. of wet sample (g)	Wt of Dry (g)	Moisture (%)	AV. Moisture	SD
$A0_1$	50.6046	51.6423	51.5779	1.0377	0.9733	6.206033	5.698185	0.718205
$A0_2$	67.4293	68.7664	68.697	1.3371	1.2677	5.190337		
$A1_1$	40.1584	41.3159	41.2504	1.1575	1.092	5.658747	7.580606	2.717919
$A1_2$	66.8763	67.9918	67.8858	1.1155	1.0095	9.502465		
$A2_1$	69.5385	70.5769	70.4816	1.0384	0.9431	9.177581	7.182009	2.822164
$A2_2$	63.3296	64.5713	64.5069	1.2417	1.1773	5.186438		
$A3_1$	40.1603	41.2626	41.2228	1.1023	1.0625	3.610632	3.453821	0.221764
$A3_2$	62.8397	63.9134	63.878	1.0737	1.0383	3.29701		
$A4_1$	63.3285	64.396	64.36	1.0675	1.0315	3.372365	3.21283	0.225618
$A4_2$	64.3523	65.4331	65.4001	1.0808	1.0478	3.053294		
$A5_1$	64.3487	65.3766	65.3512	1.0279	1.0025	2.471057	2.387523	0.118135
$A5_2$	62.8356	63.708	63.6879	0.8724	0.8523	2.303989		

Appendix E: Moisture content of Thika bentonite clay

Clay sample	Empty vial(g)	Vial + Wet Sample(g)	Vial + Dry sample (g)	Wt. of wet sample (g)	Wt of Dry (g)	Moisture (%)	Average Moisture content	SD
$T0_1$	69.5363	70.8355	70.7199	1.2992	0.1156	8.897783	10.07196	1.660542
$T0_2$	66.8808	67.9505	67.8302	1.0697	0.1203	11.24614		
$T1_1$	43.8652	44.9284	44.9187	1.0632	0.1097	10.31791	10.03126	0.405378
$T1_2$	54.9472	56.0945	56.0827	1.1473	0.1118	9.744618		
$T2_1$	50.6046	51.6423	51.6296	1.0377	0.1127	10.86056	10.03237	1.171229
$T2_2$	67.4293	68.7374	68.717	1.3081	0.1204	9.204189		
$T3_1$	69.5385	70.5769	70.5636	1.0384	0.1133	10.91102	9.768144	1.616266
$T3_2$	63.3296	64.5713	64.5642	1.2417	0.1071	8.625272		

Appendix F: Percent bleaching performance (BP %) of Athi River bentonite clay at different acid concentrations

Clay sample	BP (%)$_1$	BP (%)$_2$	Mean BP %	SD
A0	6.2884	6.43296	6.36068	0.10222
A1	91.76	91.9407	91.8504	0.12777
A2	94.7597	94.326	94.5428	0.30666
A3	88.3628	86.9172	87.64	1.0222
A4	55.15	54.4272	54.7886	0.5111
A5	67.4015	66.9678	67.1847	0.30666

Appendix G: Percent bleaching performance (BP %) of Athi River bentonite clay at different contact times

Clay sample	BP (%)					
	5 min	10min	20min	30min	40min	60min
A1	39.5013	79.8338	83.2671	91.76	91.8684	92.1214
	41.1637	82.0744	81.8937	91.9407	92.8804	92.8804
Average	40.3325	80.9541	82.5804	91.8504	92.3744	92.5009
SD	1.17553	1.58441	0.97109	0.12777	0.71554	0.53665
A2	45.6812	91.8684	92.8081	94.7597	94.3621	95.0488
	46.5486	91.6516	93.6755	94.326	94.9765	95.627
Average	46.1149	91.76	93.2418	94.5428	94.6693	95.3379
SD	0.61332	0.15333	0.61332	0.30666	0.43443	0.40888
A3	23.3466	48.6086	83.9899	88.3628	89.5555	89.4471
	27.828	49.476	84.8934	86.9172	89.1218	90.0253
Average	25.5873	49.0423	84.4416	87.64	89.3386	89.7362
SD	3.16882	0.61332	0.63887	1.0222	0.30666	0.40888
A4	11.9986	24.1778	54.897	55.15	57.3184	58.5472
	15.1066	23.5273	54.1742	54.4272	58.6917	58.8363
Average	13.5526	23.8525	54.5356	54.7886	58.0051	58.6917
SD	2.19773	0.45999	0.5111	0.5111	0.97109	0.20444
A5	23.5996	45.3921	62.1973	66.9678	67.4377	67.9436
	25.8403	43.4405	63.0647	67.4015	67.004	66.7871
Average	24.7199	44.4163	62.631	67.1847	67.2208	67.3654
SD	1.58441	1.37997	0.61332	0.30666	0.30666	0.81776

Appendix H: Percent bleaching performance (BP %) of Thika bentonite clay at different contact times

		BP (%)			
		10 min	20 min	30 min	40 min
$T1_1$		23.63571	71.95519	57.39068	58.36646
$T1_2$		24.75605	72.67799	58.33032	59.08927
	Average	24.19588	72.31659	57.8605	58.72786
	SD	0.792205	0.5111	0.66443	0.5111
$T2_1$		25.1536	56.59559	35.63426	42.64546
$T2_2$		24.17781	53.12613	32.30936	40.18793
	Average	24.6657	54.8609	33.9718	41.4167
	SD	0.68998	2.45328	2.35106	1.73774
$T3_1$		39.50126	50.63245	35.99566	35.20058
$T3_2$		37.98338	49.22299	38.38092	36.57391
	Average	38.7423	49.9277	37.1883	35.8872
	SD	1.07331	0.99664	1.68663	0.97109
$T4_1$		50.88544	54.57174	45.35598	38.34478
$T4_2$		51.68052	56.08963	46.07879	37.69425
	Average	51.283	55.3307	45.7174	38.0195
	SD	0.56221	1.07331	0.5111	0.45999
$T5_1$		42.57318	54.13806	24.50307	27.68341
$T5_2$		42.03108	51.7528	25.94868	28.11709
	Average	42.30213	52.94543	25.22588	27.90025
	SD	0.383325	1.68663	1.0222	0.30666

Appendix I: Percent bleaching performance (BP %) of Athi River bentonite clay at different clay amounts

20 min				
Clay amount (g)	BP $(\%)_1$	BP $(\%)_2$	Mean	SD
0.005	38.41706	37.04373	37.73039	0.97109
0.01	92.15757	93.02494	92.59125	0.61332
0.015	94.68739	95.62703	95.15721	0.66443
0.02	93.31406	94.10914	93.7116	0.56221
0.03	93.27792	94.50669	93.8923	0.86887
0.04	96.09686	96.81966	96.45826	0.5111
30 min				
0.005	40.98301	39.68197	40.33249	0.91998
0.01	95.08493	93.96458	94.52476	0.792205
0.015	96.45826	95.88001	96.16914	0.40888
0.02	96.92808	96.63896	96.78352	0.20444
0.03	98.30141	97.28948	97.79545	0.71554
0.04	98.80737	98.22913	98.51825	0.40888

Appendix J: Percent bleaching performance (BP %) of Thika bentonite clay at different clay amount s

	20 Min			
Clay amount (g)	BP $(\%)_1$	BP $(\%)_2$	Average	SD
0.005	35.20058	35.92338	35.56198	0.5111
0.01	73.00325	71.62992	72.31659	0.97109
0.02	76.03903	78.20744	77.12324	1.5333
0.03	78.09902	78.67727	78.38815	0.40888
0.04	78.49657	79.65305	79.07481	0.81776
	30 Min			
0.005	33.93567	32.85146	33.39357	0.76665
0.01	57.20997	58.51102	57.8605	0.91998
0.02	66.10047	67.32924	66.71485	0.86887
0.03	70.32888	67.79906	69.06397	1.78885
0.04	71.37694	71.77449	71.57571	0.281105

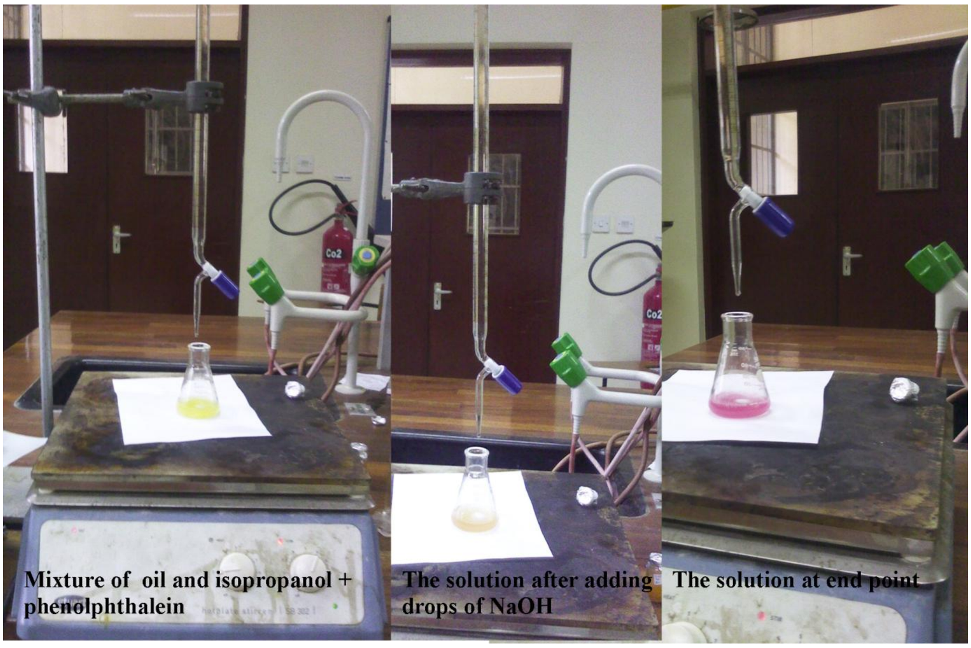
Appendix K: Percent bleaching performance (BP %) of Athi River bentonite clay at different temperatures

Clay sample	BP%								Average BP % ± SD			
	70°C		90°C		100°C		120°C		70°C	90°C	100°C	120°C
A1	73.5815	71.0517	80.9180	84.9657	89.1218	89.8446	93.0611	92.6997	72.3166 ±1.78	82.9418 ±2.8	89.4832 ±0.51	92.8804 ± 0.25
A2	80.7011	84.5320	93.8923	92.5913	93.4586	93.0972	95.3379	93.9646	82.6166 ±2.7	93.2418 ±0.9	93.2779 ±0.25	94.6512 ±0.97
A3	74.6657	69.4615	82.7611	81.6046	67.5099	66.7871	65.7029	67.0040	72.0636 ±3.6	82.1829 ±0.8	67.1485 ± 0.51	66.3535 ±0.91
A4	44.1634	45.6812	54.3549	54.7163	46.1872	48.9339	44.9584	49.1507	44.9223 ±1.07	54.5356 ±0.25	47.5605 ±1.96	47.0546 ±2.9
A5	50.5963	52.9816	63.7152	61.5468	60.8240	62.3419	60.7517	62.5587	51.78894 ±1.68	62.6310 ±1.5	61.5829 ±1.07	61.6552 ±1.27

Appendix L: Oil density after bleaching with prepared activated clay samples

Clay minerals	D (g/ml)
A1	0.9340
A2	0.9375
A3	0.9347
A4	0.9354
A5	0.9368
T1	0.9375
T2	0.9369
T3	0.9360
T4	0.9369
T5	0.9370

Appendix M: Titration of FFA



Mixture and oil and isopropanol + indicator; the solution after adding one drop of NaOH; the solution at end point.

Appendix N: Soil types (retrieved from exploratory Soil Map of Kenya)

L9: Moderately well drained, dark greyish brown, firm clay (PHAEOZEMS and PLANOSOLS)

L10: Imperfectly drained, dark greyish brown, very firm, cracking clay, humic clay

L11: Imperfectly drained, dark grey to black, firm to very firm, cracking clay, calcareous (VERTISOLS)

L12: Imperfectly drained, black to grey, very firm, cracking clay (VERTISOLS)

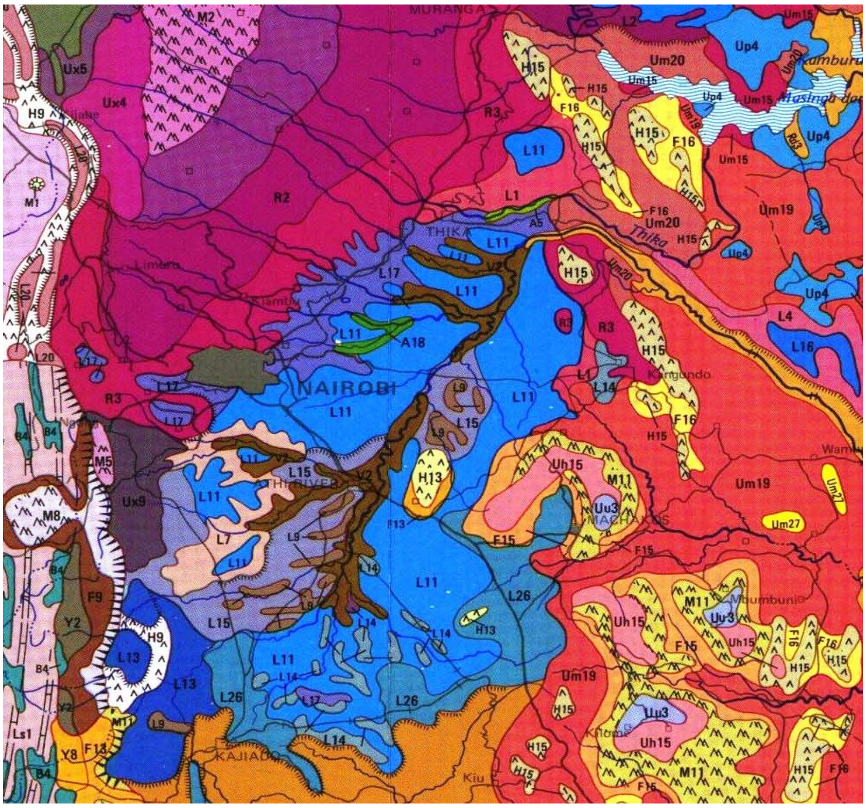
L13: Imperfectly drained, dark greyish brown, very firm cracking clay (VERTISOLS)

L14: Imperfectly drained, greyish brown, firm clay, sandy clay (PLANOSOLS)

L15: Imperfectly drained, very firm, slightly calcareous, cracking clay (VERSTISOLS)

L16: Imperfectly to poor drained, dark grey, firm, slightly calcareous, cracking clay (VERTISOLS)

L17: Poorly drained, dark brown, firm to very firm, cracking clay (VERTISOLS)



Source: Sombroek, W.G, Braun, H.M.H and Van der Pouw, B.J.A, (1982) Exploratory soil map and agro-climatic zone map of Kenya, 1980 scale 1:1,000,000, *Ministry of Agriculture-National agriculture Laboratories.* Available online and KARI library-Nairobi

Appendix O: Kenya's imports of decolourising and fuller's earth, 1997-2007 (World Integrated Trade Solutions, 2014)

YEAR	VALUE IN 1000 US$	QUANTITY, KG
1997	41.331	75,878
1998	37.065	73,375
1999	157.308	392,250
2000	47.391	133,484
2001	249.33	569,483
2002	169.417	465,000
2003	186.137	521,261
2004	190.994	545,022
2005	187.238	528,795
2006	260.124	747,890
2007	252.763	739,756

Appendix 16: Characteristics of palm oil

Parameters	CPO	BPO (A)	BPO (CBE)
Colour	Orange- red	Yellow	Yellow
FFA (%)	6.68	0.268	6.68
Peroxide value	ND	ND	ND
Iodine value	ND	ND	ND
Density (g/ml)	0.9377	0.9375	0.9361
BP (%)	6.3	98	97

ND: Not determined, CPO: crude palm oil, BPO: bleached palm oil, CBE: commercial bleaching earth, A: Athi River bentonite clay