



Effect of Activation on Clays and Carbonaceous Materials in Vegetable Oil Bleaching: State of Art Review

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Authors' contributions

This work was carried out in collaboration between all authors without conflicting issues. Author ABA designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Authors STO, AOA and JMO managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The use of clay and its minerals in vegetable oil purification has been tremendous. It has been discovered that surface modification or activation of this distinct adsorbent greatly increases its adsorptive capacity. Similarly, seed hulls also known as carbonaceous materials are being used as the only adsorbent or combined with activated clays for vegetable oil bleaching. Prominent among the modification methods is acid activation. Acid activated clay minerals and carbonaceous materials have been used extensively as adsorbent industrially for vegetable oil bleaching. However, some challenges have been identified with the use of acid activated adsorbent for vegetable oil cleansing. This paper made a review of activation of clay minerals and carbonaceous

materials and its effect on micro structure, surface area and bleaching efficiency in vegetable oil refining.

Keywords: Acid activation; clay; carbonaceous materials; bleaching; vegetable oil.

1. INTRODUCTION

Vegetable oils in their crude form are deeply coloured. These colour impurities have to be removed to make the final product attractive and acceptable to the end user. Impurities in vegetable oils include pigments such as chlorophyll, tocopherol, xanthophyll and carotenoid [1]. Other impurities are phosphatides, trace metals, traces of soap, peroxides and free fatty acids. It is desirable to remove color impurities from oil not only prior to use but also after use, thereby enabling re-using or re-cycling the oil. Processes involved in vegetable oil refining include degumming, neutralization, bleaching, filtration, and deodorization. These processes are aimed at converting the crude oil to more suitable oil for subsequent use. Degumming process is a method of removing phosphatides or gums in vegetable oil. Gums could be hydratable or nonhydratable. Greyt and Kellens [2] described degumming as the removal of phosphatides and mucilaginous material from crude oil by means of washing with hot water, dilute acid or sometimes dilute sodium hydroxide. Neutralization process involves the use of alkaline to produce soap stock which is separated from the oil [3]. Bleaching is done to remove colour impurities in vegetable oil and finally deodorization is designed to produce oil of good flavor, odour and shelf life.

Bleaching is most important among the five stages of refining because it determines the appearance, flavor, taste and stability of the final product [4]. This is achieved by using a surface active solid to adsorb the colouring matters. In the process of refining vegetable oil, bleaching clays have been used extensively as adsorbent in vegetable oil refining. The growing interest in using low cost adsorbent in vegetable oil bleaching as brought about the use of carbonaceous materials as an alternative. In the vegetable oil industry, carbonaceous materials are used either as a small part of readymade mixtures with bleaching clays, where the ratio of the carbon does not exceed 5–10% of the weight of the clay, or by bleaching with activated carbon prior to bleaching with the clay [5]. Its use as only

adsorbent in vegetable oil refining (VOR) is rarely reported.

Application of acid activated clay in the adsorption bleaching of vegetable oils has reached the limit of optimization. A lot of shortcomings have been reported for various acid activated clays used as adsorbent in VOR. Residual acid effect has been reported by David et al. [6], while the waste water from washing of the adsorbent during activation process constitute a nuisance to the environment. Several review have been made on clay activation for vegetable oil bleaching [7,8,9], the report of these researchers were focused on structural and surface properties of the clay mineral, textural characteristics, surface chemistry, modification techniques and parameters that influence the activation method. This paper therefore is aimed at reviewing various studies on the effect of activation on clays and carbonaceous materials for vegetable oil bleaching with a view to identify the challenges faced by these methods.

2. CLAY ACTIVATION

Clay is defined as a naturally occurring material composed of fine grained minerals, which is plastic at appropriate water contents and will hardened when dried or fired [10]. Clays are basically alumino-silicate containing different amounts of other materials which are usually expressed in terms of the percentage of each metallic element expressed in form of its oxide [11]. Clay in its natural form is a natural adsorbent. It has been used in the clarification of beer and wine, animal feed bond, and food additives. It has been used as adsorbent in food technology such as bleaching earth, [12,13]. However, it has been discovered that the bleaching efficiency of these clays can be enhanced through physical and chemical activation. Other methods of activation include pillaring and heat treatment. Chemical activation include acid and alkaline activation, the most common been acid activation. Farihahusnah et al. [7], made a comprehensive review of textural characterization, surface chemistry, and activation of bleaching earth and they concluded that new techniques that are more environmental

friendly should be employed, alternative source of bleaching earth should be sourced, detailed study on most effective parameters of the bleaching earth be conducted using design of experiments and that effective technique of the bleaching earth that can be used for vegetable oil purification be investigated. Activation increases the specific surface area and the adsorption capacity of the adsorbent [14].

2.1 Acid Activation

Natural clays are purified and treated with mineral acids. These acids include hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid, organic acid such as acetic, citric, oxalic and lactic. Among these acids, hydrochloric acid and sulfuric acid are the most widely used in acid activation, because they give good results regarding the specific surface area, porosity and adsorption capacity of the activated clay [15]. David et al. [1] in a United States patent titled 'oil bleaching method and composition for same' reported that sulphuric acid is preferred because it does not evaporate during the acid activation step or at the beginning of the final drying process, thus permitting a more complete activation of the clay. The authors also stated that phosphoric acid has a similar action, but poorly soluble aluminum phosphate is formed. However, it does not migrate into the pores easily. This disadvantage can be eliminated by using a mixture of sulphuric acid and phosphoric acid. Hydrochloric acid is less desirable as an activating acid, as it evaporates during activation and forms soluble salts which can be washed out of the micropores of the clay product [6].

Generally, the process of acid activation involves purification of the clay and grinding to very fine particles. The grinded clay mixed with known amount of acid and the resulting mixture heated to a temperature of between 80 and 100°C under continuous stirring for a period ranging from 2-6 hours. The clay suspension is then washed in distilled water before filtration and drying process to recover the solid acid treated clay. These acid activated clays are usually washed until ions free before being used as bleaching clay, creating a waste stream whose disposal may incur additional cost as it must be disposed off in an environmentally friendly way. Also, oil bleached with acid activated clays is neutralized with alkaline during refining thus increasing processing cost. Moreover, significant quantity of the activated clay may be lost during the washing process.

Taylor et al. [16], in a United States patent (patent no: 5008227) invented a process of making acid activated bleaching earth from crude attapulgite. The authors claimed that clay sources used in the past to produce acid activated bleaching earth of high activity has been restricted to calcium bentonite that is, clay in which the principal exchangeable cation is calcium ion, activation of this type of clay requires high acid dosages. It has been a general belief that clays rich in attapulgite do not respond to conventional acid activation but the authors surprisingly discovered that mildly acidic uncalcined attapulgite clay requires significantly low acid to reach their maximum bleaching levels.

Francisco et al. [17], studied the acid activation of Brazilian smectite clays. Different samples of Brazilian smectite clays were activated using hydrochloric acid. The activated clay was washed in distilled water by decantation until it is Cl⁻ free. The authors established that activation process involves basically the substitution of exchangeable cations by proton and dissolution of metals ions from the clay structure.

Salawudeen et al. [18], evaluated the performance of acid treated Nigerian clay for palm oil bleaching. The result revealed that HCl activated clay has relatively higher bleaching power than H₂SO₄ because H₂SO₄ activated clay forms metallic sulfate during activation thereby blocking the surface of the clay and therefore reduces the surface activities of the adsorbent. The authors also discovered that bleaching efficiency increases with increase in acid concentration. The maximum percentage colour reduction of 94.28% was achieved in HCl activated clay at 45% acid concentration while 89.46% colour reduction at 35% acid concentration was achieved with H₂SO₄ activated clay. Further increase in concentration of H₂SO₄ has no significant effect.

Nguetnkam et al. [19], assessed the bleaching capacity of Cameroonian clays on vegetable oils. The authors discovered that the bleaching capacity of natural clays were poor compared to that of industrial adsorbents. Acid activation of the Cameroonian clays was carried out using sulphuric acid solution. The activated clays were washed severally with pure water until the silver nitrate test for sulphate ion was negative.

Hulya et al. [20], studied the effect of sulphuric acid activation on crystallinity, surface area, porosity, surface acidity and bleaching power of

bentonite. The turkey bentonite, precisely, Ankara was activated with sulphuric acid by dry method at 97°C for 6hrs. The sulphuric acid content in the dry bentonite acid mixture was changed between 0% and 70%. The activated bentonite was used to bleach soybean oil.

Several other studies have been reported on production and application of acid activated clays, these include acid activation of montmorillonite by Falaras et al. [21], properties and catalytic activity of acid modified montmorillonite and vermiculite by Ravichandran et al. [22], acid activation of palygorskite with HCl by Suarez Barrios et al. [23], clarification of cottonseed oil by acid treated bentonite by Foletto et al. [24], sunflower oil bleaching by adsorption onto acid activated bentonite by Foletto et al. [25], textural properties of acid activated glauconite by Srasra and Trabeisi-Ayedi [26], synthesis and characterization of acid activated Serbian smectite clays obtained by statistically designed experiments by Novakovic et al. [27].

2.2 Alkaline Activation

Very few studies were reported on the effects of alkaline treatment of bleaching earth on the adsorption bleaching of vegetable oils capacity. Okwara and Osoka [28], studied the influence of caustic activation of Nigerian clays for palm oil bleaching. The clay samples (kaolin, bentonite and fuller's earth) were activated at 80-85°C for 35-45 minutes using caustic soda (NaOH) at concentrations of 1M, 2M, 3M and 4M respectively. The alkaline activated clays were used to bleach palm oil. They discovered that alkaline activated clay could remove reasonable amount of unwanted pigment in vegetable oil. However, the use of alkali activated clay is still receiving research attention because no conclusive information has been drawn on its effect on the general properties of vegetable oils.

2.3 Thermal Activation

Heat treatment is a physical method of clay modification. Clay structure and composition can be modified by heating at high temperature [29]. Valenzuela Diaz and Souza Santos [15] stated that thermal treatment is a method of alteration of chemical composition and/or crystalline structure by the effect of temperature. Heat treatment of clay results in loss of all or substantial proportion of chemically held water in the clay. Many impurities are also lost during heat treatment.

Regina, [30], modified the physico-chemical properties of Uri (Nigeria) clay minerals to enhance its adsorptive capacity. The author modified the samples by thermal activation at temperatures ranging from 100°C to 500°C. Such heat treated clays were used to bleach palm oil for its adsorptive capacity test.

Habashy et al. [31], characterized some Egyptians clays for use as bleaching agents. The authors reported that increase in treatment temperature from 110°C to 150°C leads to increases in the specific surface area and total pore volume of the treated clays. This is due to the loss of mechanically held water, followed by the initial loss of lattice water of hydration occurring at the first low stage, from the montmorillonitic structure present in the tested clays. However, with a further increase in the treatment temperature to 250°C, loss of the water content increased, and this leads to decrease in the specific surface area and the total pore volume of the Maadi clay.

2.4 Microwave Activation

Microwave heating can be used to significantly modify the adsorption properties of bleaching earth. Gunawan et al. [32] investigated the effect of organo-bentonite for the purification of vegetable oils by using normal heating and microwave irradiation method. The authors discovered that the amounts of free fatty acid (FFA) removed during bleaching process by microwave irradiation method are higher than the conventional heating. The results also show that there was a significant decrease in peroxide value (PV) for both methods. Korichi et al. [33] studied the effect of acid activation under microwave irradiation on the textural and structural properties of a smectite from Algeria. The results showed that, the specific surface area, micropore and mesopore of smectite increased with increasing irradiation time. The authors also reported that the temperature and time required by the microwave heating for adsorbent preparation are far shorter than the conventional thermal activation method. Their findings indicated that, the method is simple, economic, time saving and energy efficient.

However, this method of modification has not been optimized hence, its adoption in manufacturing and industrial synthesis is not yet feasible. Deng and Lin [34] stated more studies on the fundamental of the microwave heating for solid dispersion are needed in order to optimize

the synthesis process. Such studies should include investigation of the effects of heating atmosphere, microwave power, different casket materials on the heating curves, ending temperature and dispersion of the active species. The authors concluded that sorbents or catalysts with better properties could be prepared when the microwave synthesis process is further optimized.

2.5 Pillaring

Pillaring is another method of clay modification which involves combination of both chemical and physical treatment. It involves the insertion of inorganic polycation of nanodimension to the clay interlayer and subsequent thermal treatment. These polycationic metals also known as pillars can be intercalated into the interlayer of the clay to produce thermally stable activated clays. Falaras et al. [35], investigated the bleaching properties of Alumina-pillared activated montmorillonite on cotton seed oil. The Ca-rich montmorillonite was treated with sulphuric acid and pillared with a poly cation called Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ at a calcinations temperature of 500°C. In another research article by Gizela et al. [36], montmorillonite clay was modified to produce six different samples, namely raw montmorillonite (RM), activated raw montmorillonite (ARM), acid activated Al-pillared raw montmorillonite (AAIRM), purified montmorillonite (PM), acid activated purified montmorillonite (APM) and acid activated Al-pillared purified montmorillonite. Muhammed et al. [37] made a comparative study of laterite and bentonite based organoclays for the sorption of hydrophobic compound (edibleoil/grease and hydrocarbon oil) from aqueous solution. Organoclays were prepared by cation exchange reaction of lattice ions with two surfactants, hexadecyl trimethyl ammonium chloride (HDTMA-Cl) and tetradecyl trimethyl ammonium bromide (TDTMA-Br). The authors discovered that the amount of surfactant loading and the nature of the surfactant molecules used in the syntheses of organoclay strongly affect the sorption capacity of the clay mineral. It was found that both the laterite and bentonite based organoclays efficiently removed the edible and hydrocarbon oil content from lab prepared emulsions; however, the adsorption capacity of clay mineral was greatly influenced by the nature of hydrophobic compounds as well.

3. EFFECT OF ACTIVATION ON CLAY STRUCTURE

The crystal clay structure is one of the important factors that contribute to clay adsorptive property. The crystal structure with a few exceptions consists of sheets. Individual layer consists of two, three or four sheets. The sheets are formed by tetrahedrons (SiO_4)⁴⁻ or octahedrons

Such as $[AlO_3(OH_3)]^{6-}$. When an octahedral sheet is linked to one tetrahedral sheet, the clay layer is called two sheet phyllosilicate and is referred to as 1:1 layer type. Similarly, when the ratio of tetrahedral sheet to octahedral sheet is 2:1, it is called three layer phyllosilicate. The octahedral sheet is sandwiched between the two tetrahedral sheets [11].

Isomorphic substitution is an important characteristic of clay which generates negative charge on clay layers. It involves replacement of constituent metal ion of the lattice by cation of lower charge thus producing a negative charge [38]. Example of such substitution includes Al^{3+} for Si^{4+} in the tetrahedral sheets. This negative charge is balanced by the interlayer exchangeable cation. Another special feature of clay mineral is the presence of Lewis and Bronsted acidity site. Lewis and Bronsted acidity site is one of the active site that determines the chemical reactions in the clay structure. Sposito et al. [39] reported that, when isomorphic substitution occurs in the octahedral sheet, the negative charge is more delocalized and the Lewis base character (electron donor) of the siloxane surface is enhanced. The negative charge that results from isomorphic substitution is balanced by the presence of exchangeable cations which are Ca^{2+} , Mg^{2+} , K^+ and Na^+ ions. The excess negative charge smeared over all the superficial oxygen and makes the clay surface highly acidic. This subsequently have great impact on the sorption of polar and charged organic compounds.

Acid activation of clay results in leaching of cation from tetrahedral and octahedral sheets and replaces the exchangeable cation with hydrogen ion. Acid treatment of clay also opens the edges of the platelets as shown in Fig. 1, and as a result, surface area and pore diameter increases [17].

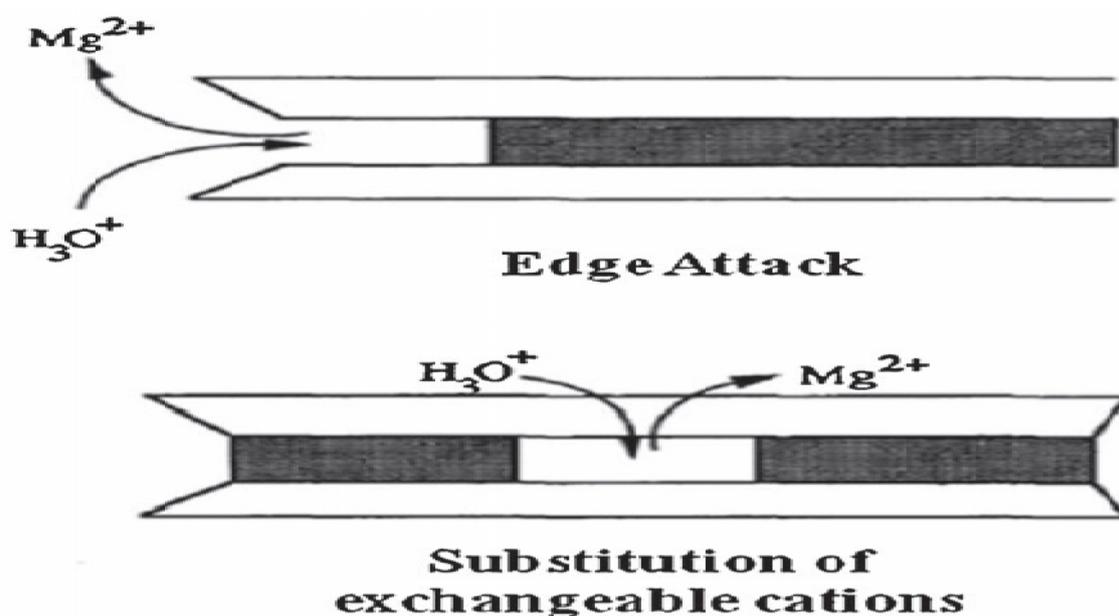


Fig. 1. Mechanism of acid activation [adapted from Kaviratna and Pinnavaia [40]

Taylor and Jerkin [41], experimentally established that acid treatment of clay increases the adsorption capacity for oil increases to an optimum value and decreases with further treatment. A similar effect was reported by Christidis et al. [42], they reported that surface area is an important characteristic of activated clay but maximum bleaching ability is not associated with maximum surface area.

Dombrowsky and Handerson [43], made a list of some changes which smectite crystal suffers after activation, these include (i) opening of the crystal edges which exposes the Al^{3+} and Mg^{2+} cations to acid and subsequent dissolution of the cation, (ii) expansion of the surface pore diameter, (iii) specific surface area of smectite increases to a maximum and reduced by additional treatment.

For industrial oil bleaching, pore size distribution of clay minerals an important factor. Gregg and Sing [44] classify pore size into three types: pore with width below 2nm are called micropores, those with width between 2nm and 50nm are called mesopores and those larger than 50nm are called macropores. Babaki et al. [45], reported that physical properties and chemical properties of bentonite such as adsorption and catalytic activity depend extensively on the micro and mesopores. They reported that micro and mesopores are located within the particles while macropores are located between particles and that the effect of macropore on adsorptive

properties is negligible compared to that of micro and mesopores.

Kashani et al. [46] studied the effect of acid activation on structural properties of bentonite. Their result showed that surface area can be increased upon acid treatment. As activation progresses, surface area increases rapidly and reaches a maximum, further activation decreases the surface area. An approximate seven fold increase in the specific surface area was achieved (from $17 \text{ m}^2/\text{g}$ to $123 \text{ m}^2/\text{g}$). Zschau [47] reported that natural montmorillonite clay has a specific surface area between $40 \text{ m}^2 \text{ g}^{-1}$ and $160 \text{ m}^2 \text{ g}^{-1}$, while the specific surface area of acid activated is in the range of $150\text{--}350 \text{ m}^2 \text{ g}^{-1}$.

A research by Onal [48] showed that crystallinity and porosity of smectite reduced greatly by heat treatment. The result showed that change by dehydration up to 400°C is reversible and reduced irreversibly after heating above 600°C . The specific micropore volume increased rapidly to a maximum of $0.045 \text{ cm}^3/\text{g}$ when the temperature rises to 400°C by the effect of dehydration and decrease rapidly by effect of dehydroxylation and finally reached zero at 900°C by effect of decrystallisation.

Illic et al. [49] reported that water absorbed in pores and on surface were released at temperature below 200°C . Mass loss of water attributed to pre-dehydration occurred between 200°C and 400°C which is as a result of reorganization in the octahedral layer.

Dehydroxylation of kaolinite and formation of metakaolinite takes place at temperatures between 450°C and 650°C. Mullite was formed at about 1000°C. Table 1 presents the specific surface area of raw and activated clay minerals investigated by some researchers. The table shows that specific surface area is greatly increased after activation.

Table 1. Specific surface area of raw and activated clay and clay minerals

Adsorbent	Raw clay (m ² g ⁻¹)	Activated clay (m ² g ⁻¹)	References
Glaucanite	49	326	[26]
Bentonite	69	238	[4]
Smectite	63	238	[27]
Montmorillonite	93	107	[21]
Sepiolite	150	263	[50]
Palygorskite	183	286	[51]
Glaucanite	78	324	[52]
Saponite	35	367	[50]
Phlogopite	4	91	[53]
Vermiculite	8	162	[53]

Adapted from Farihausnah et al. [7]

4. BLEACHING OF VEGETABLE OIL USING ACTIVATED CLAYS

Clay has been used for bleaching edible vegetable oil due to its high adsorptive ability. Several studies have shown that activated clays have higher adsorptive capacity compared to that of natural clay. This can be attributed mainly to increase in specific surface and pore diameter during activation [4]. Apart from the coloured pigments, other impurities such as soap, sulphur, phosphates, trace metals and oxidation product are removed from oil by bleaching [21]. The bleaching power of clay is dependent on the surface area, surface acidity, porosity and pore size distribution [48]. The bleaching process is carried out under a vacuum with typical contact temperature in the range 80°C - 120°C and contact time ranging from 20-40 mins. The dosage of bleaching clay is variable depending on both the process and the oil type. Chemical refining uses 0.5-2% on weight basis while physical refining consumes about 0.25-2%. However, the dark oil and fats may require as much as 2-4% to meet final color requirement [17].

Salawudeen et al. [18] bleached palm oil using hydrochloric acid and sulphuric acid activated clays. Their result showed that the ability to remove colour impurities from palm oil is up to 94.28% in HCl activated clay and 89.40% in

H₂SO₄ activated. A research article by Folleto et al. [24] showed that bleaching efficiency for sunflower oil was strongly dependent on the concentration of acid used for clay activation. The authors activated natural bentonite clays with 4N and 8N of sulphuric acid and the activated clays were used to bleach sunflower oil. The bleaching capacity of the clay activated with 8N sulphuric acid was similar to that of commercial sample.

Sabha and Madjan [54], removed phosphorus from rape seed oil using acid activated sepiolite. The sepiolite was activated using HNO₃. The adsorption of phosphorus was carried out at 80°C and 100°C respectively. There was decrease in the adsorption of phosphorus with acid activated sepiolite at both temperatures which result from the fact that the adsorption site remains unsaturated during the bleaching process. The authors claimed that at low clay/oil ratios, the removal phosphorus was more efficient since most active sites were occupied by phosphorus. For higher clay/oil ratios, competition between phosphorus and other colour bodies in the adsorption process occur.

In a US patent by David et al. [6], bleaching clay was produced by aging hormite clay for 1 month and adding extremely small quantity of acid to the aged clay. The hormite clay produced was used to bleach soybean oil. The oil initially had a red value of 10, yellow value of 70, and 0.1084ppm of chlorophyll. After heating with the bleaching clay, these values dropped to less than 1ppm and as a result the oil becomes clearer. As more acid was added to the clay, the pH value of the oil dropped and the value of acidity became high. This implies that there is a limit on the amount of acid that should be used because a high residual acidity may be created which increases acid value in the oil being treated, whose presence is undesirable.

Gizela et al. [36] determined the bleaching capacity of acid activated Al-pillared by measuring the absorbance of raw sunflower oil. The result showed that there was elimination of moisture content and volatile materials but there was no significant influence on acid and peroxide values of the raw sunflower oil.

Oboh and Aworh [55], bleached palm oil using organic and inorganic acid activated Nigerian clays. They activated the clay using hydrochloric acid, sulphuric acid and acetic acid. The result showed that clays treated with hydrochloric and

sulphuric acids have high bleaching power compared to clay treated with acetic acid.

Regina [30] determined the adsorptive capacity of Udi modified clays on palm oil. The author modified Udi clay by thermal and acid activation and discovered that bleaching efficiency increased from 29.67% to 75.3% and 92.74%, for thermally and acid activated samples, respectively.

Sabah and Çelik [56], reported the use of sepiolite as an adsorbent in the bleaching of rape seed oil. The authors discovered that in addition to producing a pale color, the adsorbent was also able to reduce levels of free fatty acid, peroxide value, anisidine value, and phosphorus content in oil. Furthermore, the research also reported that the performance of the process increased along with the increase of adsorbent concentration.

James et al. [57], studied the bleaching performance of raw and activated Nigerian (Yola) montmorillonite clay on palm oil. The authors discovered that the bleaching performance of the clay was enhanced upon activation. Clay samples were activated at varying acid/clay ratio, and the best bleaching performance was obtained with clay samples activated with 5M H₂SO₄ at acid/clay ratio 0.7, bleaching temperature of 120°C and at 10 mins stirring time. The activated clay sample at this condition compared favourably with the imported industrial sample and they concluded that it could be a local substitute for the industrial standard.

5. CARBONACEOUS MATERIALS

The growing interest in the use of low cost adsorbent in vegetable oil refining has brought about the use of carbonaceous materials as alternatives to expensive commercially available bleaching earth. Carbonaceous materials can be classified into chars and activated carbon [58]. Chars are the carbonization products from wood, fruit shells, seed hulls, brown coal and highly volatile coals. Activated carbons are produced by partial gasification of chars with steam or carbondioxide or mixture of both to increase the porosity or by chemical activation. In the vegetable oil industry, carbonaceous materials are used either as a small part of readymade mixtures with bleaching clays, where the ratio of the carbon does not exceed 5–10% of the weight of the clay, or by bleaching with activated carbon prior to bleaching with the clay [59]. Iwuoha and

Agunanne [60], activated palm kernel shells by treatment with hydrochloric acid, sulphuric and phosphoric acids, and tested the bleaching efficiency of the activated carbons on palm kernel oil.

Salma et al. [58], evaluated some seed hulls as carbonated materials for bleaching of vegetable oil. The seed hulls considered were cottonseed, peanut, sunflower, faba bean and lupine. The six hulls were activated by carbonization, steam activation and acid activation. Fuller's earth and tonsil were used as reference standards for the research work. The authors bleached crude soyabean oil with the carbonaceous materials produced. Their result showed that carbonized hull yielded oils with least free fatty acid content and highest oxidative stability, acid activated hull carbon gave oils with best colour and least peroxide and phospholipids. Also, acid activation of the hulls gave the highest increase in surface area, pore volume and least pore dimension.

Similarly, Ravin et al. [61], studied the structure and performance of soybean hull carbon adsorbent as affected by pyrolysis. The structure of the soy hull carbon was studied by scanning electron microscope, x-ray diffraction and Fourier-transform infrared spectroscopy. The crude soy oil was processed with the soy hull carbon products at 2% (w/w) in the laboratory under commercial bleaching conditions. Free fatty acids (FFA), peroxide value, phospholipid phosphorus (PLP), and lutein content of the treated soy oil samples were determined. SEM of the samples revealed particle size ranging from 1 to 2 mm. FTIR spectra of the carbon samples showed major differences in peak intensities at 3600 to 3200, 1600, and 1450cm⁻¹ due to pyrolysis temperature. XRD revealed a predominantly amorphous structure with increasing pyrolysis temperature, which also resulted in an increased alkaline surface. The free fatty acid and peroxide content of the treated oil decreased compared to that of crude oil. There was no observation as regards the adsorption of PLP and lutein.

Hassanaein et al. [62] evaluated peanut hull as an alternative to bleaching clays. The peanut hulls were carbonized at different temperatures and times. Mixtures of adsorbents were formed by mixing the peanut hull with some commercially available bleaching clays (tonsil, fuller's earth and O-passive) at different ratios. Highest reduction in Peroxide value and phospholipids, and highest bleachability were

Table 2. Insight to previous research (summary)

Activating agents	Effect on final product in terms of acid value (AV) and free fatty acid (FFA)	Challenges	References
Sulphuric acid	High acid content	Washing is required Generation of waste stream Cost of acid is high Washing is required	[18]
Sulphuric acid	High acid content	Generation of waste stream Cost of acid is high Not suitable for certain types of edible oil	[64]
Aging for one month and addition of extremely small quantity of sulphuric acid	High acid content	Cost of acid is high Longer activation period Still needs to be chemically activated to bleach oil effectively	[6]
Pillaring			[8]

achieved for soybean oil bleached with 2% peanut hull carbonized at 500°C for 30 mins. Mixtures of peanut hull with the three commercial bleaching clays 1:2 indicated that peanut hull and tonsil in ratios 1:2 gave the highest bleachability.

Lin and Lin [63], studied the performance of peanut hull ashes in the bleaching of water degummed, and alkali refined soybean oil. The results indicated that the influence of time was not clear, but that 500-700°C showed potential as the best calcination temperature for preparing an effective adsorbent.

6. CONCLUSION AND RECOMMENDATIONS

This review paper have been able to present numerous research carried out on clays and carbonaceous materials modifications for use as adsorbent in vegetable oil refining. Despite the numerous research carried out, there is very little information on the development of less expensive and more environmental friendly process of activation. Acid activated adsorbent required thorough washing before being used as bleaching clay. The washing generates a waste stream which is a threat to the environment or otherwise must be disposed off in an environmentally friendly manner. Moreover, the use of acid activated adsorbent as bleaching agent increases the acid value of the oil hence; neutralization process is a compulsory step in

vegetable oil refining which add to the cost and time of production.

The aforementioned problems can be addressed if (i) the use of alkaline activated adsorbents are employed as this will eliminate washing and neutralization process during oil refining process thereby reducing cost and time of refining; (ii) activation and bleaching processes are optimized; (iii) agricultural wastes are modified on large scale for use as adsorbent in vegetable oil refining. Table 2 shows the summary of previous research carried out on clay activation for vegetable oil bleaching and the challenges faced by the methods used.

COMPETING INTERESTS

Authors declare that there are no competing interests.

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