

Bleaching Edible Oils using Clay from Kangole, Moroto District, North Eastern Uganda

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Abstract

The effectiveness of raw and acid activated clays developed from local Ugandan clay from Kangole, Moroto District of North Eastern Uganda for bleaching cotton and sunflower seed oil was studied. Two acids namely hydrochloric and sulfuric acids of varying strengths 0, 10, 20 and 30% were used for the activation. Mixture of the degummed, neutralized oil and appropriate clay powders placed in Pyrex glass flasks, fitted with a magnetic stirrer was placed in a thermostatic iso-electric mantle at various temperatures in a nitrogen atmosphere for duration of 10 to 60 minutes before being cooled and filtered to record absorbance. Minerals were identified by means of XRD, chemical composition and other related studies were conducted to explore the activation potential of these clays. The clay was montmorillonite in character with subordinate Kaolinite and Illite and unaltered tuff in form plagioclase and feldspars. Samples were subjected to hydrochloric and sulfuric acid activation under varying the conditions. Temperature, solid liquid ratio was kept constant whereas the time and the acid concentrations were varied to get optimum values for activation. Bleaching efficiency of the process was tested on cotton and sunflower oils. Study revealed that maximum decrease in absorbance of bleached oil was attained with clay leached in 30% acid when the oil was in contact with clay for 30 to 40 minute at 90°C. Results obtained in which the performance of locally prepared clays was expressed in terms of percentage decrease in absorbance of oil showed that, the acid-activated samples were more effective in the bleaching of oils than raw clay. The percentage decrease in absorbance of sunflower oil of 80% was achieved with clay leached in 20% hydrochloric acid. Yet cotton oil attained highest percentage absorbance of 55% during the bleaching step. The performance was high enough.

Keywords: Adsorptive bleaching; Acid-activated clay; Edible oil refining; Degumming; Neutralization.

Introduction

Chemical Analysis of Clay

A variety of chemical analyses are offered. Samples which can be taken into solution for example in nitric acid are analyzed by ICP-MS or ICP-OES. Analysis of various materials by X-ray fluorescence (XRF) can also be arranged. XRF is often more appropriate for many geological materials where total elemental analysis is required, such as many rocks and soils. These types of sample are often difficult to take in solution in a matrix suitable for analysis by ICP, so XRF analysis is more appropriate when it is important to know true total elemental concentrations.

Quantification of heavy and trace metal contamination in clay can be arduous, requiring the use of lengthy and intricate extraction procedures which may or may not give reliable results. Of the many procedures in publication, some are designed to operate within specific parameters while others are designed for more broad application. Most procedures have been modified since their inception which creates ambiguity as to which procedure is most acceptable in a given situation.

Clays can be the reservoir for many harmful constituents, elemental and biological, including heavy metals and trace metals. Total metal content of soils can be useful for many geochemical applications but often the speciation (bioavailability) of these metals can be more interesting agriculturally in terms of biologically extractability. Speciation is the identification and quantification of the different, defined species, forms or phases in which an element occurs. It is essentially a function of the mineralogy and chemistry of the soil sample examined. Quantification can be done using chemical solutions of varying, but specific, strengths and reactivity to release metals from the different fractions of the examined soil.

The Leaching of Clays

Activation of clay is a chemical or physicochemical treatment applied to clay to develop capacity to adsorb coloring matter and other impurities in vegetable, animal or petroleum oils [1]. The activity of clay denotes surface chemical and physicochemical reactivity leading to increase in surface area of solid. Activation of clay aims at producing modifications on surface of material for use as adsorbent for liquid, solid or gas or obtain high rate of reaction or

dissolution. Thermal dehydroxylation occurs at high temperature between 600 and 1000°C follows the chemical reaction shown below in equation 1.1,



Acid activation involves removal of exchangeable interlayer ions as well as dissolution of tetrahedral and octahedral ions from alumina and silica layers [2] and replaces them with hydrogen causing structural deformations. The composition and texture of clay changes when leached [3,4].

Presently the expressions activation of clay or a clay mineral and activated clays cover a wide range of chemical treatments, most of them aimed at producing modifications on the surface of the clay mineral crystals. Besides the acid activated smectites or bentonites the following are some of the treatments used: sodium exchanged smectites, quaternary ammonium exchanged smectites (organophilic bentonites); organic clad kaolinites (oleic acid; silanes; organic polymers); surface modified kaolinites; intercalated inorganic polyhydroxycations; pillared smectites; thermally activated kaolinites and palygorskite-sepiolite; thermally activated bauxites (crystalline aluminium hydroxides).

The classes of methods used to enhance or to activate the properties of a natural clay or clay mineral for several industrial uses include physical alteration of particle size (specific surface area), thermal alteration of chemical composition and/or crystalline structure by the effect of temperature, chemical alteration which is usually limited to ionic exchange: therefore, it does not include massive chemical destruction of the clay mineral structure and pillaring regarded as using chemical and physical restructuring of the clay mineral structure to increase capacity for adsorption or to make spaces that encourage adsorption of specific ions.

The adsorptive capacity of clays can be enhanced by acid treatment and heating in processes referred to as activation. While heating modifies clay through calcining, dehydration, sintering and dehydroxylation, leaching with acids removes octahedral and tetrahedral cat-ions leaving a silica skeleton [5]. This creates of Lewis and Bronsted acidity, which increases the ability to clarify oils. Clays adsorb carotenoids, amines and other olefins via surface reactions. The capacity of clay to bleach was reported to increase with concentration of acid and temperature. The presence of Bronsted and Lewis centers and kaolin, illite and nontronite phases in the material was cited as being responsible for the gain in decolorizing power as concentration of acid and temperature increased.

Materials and Methods

Sample Collection and Preparation

When the concentration of impurities on the adsorbent exceeded what the clay could hold, the Freundlich and Langmuir isotherms deviated from linearity because it became saturated with the adsorbate [6]. A number of attempts have been made in the refining of edible oils using local clays from Uganda as adsorbents [7 – 9] in much the same way as Local Nigerian clays were used to bleach palm oil [10-13].

Visible spectra of the neutralized cottonseed oil and bleached oils were reported to give five absorption maxima due to presence compounds namely, chlorophyll-a, β -carotene and their relative compounds, respectively [14, 15]. It was further reported that these absorption maxima disappeared in the absorption spectra of oil bleached using bentonite leached in 25% acid showing that the acid activated clay was effective in removing almost all coloring bodies. There was initial increase in bleaching capacity with increasing concentration of sulfuric acid probably due to formation of active acid sites on the montmorillonite flake resulting from structural modifications caused during activation. There was subsequent decrease in bleaching ability when the concentration of acid was above 25% due to the collapse of the clay lattice structure to some extent [16].

This study has aimed at developing local clay with effective adsorptive capacity for impurities in cotton and sunflower oils.

The effectiveness of these locally prepared adsorbents can be expressed as a measure of percentage decrease in absorbance of the bleached cotton and sunflower oil. The effectiveness of these local clays improved when two of them were selected and activated using acids. State, with a view to initiating the utilization for bleaching earth manufacture and reasonable percentage color reduction was achieved. The increasing manufacture of oils and edible products from vegetable oils in Uganda and high cost of bleaching earths possess a great challenge for the provision of high quality local substitutes. There is therefore, the need to continuously find new ways and means of improving the quality of oils by developing low cost adsorbents that can be used during the bleaching process. In this work however, local clays mined from pitch black soils at Kangole, Moroto District in North Eastern Uganda and have been prepared as raw and acid-activated earths. These raw clays were analyzed for chemical and mineral compositions.

Composite sampling method was used because the average value of clay properties was needed at low analytical costs. A number of field samples representing the clay from Kangole, Moroto District in North Eastern Uganda were thoroughly mixed to form a composite which used in the laboratory. This sampling plan was used because physical distance does not alter chemical properties of the clay. It measures the mean. There was no need of estimating of variance. In all cases the clays were dug by removing the top soil and clays scooped from the underlying horizons. The samples were collected through removing the top soil from the surface to minimize the effect of weathering and contamination and scooping 1kg of clay from the layers below. A total of ten samples weighing nearly 1kg each were scooped from the ten spots at Kangole. All the samples were put in one polythene bag as a composite and transported to the laboratory for purification and analysis [17].

Sunflower seeds, cotton seeds and date palms were collected from Kampala's St Balikuddembe market and Jinja oil mills, pressed to collect the different oils.

Purification of Samples

Clay powder (30 g) was suspended in distilled water (700 ml) in a 1000 mL large plastic beaker. Using an ultrasonic probe the clay was disaggregated for approximately 20 minutes. The beaker containing the suspended sample was removed from the ultrasonic probe enclosure and covered the beaker. The beaker was placed on a vibrationally stable surface and to allow the sample to settle gravitationally without interruption for 47 minutes per cm depth of water. The supernatant solution was decanted off to other plastic beaker and allowed to stand for 2 days. The remaining supernatant solution was decanted off and allowed to evaporate to dryness, ground to powder and used in experiments. The sediment in the beaker was discarded.

Elemental Chemical Analyses of Clays

The chemical analyses of elements like aluminium, iron, calcium, sodium and potassium in clays were carried out three times for clay and done by decomposition using sodium carbonate fusion method in platinum crucibles. Silica was determined by gravimetry and the other elements were analyzed using the Perkin–Elmer 3030 model Atomic absorption spectrometer after dissolution of the sample in the hydrofluoric acid–perchloric acid digestion mixture.

Infrared Spectroscopic Studies

Infrared spectroscopy (IR) gives a unique chemical overview of a clay sample, with all the chemicals present contributing to the spectrum produced. The technique allows the qualitative analysis of a large variety of samples ranging from biological samples to clay minerals. Identification of unknown clay is possible through expert interpretation of spectra, in conjunction with the use of spectral libraries. Although the analysis done using IR is largely qualitative, quantitative work is also possible. The search facility can be very useful to identify/characterize unknown clays but care should be taken to ensure that spectral libraries are used appropriately, especially where spectra are of complex mixtures. A high match index does not necessarily mean a successful identification hence close comparison of the unknown sample spectrum and the search match spectrum by the analyst is highly recommended before a conclusion is reached. It should also be noted that all the bands have to match the reference clay spectrum not just one or two bands for a positive identification.

Typically, many of the samples analyzed using the FTIR spectrometers have been used in identification of components in complex mixtures clays. The use of the FTIR microscope ranges from the identification of fibers to mapping of chemical compositions. The IR spectrum is a chemical fingerprint of the sample, made by plotting absorption on y-axis versus frequency in the x-axis, the unit of frequency is the wave number (cm^{-1}). Absorption band intensities are determined by the strength of the change in dipole moment involved in the particular inter-atomic vibration. The stronger the dipole moment change the greater the band intensity.

Different groups in clays show different stretching modes at different frequencies in the infra-red region of the electromagnetic spectrum. The IR absorption spectrum for the smectite-rich natural clay was shown to have absorption band at 3640 cm^{-1} attributed to stretching vibrations of the OH group while that at 3454 cm^{-1} , the presence of interlayer water. The amount of adsorbed water in clays is related to the deformation vibrations of the H–O–H group (1664 cm^{-1}). The bands at 1042 and 798 cm^{-1} are attributed to Si–O stretching vibrations [18]. The bands at 526 and 466 cm^{-1} correspond to deformation vibrations of Si–O–Al and Si–O–Si, respectively and they were used to identify kaolinites and smectites [8, 9].

The clay powder (3 mg) was mixed with KBr (100 mg) ground to powder and pressed into discs. The infrared spectra were run using the KBr discs using B10RD FT540 Fourier Transform IR spectrometer in the frequency range of $3700 - 400 \text{ cm}^{-1}$.

X-ray Powder Diffraction (XRD) is a versatile technique that can be used to identify any crystalline substances, such as most minerals. It can also be used to quantify the proportions of different minerals or indeed many other substances when they are present in a mixture. Typically, clay mineral analysis involves the separation of a clay sized fraction (usually $< 2 \mu\text{m}$) from the sample. Once obtained the clay fraction is prepared by collecting it on a filter and transferring the layer of clay to a glass slide substrate. This 'filter peel' method enhances the preferred orientation of the platy clay particles which helps to obtain a good diffraction signal from the diagnostic basal planes of the clay minerals. It is also the best way to make a homogenous sample, essential is quantitative results are required. These oriented samples are run on the diffractometer (air-dried) and then run again following various treatments such as solvation with ethylene glycol, and heating to specified temperatures for specified times. Other treatments may be appropriate for the identification of some clay minerals. Peak positions, shapes and intensities and changes in these between treatments are diagnostic for the identification of different clay minerals. Following identification, quantitative analysis may be made by an intensity ratio method whereby the integrated intensity (peak area) of selected clay mineral peaks is related to their weight fraction in the mixture by means of a predetermined constant of proportionality termed mineral intensity factors (MIF) or more generally known as Reference Intensity Ratios (RIR). These are most readily determined from calculated one dimensional X-ray diffraction patterns, using for example the NEWMOD program as described by Moore and Reynolds. Precise identification of clay minerals is the first step in any clay mineral analysis, and should be based on experience of the interpretation of diffraction pattern.

The mineralogy of clays was determined using x-ray Powder diffraction (Philips diffractometer with PW1710 control unit operating at 40kV and 30mA using the Ni-filtered $\text{Cu K}\alpha$ radiation). The diffractograms were automatically matched with JCPDS-cards in the computerized XRD CD-rom. Bulk mineralogy was studied with randomly oriented air-dried samples [19].

XRD studies on montmorillonite [20] were used to show that clay exchanges oxygen in form of hydroxyl (SiOH) and (HOH) with hydration of oxygen to surface exposing fresh oxygen previously in the body of the oxide. XRD hot stage analysis was also used to demonstrate the presence of a more thermally stable polymorph of the kaolinite [8,9].

Activation of Samples

For preparation of the activated clays, varying concentrations (0, 10, 20 and 30%) of hydrochloric and sulfuric acids were used. 200 g of the purified sample was placed in a 500 mL beaker. Water (200 mL) was added and a pasty slurry was made. Activation was carried out by adding the acid of a known concentration to the clay slurry and the mixture was boiled for 2 hours at a regulated temperature of 105°C. After slow cooling, the slurry was filtered via a Buchner funnel to separate clay and acid. The residue clay was thoroughly washed with distilled water to remove the residual acid. The sample was dried to constant weight in a thermostated oven at 80°C. The lumps of the prepared clays were ground using a mortar and pestle, sieved to 240 micrometer and stored for use in the bleaching process.

Degumming of Vegetable Oils

Crude oil (100.0 g) was placed in a flask, 85% phosphoric acid (1.0 g, 0.1 mmol) added, the mixture heated at 90°C while stirring at 900 revolutions per minute for 10 minutes under nitrogen blanket. The oil was filtered under nitrogen.

Neutralization of Oil

Mixture of the degummed oil (200.0 g, 0.85 mol) and 0.1 M sodium hydroxide (10.0 cm³) was placed in 250 cm³ Pyrex glass flasks, fitted with a magnetic stirrer. The mixture was stirred vigorously for 10 minutes at room temperature and filtered.

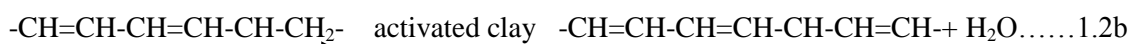
Bleaching Vegetable Oils

Bleaching of oils is a process whereby the clay adsorbent mixed with oil under specified conditions removes unwanted color bodies and contaminants. The primary function of the bleaching process is to remove pigments, gums, trace metals, peroxides and secondary oxidation products. Four basic steps are used to refine oil: neutralization and separation, bleaching and deodorizing. Diatomaceous earth, clays, peroxides or carbon is added to bleach and adsorb the dark colored impurities in the oil in order to give it a clear color [21, 10]. The bleaching process combines catalytic action such as peroxide decomposition and equilibrium adsorption of pigments from oil. The peroxides decompose to volatile aldehydes and ketones due to further oxidation as shown below in equations 1.2a-1.2c, and then they get adsorbed onto clay.



(Peroxide)

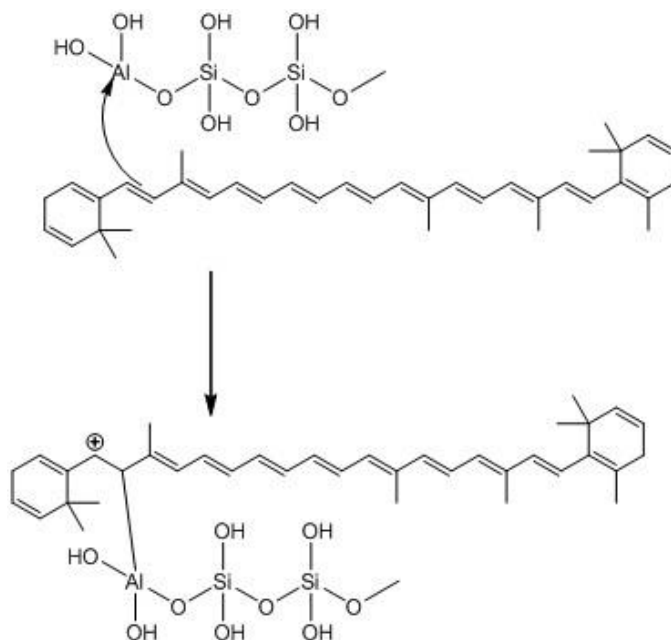
(Secondary oxidation product)



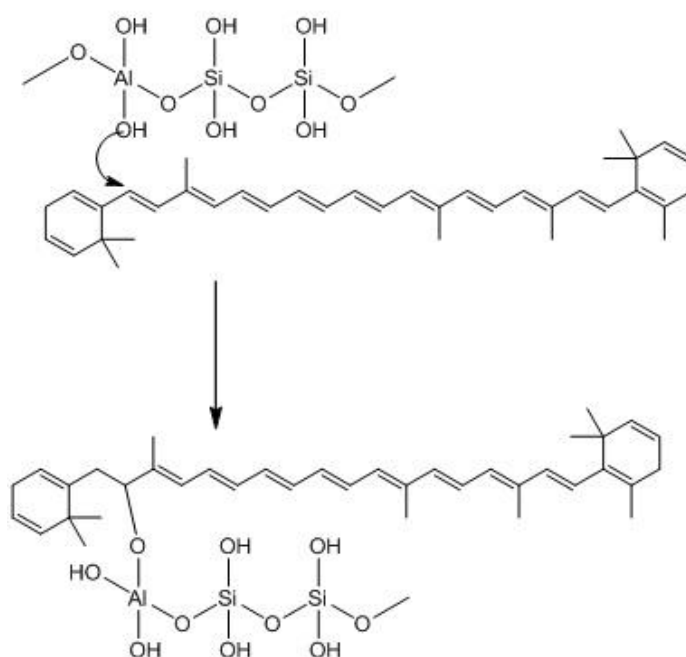
Bleaching is carried out under steam, nitrogen or vacuum to minimize oxidation of oils by oxygen at elevated temperatures.

Clays bleach by interacting with the medium in which the materials or impurities to be removed are present. A nutritive component of crude oils, β-carotene, decomposes on exposure to light or oxygen. Decomposition

of β-carotene is catalyzed by metallic ions like Fe³⁺ or Cu²⁺ which may be present on clay surface. Metal ions catalyze the reaction or serve as active sites for the chemisorption of β-carotene. Pigments dissolved or dispersed in crude oil have olefinic groups which can be protonated by the acidic clay groups. Adsorption of carotenoids can be catalyzed by Brønsted and Lewis acidity as shown in equations 1.3a and 1.3b below.



1.3a



1.3b

β -carotene attaches to clay surface in form of carbocations either through formation of coordinate bonds with Lewis sites or by formation of hydrogen bonds with Broensted sites of the bleaching earths. β -carotene behaves as both electron donor and acceptor, so it reacts with acid centers of bleaching earth's surface by means of its seventh atom. The pigment molecules are held on the clay surface by electrostatic attraction.

Mixture of the degummed, neutralized oil (200.0 g, 0.85 mol) and appropriate clay powders (4.0 g, 1.24 mmol) was placed in 250 cm³ Pyrex glass flasks, fitted with a

magnetic stirrer. The flask was immersed in a thermo-stated iso-electric mantle at various temperatures. The mixture was heated while stirring continuously for a further two hours at the set temperature under high vacuum. The hot oil and clay mixture was filtered in nitrogen atmosphere and tested by measuring absorbance. The absorbance of bleached oil was determined using ultra violet-visible spectrophotometer, Shimadzu, 1201. The absorbance of the bleached oils at 550 nm was determined for each oil sample obtained at the different temperatures of activation. The percentage decrease in absorbance, BE, was calculated as given in equation 1.

Where,

T = Absorbance of unbleached oil

Ts = Absorbance of bleached oil

To investigate the effect of mass percent of clay on the percentage decrease in absorbance of bleached oils, the procedure above was repeated using different clay dosages of 2, 4, 6 and 8%; the operating temperature was 90°C and contact time was 30 minutes.

Solution Absorption Isotherm

The Freundlich isotherm equation has been widely applied to adsorptions from dilute solutions. The equation was derived by assuming an exponential distribution of adsorption potential energies. The equation takes the form given in 2 below,

$$x/m = kC^n \dots\dots\dots (2)$$

Where x is the amount of solute adsorbed by m grams of the adsorbents at concentration C in the solution. k and n are

constants.

Expressing equation 2 in logarithmic form,

$$\log x/m = n \log C + \log k \dots\dots\dots (3)$$

A plot of log x/m against logC gives a straight line known as the Freundlich isotherm has a vertical intercept as logk and slope n.

Results and Discussions:

Characterization of Clay

Table 1 shows the results of the analysis of mineralogy content of the clay composite sample investigated. Result showed the presence of SiO₂, Al₂O₃, MgO, K₂O, CaO and Na₂O in slightly varying amount may be due to errors in forming the composite studied.

Table 1: Chemical composition of Kangole clay

Element%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	LOI	Total
A1	45	18.3	5.7	2.3	3.5	2.4	9.7	86.9
F1	44.3	19.4	6.2	2.4	3.4	2.6	9.9	88.2

The chemical analyses presented in Table 1 showed the Kangole clay had high content of Na₂O (3.45%) and Na₂O/CaO ratio greater than one, which indicated the presence of swelling clay. This has been used as indicating presence of montmorillonite. The presence of iron oxides and aluminium oxide in Kangole deposits in high concentrations of 6 and 20% respectively may be responsible for their high bleaching capacities when acid-leached. The percentages of iron, aluminium and silicon among bentonites worldwide are approximately 11, 18, and 60% respectively. Basing on this, clay from Kangole resembled bentonites and can substitute commercial bleaching earths and cracking catalysts. On the basis of relative percentages of aluminium, silicon and alkaline metals or alkaline earth metals [22], the clays

studied have been found to satisfy the formulae $(\frac{1}{2}Ca, Na)_{0.33}(Mg, Fe^{+2})_3(Si, Al)_4O_{10}(OH)_2 \cdot 4H_2O$ and $Ca_5(Si_7Al_8Fe_2)(Fe_{3.5}Al_4Mg_1)O_{20}(OH)_4$ for montmorillonite and nontronite respectively [22].

The dominant clay mineral in clay deposits at Budadiri, Chelel, Siron and Mutufu was published as being nontronite, a smectite and this coincides with studies on clays formed from volcanic sediments [7-9]. The presence of bentonite among volcanic sediments is well documented in literature. The main smectite mineral present in the Kangole clay deposits was nontronite, di-octahedral clay as shown by the X-ray diffractograms in Figure 1. Tri-octahedral smectites were not detected.

Figure 1 shows that Kangole clay contains smectite (S), illite (I), kaolinite (K), K-feldspars (Kf), plagioclase (Pc) and quartz (Q). The presence of feldspars and plagioclase in these clays showed that the parent rock has not yet completely metamorphosed. Key: smectite (S), illite (I), (K), K-feldspars (Kf), plagioclase (Pc) and quartz (Q)

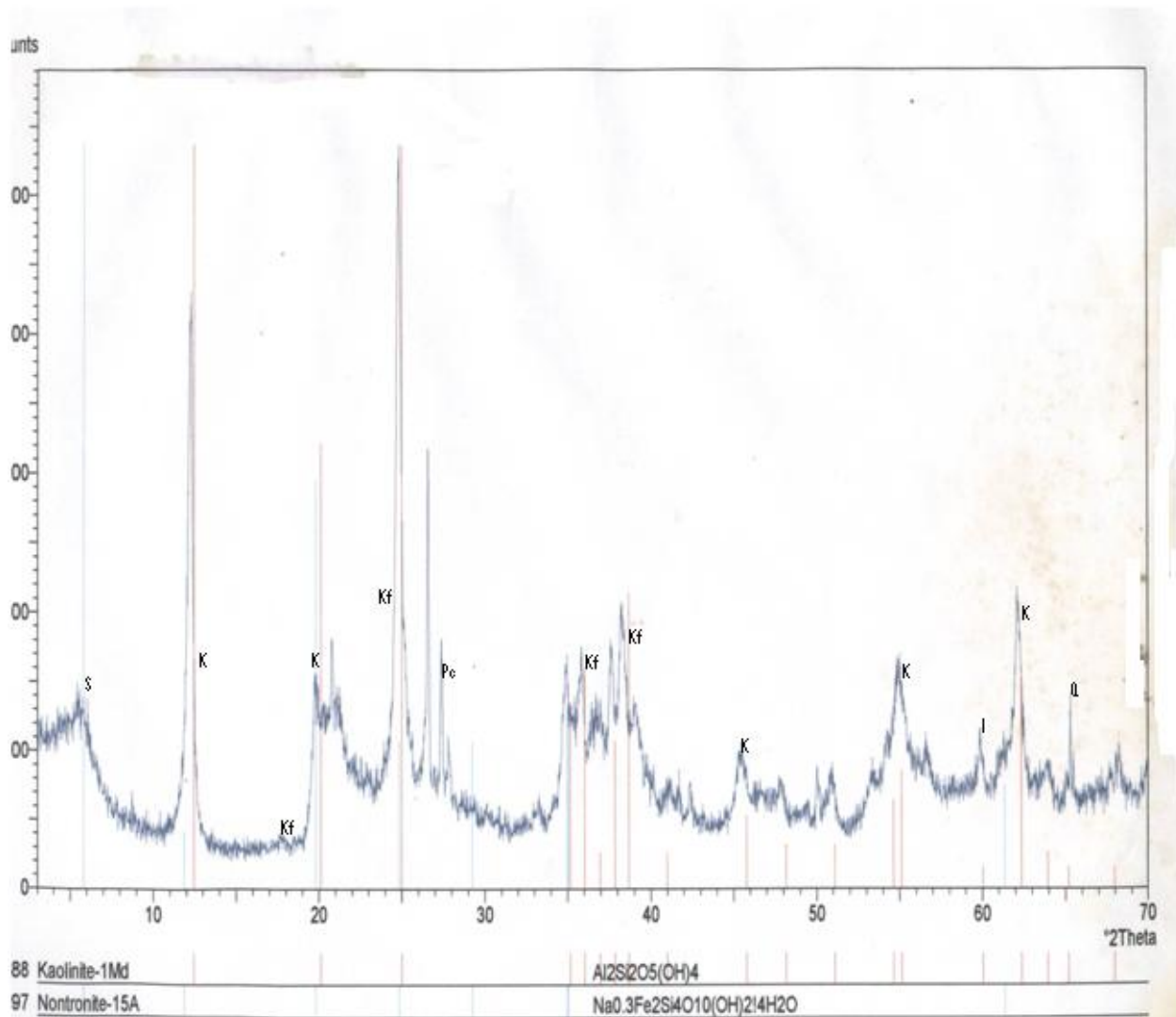


Figure 1: XRD pattern for Kangole clay

Using Reynold's quantitative method, the mineral composition of Kangole clay was determined as follows: feldspars 20%, illite 5%, Kaolinite 7%, plagioclase 5%, quartz 10% and smectite 50%. This indicated the dominant clay in the Kangole sample is smectite. Presence of different clay phases like illite, kaolinite, feldspars, plagioclase and montmorillonite was used to predict that the clay would develop high bleaching capacity when leached in acid.

The Kangole clay was heterogeneous because it had Broensted and Lewis centers and as well contained different phases of clays, such as kaolinite, montmorillonite and illite layers, which also have active centers on their surfaces. It was reported that heterogeneity of Cyprus bentonite was attributed both to different active centers on the smectite surface (Broensted and Lewis centers) and to the different phases present in bentonite, such as illitic layers and clinoptilolite, which also have active centers on their surfaces as the clay was a mixture of illite and smectite.

Table 2: Composition of raw clay and acid-leached clay from Kangole.

%oxide	A0	A10	A20	A30	F0	F10	F20	F30
SiO ₂	45.21	54.16	60.28	68.10	44.3	59.76	64.48	67.31
Al ₂ O ₃	18.32	20.34	15.63	11.23	19.42	15.42	13.06	12.30
Fe ₂ O ₃	5.71	2.41	1.49	1.23	6.21	1.52	1.21	1.00
MgO	0.68	0.63	0.51	0.41	0.63	0.52	0.05	0.03
CaO	2.30	0.60	0.50	0.45	2.41	1.03	1.02	1.00
K ₂ O	2.42	0.86	0.72	0.64	2.66	0.64	0.87	0.72
Na ₂ O	3.5	0.64	0.59	0.42	3.4	0.52	0.50	0.33
LOI	9.71	11.84	12.30	12.90	10.84	12.49	12.90	13.11

Raw clays contained lower silica content than acid-leached clay. Because silica did not dissolve during leaching in acid, its content increased progressively with increase in acid concentration because of removal of ions from the interlayer and octahedral sheets of the clay. Exchangeable ions like calcium, sodium and potassium ions were removed under mild treatment with the acid and this was revealed by the decrease in the percentages in Table 2. There was more significant decrease in percentage of iron and aluminum as the concentration of acid increased than decrease in quantity of calcium and potassium ions remaining in clay matrix. The insignificant change in calcium and potassium content as concentration of acid increased was probably due to passivation. Removal of Al³⁺, Fe³⁺, and Mg²⁺ ions the clay layer must have left unoccupied octahedral sites which may lead to increased bleaching capacity and surface area. The

surface area must rise as a result of the unoccupied octahedral spaces. The loss on ignition increased with increase in concentration of acid used because when octahedral ions were removed, hydrogen and hydroxyl groups replaced them. And on heating, hydrogen and hydroxyl groups decompose to give water. So the amount of water lost from the leached material increased.

Effect of Bleaching time on Adsorption

The effect of contact bleaching time for both raw and acid-activated samples was investigated by measuring absorbance of oils bleached at differing temperatures and times. The percentage decrease in absorbance was observed to increase with contact time, concentration of acid and temperature of activation of clay. The data on absorbance of bleached oils is given in Table 2.

Table 2a and b: Absorbance of bleached oils

2a. Cotton oil

Contact time min	10	20	30	40	50	60
A0	3.147	2.977	2.774	2.673	2.436	2.402
A10	3.011	2.808	2.632	2.537	2.334	2.097
A20	2.876	2.470	2.368	2.300	2.199	2.030
A30	2.673	2.300	2.233	2.165	1.999	1.962
F0	3.214	3.045	2.909	2.774	2.632	2.571
F10	3.079	2.876	2.704	2.639	2.470	2.436
F20	2.977	2.639	2.470	2.402	2.334	2.300
F30	2.808	2.470	2.334	2.667	2.199	2.233

2b.Sunflower oil

Time, min	10	20	30	40	50	60
A0	2.513	2.463	2.403	2.373	2.312	2.311
A10	2.473	2.413	2.353	2.333	2.282	2.203
A20	2.433	2.313	2.283	2.263	2.233	2.201
A30	2.373	2.283	2.243	2.223	2.173	2.172
F0	2.533	2.483	2.432	2.412	2.362	2.361
F10	2.493	2.433	2.393	2.372	2.313	2.312
F20	2.463	2.363	2.313	2.293	2.282	2.283
F30	2.413	2.313	2.282	2.253	2.251	2.252

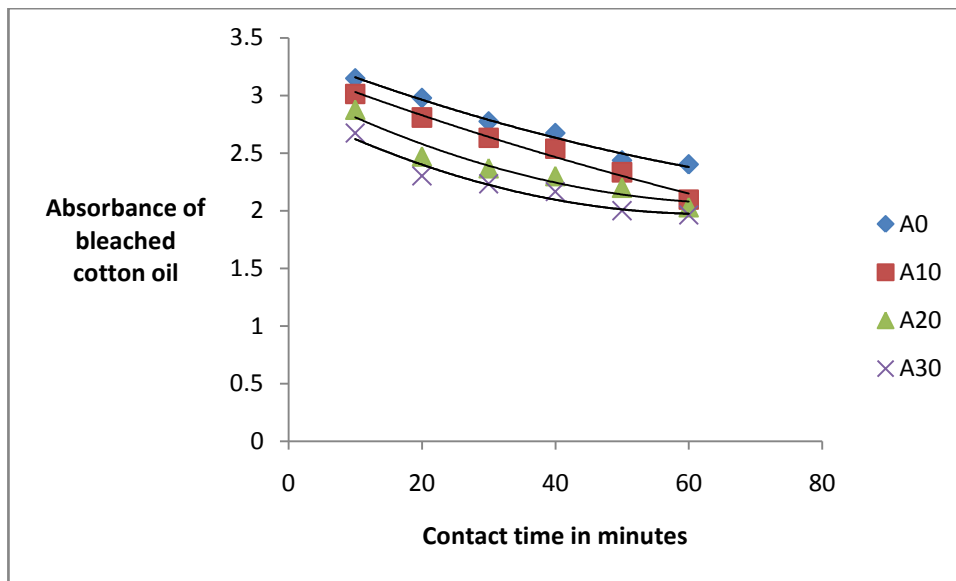


Figure 1a: Representative plot of Absorbance versus contact time minute for cotton oil bleached with clay leached in HCl

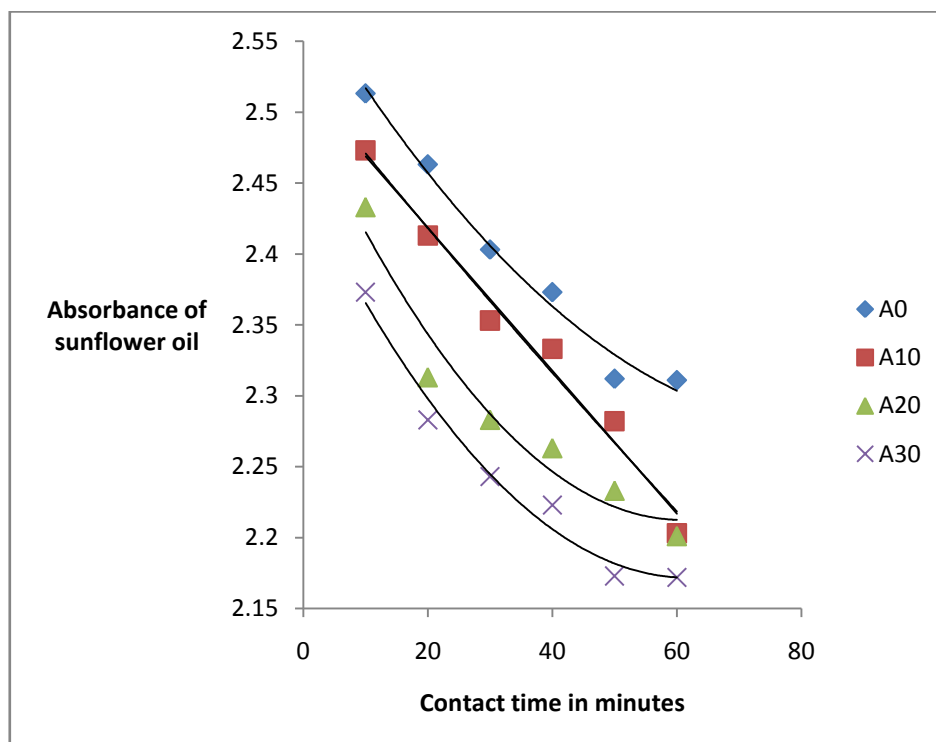


Figure 1b: Representative plot of Absorbance versus contact time minute for sunflower oil bleached with clay leached in HCl.

The absorbance for unbleached, crude sunflower-seed and cotton-seed oils were respectively determined to be 2.583 and 3.383 at 550nm. The values of absorbance for the bleached sunflower seed oils processed at different temperatures using clays activated with acids of varying concentrations were obtained. The data was used to calculate the changes in absorbance and relative absorbance.

The absorbance of bleached oil decreased as the temperature of clay activation, contact time and concentration of the leaching medium increased. The amount of pigment adsorbed, x , increased and the residual relative amount at equilibrium, X_e , decreased in the bleaching of sunflower and cotton seed oils.

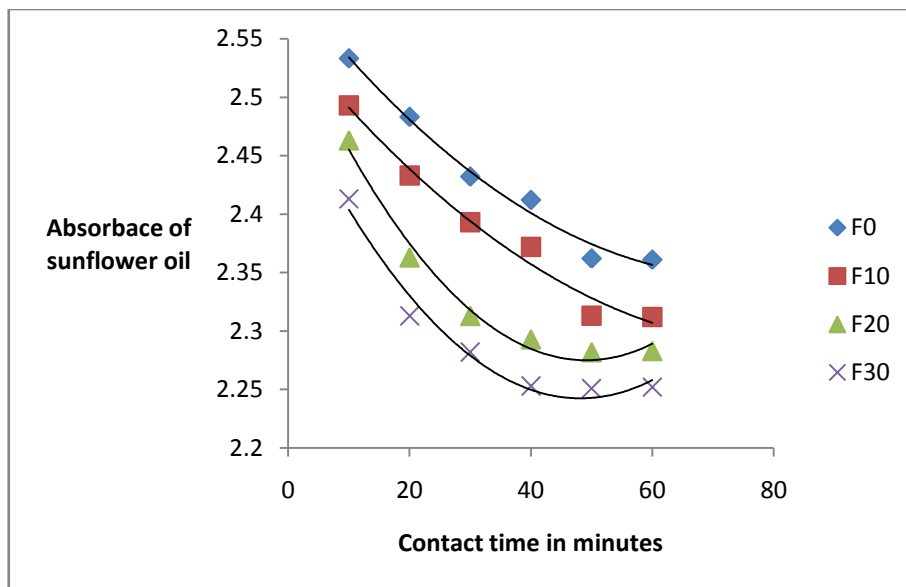


Figure 1c: Representative plot of Absorbance versus contact time minute for sunflower oil bleached with clay leached in H_2SO_4

The decrease in absorbance with increase in temperature and concentration of acid used showed that the bleaching capacity of the clays studied increased [23]. The increase in bleaching ability was caused by removal of octahedral ions from the clay matrices by the acid and dissociation of water, to produce hydroxyl groups on the clay surface. For sunflower and cotton seed oils, the relative changes in pigment adsorbed, x , mass of clay used, m , and the residual

relative quantity in equilibrium, X_e , showed that effective bleaching occurred. The absorbance of bleached cotton-seed oils decreased as the temperature of activation and concentration of the acid in the leaching medium increased. This showed that the amount of pigment adsorbed, x , increased and the residual relative amount at equilibrium X_e , decreased for the cotton-seed oils which were bleached

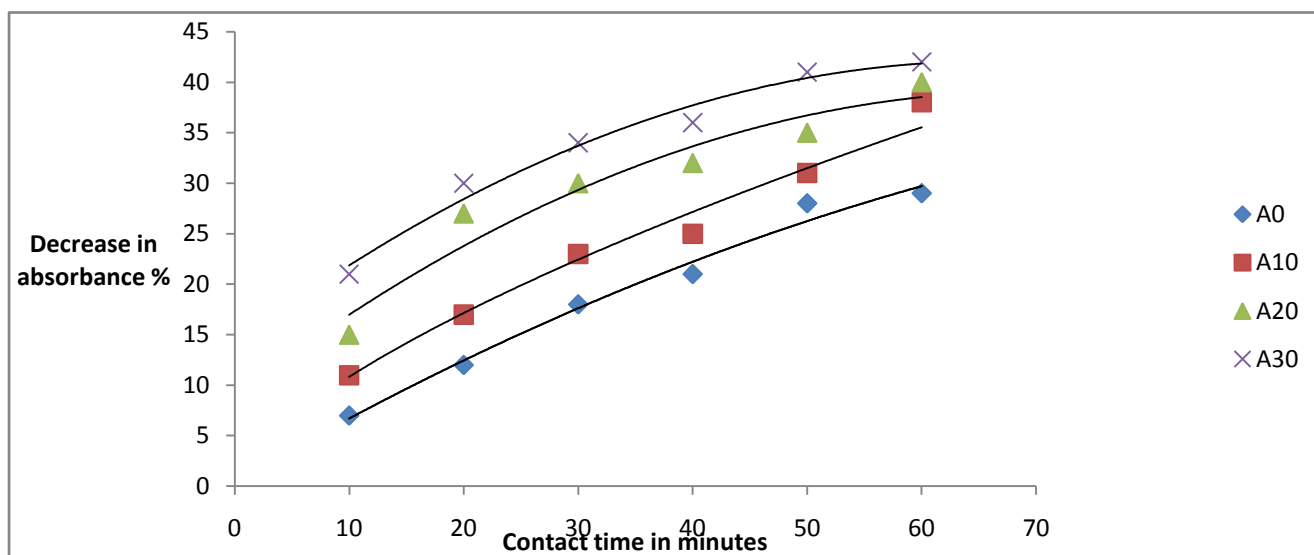


Figure 2a: Percentage decrease in absorbance versus contact time in minutes sunflower oil bleached using Kangole clay leached in HCl .

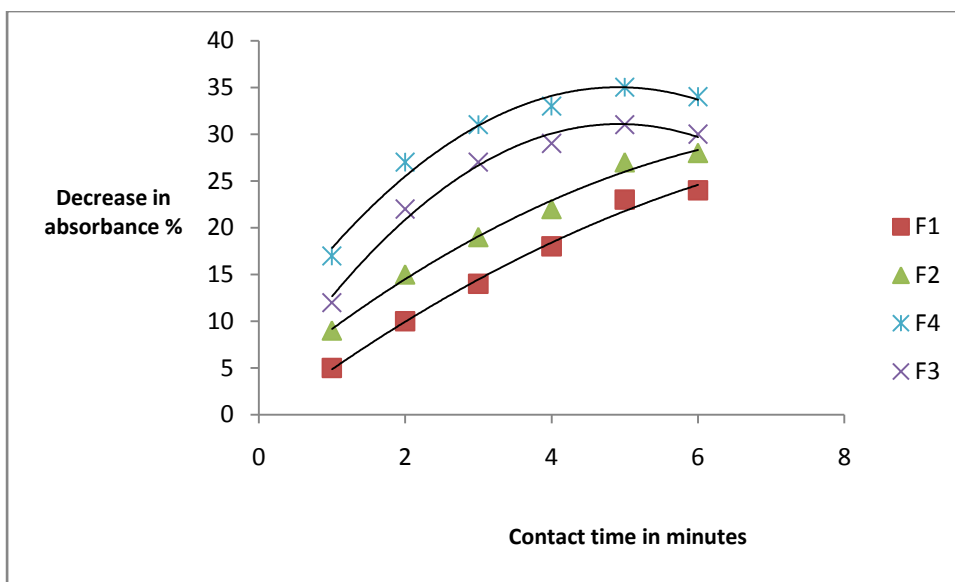


Figure 2b: Percentage decrease in absorbance versus contact time in minutes Cotton oil bleached using Kangole clay leached in H_2SO_4 .

No significant percentage change in absorbance was observed after this time. However, shorter bleaching times were observed while using acid-clays. The highest bleaching time established for both hydrochloric and sulfuric acid-leached clays were 30 and 40 min respectively.

No significant increase in bleaching efficiency of both cotton and sunflower oil when those contact times were exceeded. Earlier researchers using palm oil stated that the contact time for effective bleaching ranges from 15 to 45 minutes[24 - 26].

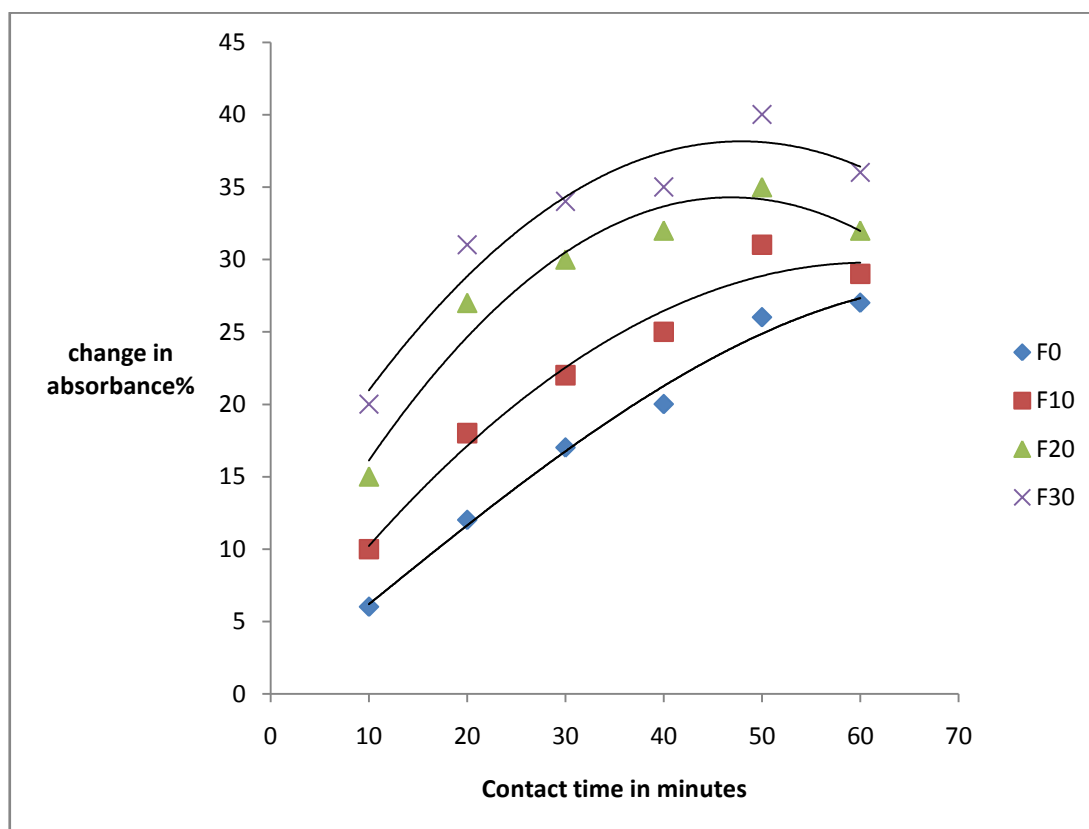


Figure 2c: Percentage decrease in absorbance versus contact time in minutes sunflower oil bleached using Kangole clay leached in H_2SO_4 .

The Percentage decrease in absorbance of oil increased to an optimum value for the raw clay A1 and F1 at adsorbent dosage of 6%. The effect is shown in Figures 3a and 3b.

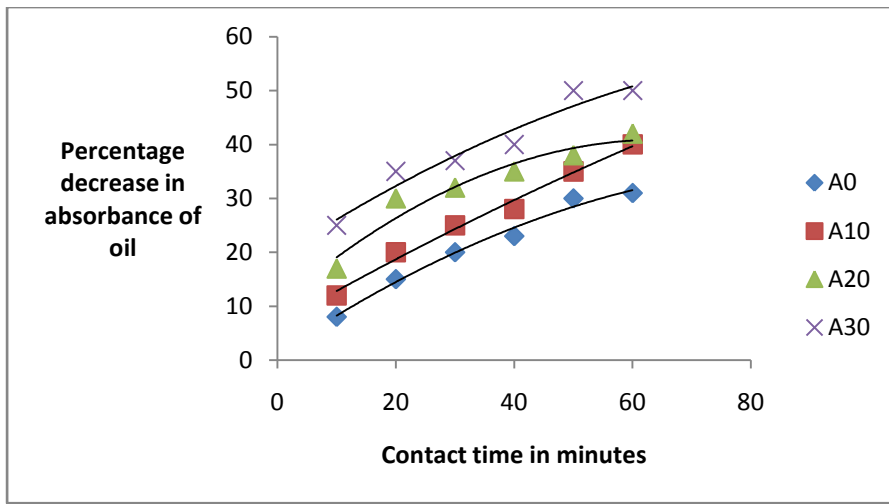


Figure 3a: Contact time versus percentage decrease in absorbance for sunflower oil bleached with HCl leached clay

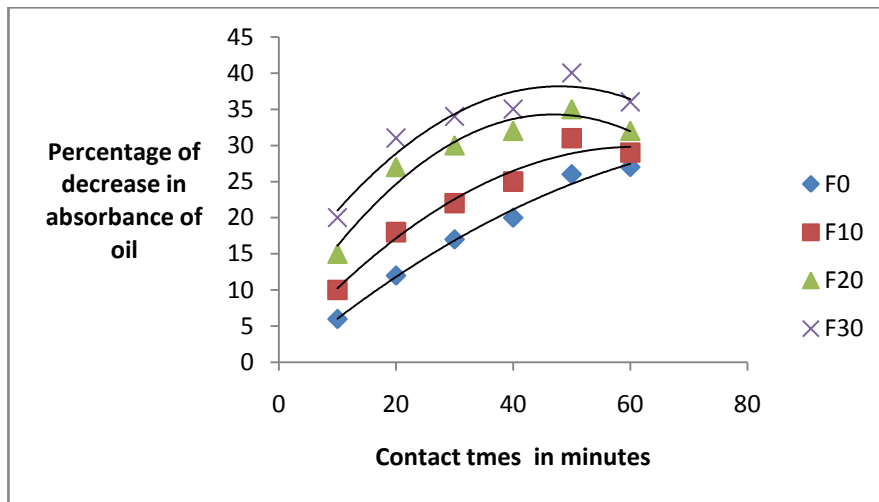


Figure 3b: Contact time versus percentage decrease in absorbance for sunflower oil bleached with H₂SO₄ leached clay

Effect of dosage on percentage decrease in absorbance of oils

The effect of adsorbent dose expressed in percentage weight of clay dose to weight of oil was also investigated with the aim of establishing the most favorable dose of clay to bleach

oil optimally. The data obtained was plotted in Figures 4a and 4b. The data indicated that the percentage decrease in absorbance of oils bleached using Kangole leached with hydrochloric and sulfuric acid increased to an optimum value at adsorbent dosage of 4%. Beyond 4% increase in percentage of clay did not cause significant decrease in percentage decrease in absorbance of bleached oils.

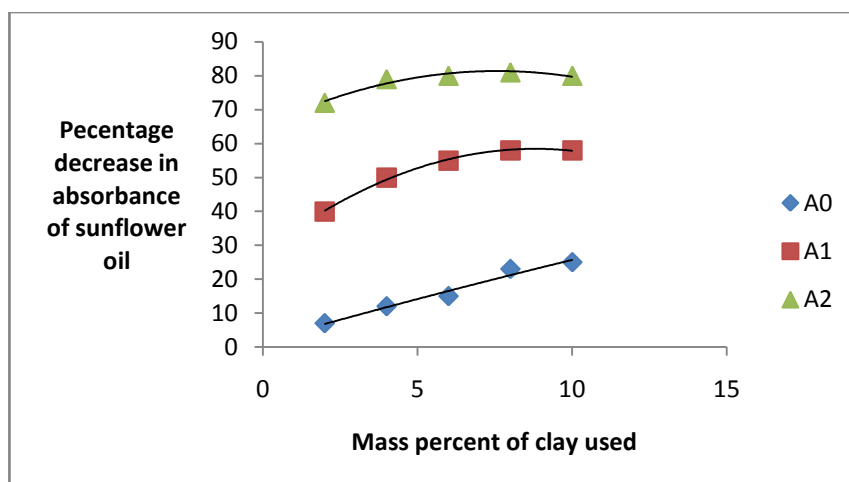


Figure4a: Plot of percentage decrease in absorbance of bleached oil against mass percent of clay

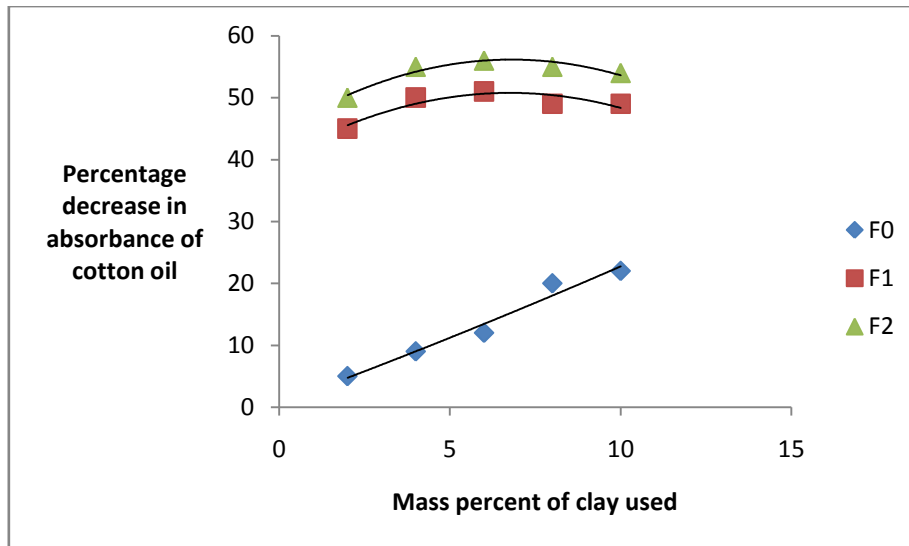


Figure 4b: Plot of percentage decrease in absorbance of bleached oil against mass percent of clay

For all activated clays used, there was increase in percentage decrease in absorbance of oil as mass percent of clay increased showing that effective bleaching was increasing as mass of adsorbent was increased. However, when the percentage was increased beyond 4% there was no significant increase in the bleaching power of the activated clay except raw clay. The failure for the decrease in absorbance of oils to increase after adding clay that is greater than 4% by mass was explained by the fact adsorption equilibrium had been attained between the activated clay and oil mixtures, there by, preventing further color removal by the excess adsorbent dosage [27]. Earlier reports showed that palm oil required as much as 2 to 4% or more to meet final color requirements. Clays leached in 20% acid were optimally effective in decreasing absorbance of oils.

Adsorption Isotherm

The Freundlich model is used to estimate the adsorption affinity of the sorbents towards the adsorbate[28]. The constants k and n indicate the adsorption capacity and the adsorption intensity. The linearity of the plot showed the representative nature of adsorption on the clay. From the solution adsorption isotherm plots, the

amount of color pigments adsorbed was found to be proportional to change in concentration of solute in the solution as measured before and after bleaching has occurred. The value of n depicted that the clay was a very good adsorbent. According to James et al. [21], when the value of n is below 0.5, it depicts that the clay is a very good adsorbent. Rossi et al. [29] stated that if n is high, the adsorbent will be effective for removing the first portions of color but less efficient for reaching highest bleaching degree. The value of k determines the decolorizing power or activity of the adsorbent for a specific solute [23]. Freundlich isotherm model adequately described the adsorption data for all the clay samples investigated with regression coefficient values greater than 0.80. The same conclusion was reported by Nwabanne and Ekwu [11]. This conforms to Rohani [30] observation that Freundlich isotherm is more applicable to a liquid phase in Figures 5a to 5d. Percentage color reductions of 80% for sunflower oil and 55% for cotton oil were obtained with Kangole clay activated using 20% acid respectively as deduced from Figures 4a and 4b. The Freundlich isotherms developed on Kangole clays are shown in Figures 5a to 5d. Figures 5a to 5d are highly linear depicting effective adsorption of coloring bodies occurred during the bleaching of oils. The linearity of Freundlich isotherms developed using Kangole clays followed the following equations;

$$\text{Log } x_e/(x/m) = -0.0974x_e - 0.285 \text{ with linearity coefficient of } R^2 = 0.9926 \text{ for C40;}$$

$$\text{Log } x_e/(x/m) = -0.0993x_e - 0.2584 \text{ with linearity coefficient of } R^2 = 0.9991 \text{ for C30;}$$

$$\text{Log } x_e/(x/m) = -0.1096x_e - 0.2187 \text{ with linearity coefficient of } R^2 = 0.9651 \text{ for C20;}$$

$$\text{Log } x_e/(x/m) = -0.199x_e - 0.2972 \text{ with linearity coefficient of } R^2 = 0.9751 \text{ for C10;}$$

$$\text{and } \text{Log } x_e/(x/m) = -0.1272x_e - 0.1643 \text{ with linearity coefficient of } R^2 = 0.9325 \text{ for C0.}$$

This showed that the acid leached clay matrices did not have limitations resulting from overcrowding, steric interference, thermodynamic instability at high impurity concentrations. The clays were strongly adsorbing as

depicted by the high linearity of Freundlich isotherms. These strongly adsorbing clays are better described by the Freundlich isotherms within lower concentration ranges [31].

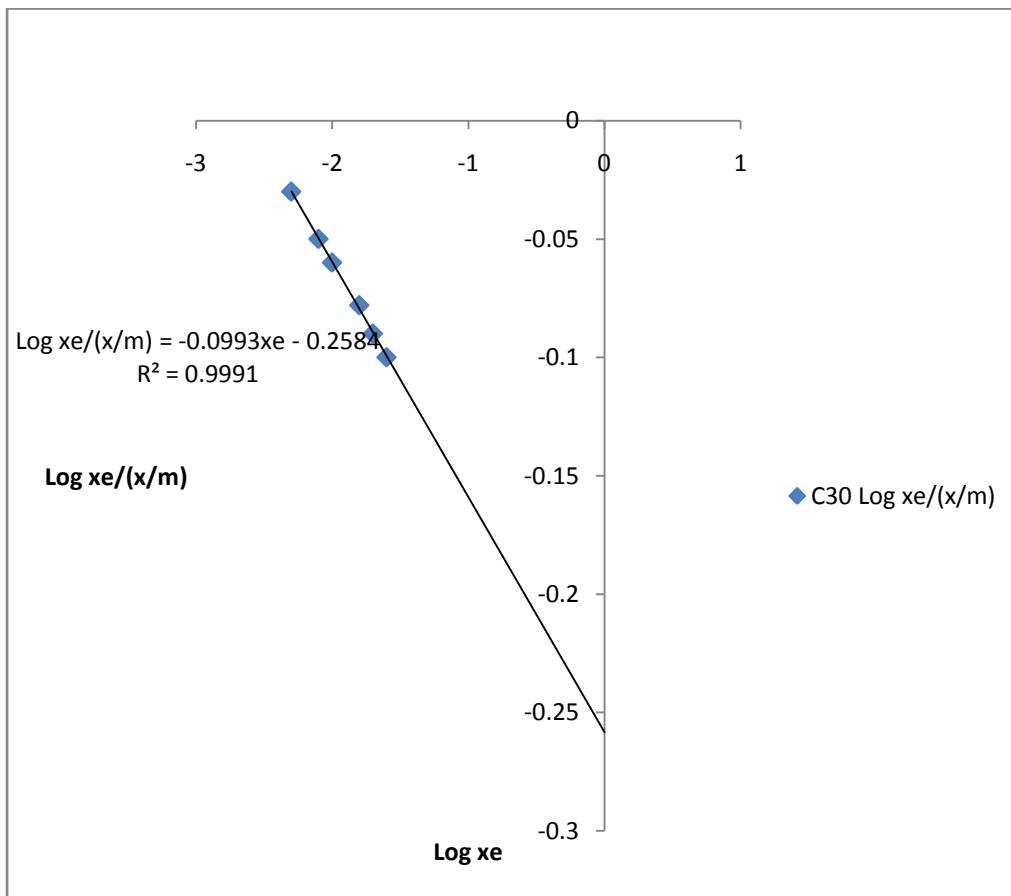


Figure 5a

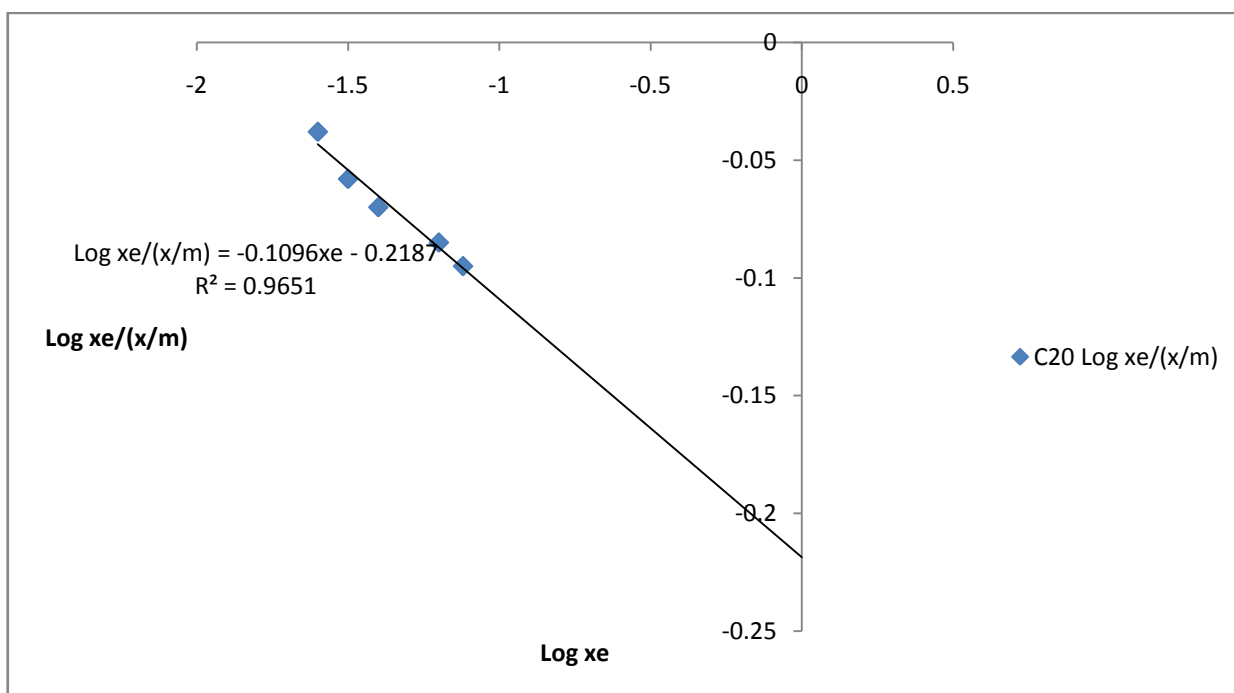


Figure 5b

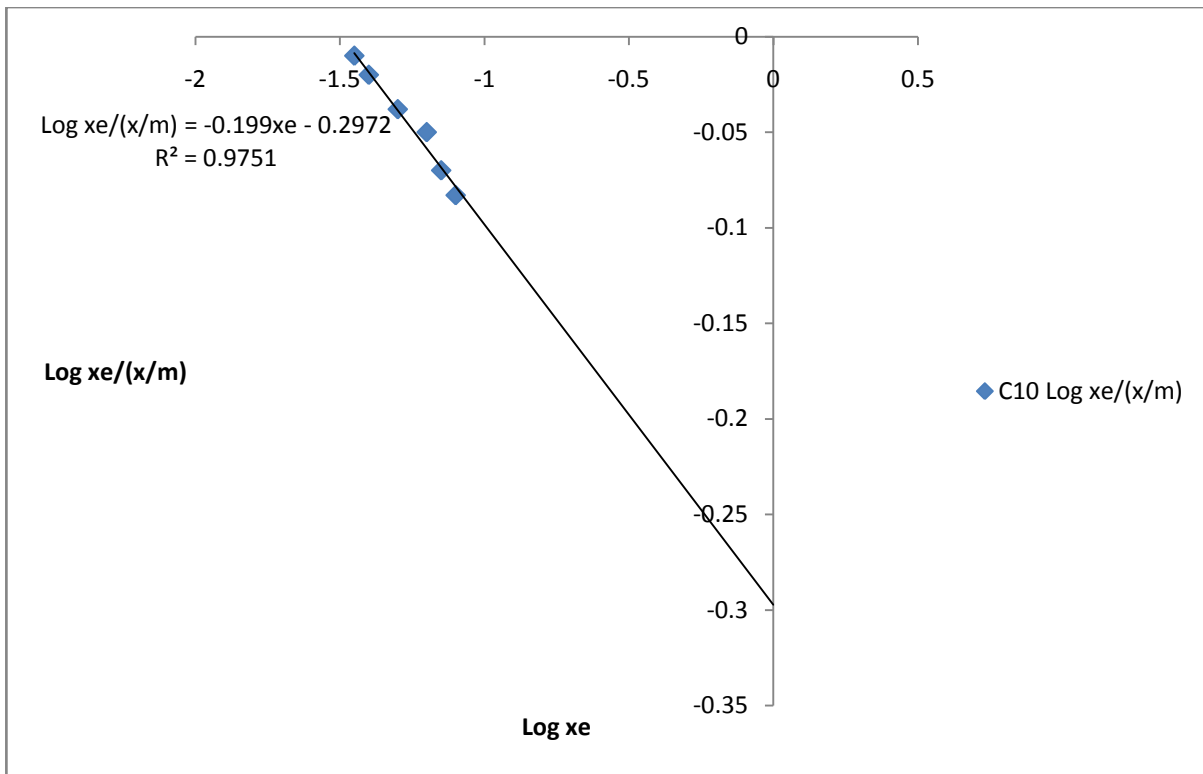


Figure 5c

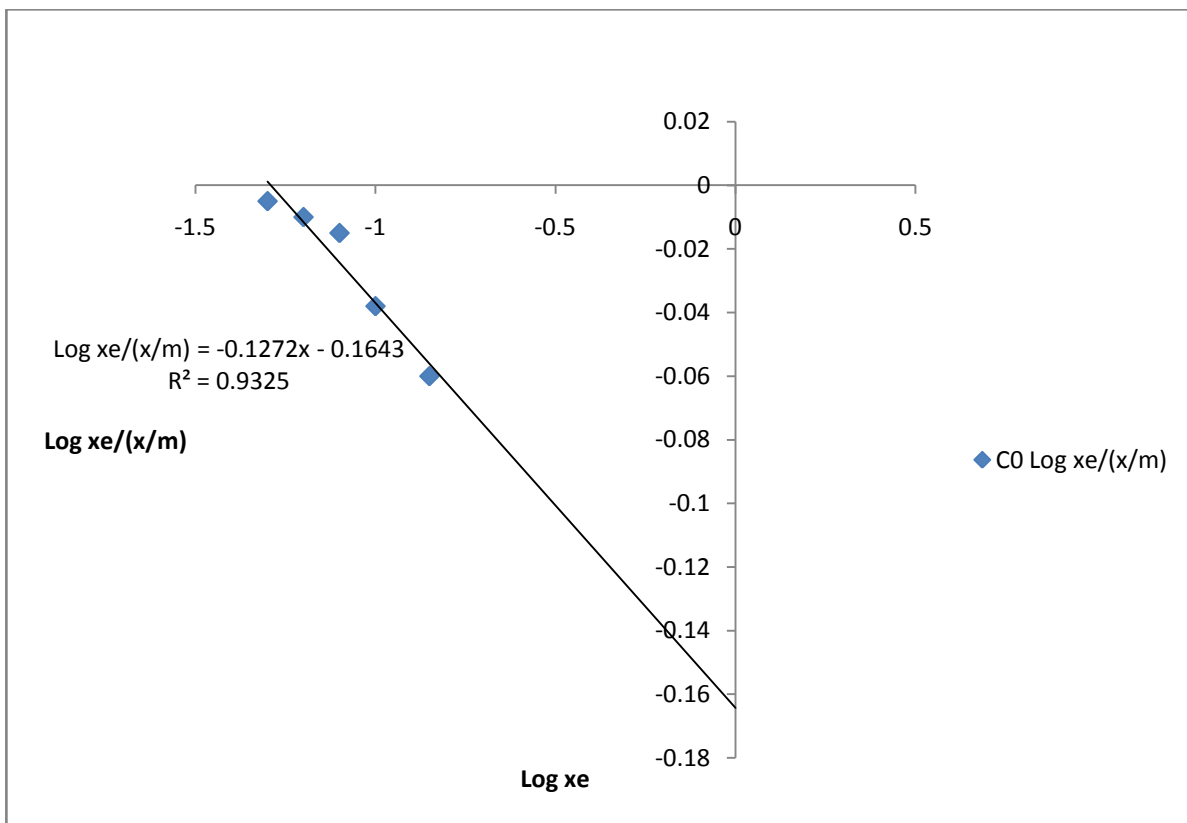


Figure 5d

Figures 5a – 5d: Representative Freundlich isotherm for oil bleached using Kangole clay.

Freundlich isotherms assume monolayer adsorption capacity, complications arise when clays and clays minerals exhibit multi-layer adsorption tendencies and this causes decrease in linearity coefficients of the isotherms. It was the raw clay that had the least linearity coefficient showing that steric hindrance may have affected it due to its low capacity to adsorb. Clays with low adsorption capacities deviated from Freundlich isotherms because they easily got saturated with impurities from oils leading to steric interactions between the adsorbed and unadsorbed impurities [6]. The amount of impurities in vegetable oils that get adsorbed on clays change with small changes in the equilibrium bulk concentration and this is reflected in the deviation from linearity of Freundlich adsorption isotherms. Commonly, if the clay becomes saturated with impurities, repulsion sets in and data obtained after the clay is saturated gives nonlinear Freundlich isotherms. Kangole clay showed high degree of linearity of Freundlich adsorption isotherms it was smectite-rich clays; had high increase in surface acidity and surface area [32]. Acid activation of clays changes the crystal structure of the clays through loss of octahedral ions, thereby increasing pore sizes in the clay matrix. So highly linear Freundlich isotherms were obtained for acid activated Kangole clays.

The values of the Freundlich constant k and n were obtained from plots of $\log X_e(x/m)$ against $\log X_e$. The vertical intercept is k and slopes of the linear graphs is, n characterizing the bleaching power of the clay and the manner in which impurities adsorb on the clay respectively [33,34]. The values of these constants were as follows;

$n = -0.0974$ and $k = -0.285$ for C40;

$n = -0.0993$ and $k = -0.2584$ for C30;

$n = -0.1096$ and $k = -0.2187$ for C20;

$n = -0.199$ and $k = -0.2972$ for C10;

and $n = -0.1272$ and $k = -0.1643$ C0.

The larger the value of Freundlich constant, k , the better the clay at removing impurities from the vegetable oils. Generally, the magnitude of values of k for Kangole clays increases with increase in strength of the acid used to the clay. Leaching with more concentrated acids resulted in creation of more impurity adsorption sites in the resulting activated clay. The highest 'k' value obtained with Kangole

clay which was leached with 40% acid, which in turn gave acid-leached clay with highest bleaching strength. This is attributed to the Kangole clay being a smectite, which made the clay applicable as bleaching agent.

The value of the Freundlich constant n is used to determine the range of decolorization within which the adsorbent is most effective. Adsorbent clay with a higher value of n will be relatively effective at binding impurities in oils, but inefficient at bleaching oil to a low color value. The opposite is true for an adsorbent with a low n value. A high n value is desirable but not at the expense of k [23, 35]. Basing this, clay leached in 10 and 20% would satisfactorily bleach.

Conclusion

The use of bleaching earths developed using local clay from Kangole in North Eastern Uganda in bleaching of cotton and sunflower oil have been studied. The results have indicated that this clay has great potential in the removal of color pigments from oil. The percentage decrease in absorbance of sunflower oil of 80% was achieved with clay leached in 20% hydrochloric acid. Yet cotton oil attained highest percentage absorbance of 55% during the bleaching step. The overall performance of hydrochloric acid leached clay was found higher than those activated using sulfuric acid. Also, the overall performance of clays activated with dilute acids was higher than those activated with concentrated acids. The values of Freundlich constants k and n showed that the acid-activated clays were very effective in bleaching cotton and sunflower oils.

Recommendation

The results produced in this research need to be tested in industrial settings.

Acknowledgement

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