Production Of Acid-Activated Bleaching Earth From Bentonite Clay For Edible Oil Bleaching

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Abstract.

The main aim of this study was to produce acid-activated bleaching earth from bentonite clay for edible oil bleaching, which is a clay mineral that can be used in its natural or acid-activated states to clarify and reduce the colour intensity of fats and edible oil. This study was conducted in two stages. The first involved the characterization of activated bentonite clay (moisture content and bulk density determination) and choosing an effect on acid-activated bleaching earth performance by considering the significant parameters, which are sulfuric acid concentration (1, 3, 5M), bleaching time (25, 40 and 60min) and dosage of acid-activated bleaching earth per millilitre of impure edible oil (1.5, 4.5, 6g). The raw bentonite clay acquired from Afar Bentonite Mineral Mining Plc. was activated by diluted sulfuric acid at a temperature of 90°C, neutralized, and the impure edible oil was prepared. A 3M acid concentration at a bleaching time of 40 min and 4.5 g of acid-activated bleaching earth dosage resulted in the highest percentage of colour reduction, which was 97%. In general, the findings of this study support the notion that bentonite clay is an effective adsorbent for edible oil bleaching. This study has strengthened the idea that acid-activated bentonite can eliminate pigments that are the result of different impurities, while also reducing the health impact of unqualified edible oil products.

Keywords: *Bentonite clay; Acid activation; Characterization; Bleaching and Acid activated bleaching earth.*

I. INTRODUCTION

The clay called “bentonite or montmorillonite is an old naturally occurring clay due to volcanic eruption. The main constituents of these clays are aluminium, silicon, and iron oxides. Clay has been used for different purposes, such as removing impurities on the skin, such as oils and toxins, from the body for thousands of years. Although the bentonite industry is slightly over 70 years old, the name bentonite was applied as early as 1848 by Knight to a highly plastic clay material occurring near Fort Benton(Hada & Goitomgebreyohannesmueduet, 2023).Bleaching is the final step in the conversion of crude vegetable oil or fat to an acceptable product for human consumption. During the deodorization process, the remaining impurities are either removed or reduced to a sufficiently low level for the production of acceptable flavour and functional edible oils and fats.

While oils and fats do not harbour growth bacteria and other organisms, one of the benefits of bleaching is the complete sterilization of the final product(Usman et al., 2012).The most commonly used method for bleaching fats and oils is to treat them with surface-active surfactant powdered materials. These bind (also known as “adsorb”) the pigmented substances in the oils to the extensive surface area provided by their powder form. The adsorptive capacity of sorbent minerals depends on their mineralogical structure and adsorptive properties, such as surface area, particle size distribution, porosity, and surface acidity. Modern bleaching processes use a substantial range of different bleaching agents to remove various specific impurities in addition to pigments. The agents normally used include(Helwig et al., n.d.)

Table 1. Demand for acid activation bleaching earth

Year (E.C)	Projected output of Edible oil in tone	Projected demand for AABE earth in tone.
2006	145,000	4350
2007	146,000	4380
2008	147,159	4414
2009	148,800	4464
2010	149,483	4484
2011	150,220	4506
2011	150,220	4506
2012	151,005	4530

2013	152,000	4560
2014	153,000	4590
2015	154,707	4641
2016	155,737	4672
2017	156,838	4705

Source: Ethiopian Revenue and Customs Authority

Natural clays are purified and treated with mineral acids. These acids include hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, and organic acids such as acetic, citric, oxalic, and lactic acids. Among these acids, hydrochloric acid and sulfuric acid are the most widely used in acid activation because they provide good results regarding the specific surface area, porosity, and adsorption capacity of the activated clay(Efstathiou et al., 1991).Acid activation of clay results in the leaching of cat ions from tetrahedral and octahedral sheets and replaces the exchangeable cat ions with hydrogen ions. Acid treatment of clay also opens the edges of the platelets, and as a result, the surface area and pore diameter increase (Usman et al., 2013).

II. METHODS

1.1. Raw materials and chemicals

The main raw materials used to prepare acid-activated bleaching earth (AABE) are raw bentonite clay. It is the type of clay most often found in the Afar region around volcanic eruptions. Bentonite clay rock obtained from Afar Bentonite Mineral Mining and Production Plc.

Fig 1. Uncrushed raw bentonite clay

The other materials that are required are unbleached oil or impure oil to test the acid-activated bleaching earth purification ability. Impure oil obtained from fast food sellers in Debre Berhan.The main chemicals used in this study were distilled water used for washing raw bentonite and activated bentonite, preparation and dilution of the solution, and pure H_2SO_4 (dilute) used to activate the raw bentonite clay. In addition, impure oil was used to test the acid-activated bleaching earth purification performance. Petroleum ethyl is another chemical used to measure the absorbance of impure and bleached oil.The equipment used in this study was a weight balance (Yassin et al., 2022)for weighing solid samples, which were powdered and sieved by a ball mill (Germany,55743-Oberstein,) and universal hot air oven (DHG-9055A) for drying the sample and preparing it for further milling and to obtain the required particle size. Beakers were used for holding sample chemicals, measuring cylinders were used to measure distilled water and sulfuric acid samples, volumetric flasks were used for preparing a sulfuric acid solution, conical flasks were used for performing the activation process in a water bath, stirrer was used for mixing purpose, and vacuum filter was used to separate the activated sample from sulfuric acid solution. Bleaching was performed using a rotary evaporator. Finally, a UV-visible spectrophotometer was used to identify the absorbance difference between impure and bleached oils.

1.2. Collection and preparation of the raw bentonite clay

First, the Bentonite clay rock was obtained from Afar Bentonite Mineral Mining and production Plc. Addis Ababa branch. After collection, crushing was performed using a ball mill. The crushing process was repeated many times combined with drying until the required particle size (74µm) gained. Next, sieving was performed, and the powdered raw bentonite was activated.

Fig 2. Powdered bentonite clay

Source: Current work

1.3. Characterization of Raw Bentonite

1.3.1. Moisture content determination

According to (Zheng et al., 2017) A 50 g raw bentonite sample that was weighed and stored in an oven at 105°C for an hour was used to calculate the percentage moisture content of bentonite clay before and after activation to ensure whether it was inacceptable range or not.

$$\text{moisture content} = \frac{(m_1 - m_2)}{m_1} * 100\% \text{---------- Equation (1)}$$

Where m_1 = mass of wet sample, g, and m_2 = mass of dry sample, g.

1.3.2. Bulk density determination

The mass of the empty 10-ml graduated cylinder was measured and recorded. Then, the amount of bentonite before and after activation was transferred to the graduated cylinder, and the final mass of the cylinder was weighed (MSC) and recorded. Finally, the bulk density of the raw bentonite was calculated as follows:

$$\rho_B = \frac{(m_{sc} - m_{ec})}{(v_{cyl})} \text{----------Equation (2)}$$

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

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

m_{ec} = mass of empty cylinder, g

v_{cyl}= volume of cylinder, ml

1.4. Preparation of acid-activated bleaching earth from bentonite

Raw bentonite clay from Afar Bentonite Mineral Mining and Production Plc. was crushed manually and milled using a medium ball mill to facilitate drying. Then, the crushed sample was taken into an oven at 105°C for 1hr. After that further milling was carried out and sieved, and then the particles 74 micrometres were taken (Bayram et al., 2021). Three different sulfuric acid concentrations, 1, and 3,5M dilute solutions, were prepared. Next, 50g of powdered bentonite clay was mixed with the acid water solution at different acid concentrations.The activation was performed by heating the mixture in a shaking water bath 90°Cfor 4 h. The activated samples were filtered under vacuum filtration, and the residue cake was washed with distilled water until it was free of H_2SO_4. The samples were then dried for 4 h at 80°C. Each sample differs only in acid concentration. Then, unbleached (impure) oil was heated to 90°C and acid-activated bleaching earth was added to the heated oil. The mixture is placed in a rotary evaporator in which the bleaching process occurs. Next, bleaching centrifugation was performed to separate the bleached (pure) oil from the acid-activated bleaching earth. Finally, the acid-activated bleaching earth bleaching performance was investigated by considering the concentration, time, and dosage effect using a UV-visible spectrophotometer (Yener et al., 2020).

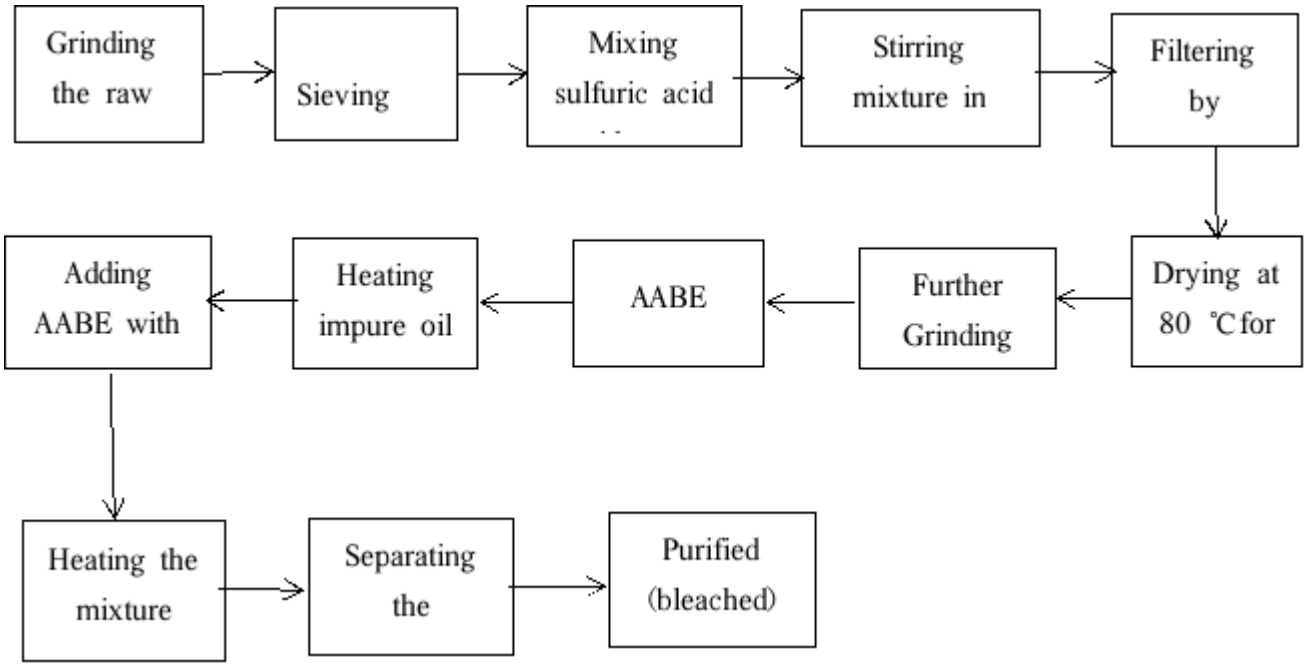

Fig 3. Block diagram for the production of AABE from bentonite clay

1.5. Experimental design and operating conditions

Three variables, acid concentration, which was used for the activation process, bleaching time, and acid-activated bleaching, were considered by keeping the temperature constant. Nine trial runs were conducted in all.

Table 2. Operating conditions

Number	Parameters	Value
1.	Activation temperature (℃)	90℃
2	Bleaching temperature (℃)	90℃
3.	Raw bentonite clay powder mass	50g
4.	Diluted acid concentrations (M)	1,3,5M
5.	Bleaching time (min)	25,40,60min
6.	Acid-activated bleaching earth dosage (g)	1.5,4.5,6g
8.	Volume of impure oil (ml)	30ml

1.5.1. Investigation of the Concentration Effect on Bleaching Performance

This study examined the colour of impure oil. In addition, a UV-visible spectrophotometer was used to assess the absorbance of oil bleached by acid-activated beaching earth at various acid concentrations (1, 3, 5M). The oil absorbance was assessed using the following method: petroleum ether was used as a reference, and 0.1g of bleached oil was diluted in 7.5 ml to estimate the sample absorbance at 445 nm. The following formula was used to determine the percentage of colour reduction(Balci, 2018).

$$\%CR = \frac{Abo - Abx}{Abo} * 100 \text{----------Equation (3)}$$

Where: - %CR = percentage color reduction, %

Abo = absorbance of impure oil

Abx = absorbance of the bleached oil

1.5.2. Investigation of the Time Effect on Bleaching Performance

In this study, the effect of bleaching time on the performance of acid-activated bleaching earth was studied by considering other factors as constant and varying the bleaching time for 25, 40, and 60 min. The absorbance of the oil before and after bleaching was determined using a UV spectrophotometer.

1.5.3. Investigation of the Dosage Effect on Bleaching Performance

In this study, the dosage effect of acid-activated bleaching earth on bleaching performance was studied using 1.5, 4.5, and 6 g impure oil. The absorbance of oil before and after bleaching was determined using a UV-Visible spectrophotometer.

1.5.4. Percentage colour reduction

The percentage colour reduction of the oil before and after bleaching was determined using equation 3.2 after measuring the absorbance oil using a UV-Visible spectrophotometer. The maximum absorbance of the samples was observed at a maximum wavelength of 450 nm using distilled water as a reference. The samples were diluted in n-hexane in the proportion of 0.1 g of oil to 2 ml of solvent. The bleaching performance of the acid-activated bleaching earth was determined in terms of percentage colour reduction.

III. RESULTS AND DISCUSSION

Before and after drying, the moisture content of the acid-activated bleaching earth was measured; this was followed by a determination of the amount of free moisture still present.

Table 3. Moisture content determination

Sample	1	2	3
Mass of raw bentonite clay	50g	50g	50g
H_2SO_4 Concentration	1M	3M	5M
Mass of AABE before drying(g)	52	53	58
Mass of AABE after drying (g)	47.5	47	46
Moisture content(g)	4.5	6	12
Moisture content (%)	8.65	11.3	20

The moisture content for the clay lies within 8–18% recommended by Wiedermann (1981) as being appropriate to ensure that the clay structure does not buckle and lose its adsorptive capacity. From the results obtained in this study, the optimum moisture content was obtained from 3M sulfuric acid concentration, which was used for the activation process. The 1M acid concentration gave less moisture content in acid-activated bleaching earth, which is an indicator of an ineffective activation process. On the other hand, from a 5M acid concentration, 20% moisture content was obtained(Usman et al., 2012). This shows that as the acid concentration increases, the strength of acid attack on bentonite clay increases and forms more surface area and porosity, which allows the bentonite clay to better hold water molecules in its structure.

Increasing the moisture retention property until the optimum is an indicator of the presence of acid activation of bentonite clay.

Table 4. Bulk density determination

Sample	1	2	3
Mass of raw bentonite clay	50g	50g	50g
H_2SO_4 Concentration	1M	3M	5M
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Moisture content(g)	4.5	6	12
Moisture content (%)	8.65	11.3	20

1.6. Parameters affecting bleaching performance

Many types of parameters affect the bleaching performance when impure oil is treated. The most important factors are temperature, acid type and concentration, bleaching time, and the dosage of acid-activated bleaching earth, which is the ratio of acid-activated bleaching earth to impure oil.

Fig 4. Impure and bleached edible oil

1.7. Effect of acid concentration

The effect of acid concentration on the bleaching of impure oil was studied at 90℃ with an acid-activated bleaching earth dosage of 4.5g in 30 ml of unbleached (impure) oil for 40 min. The effect of acid concentration, which was used for the activation process of bentonite clay, on the bleaching performance is shown in the absorbance of oil before and after bleaching.

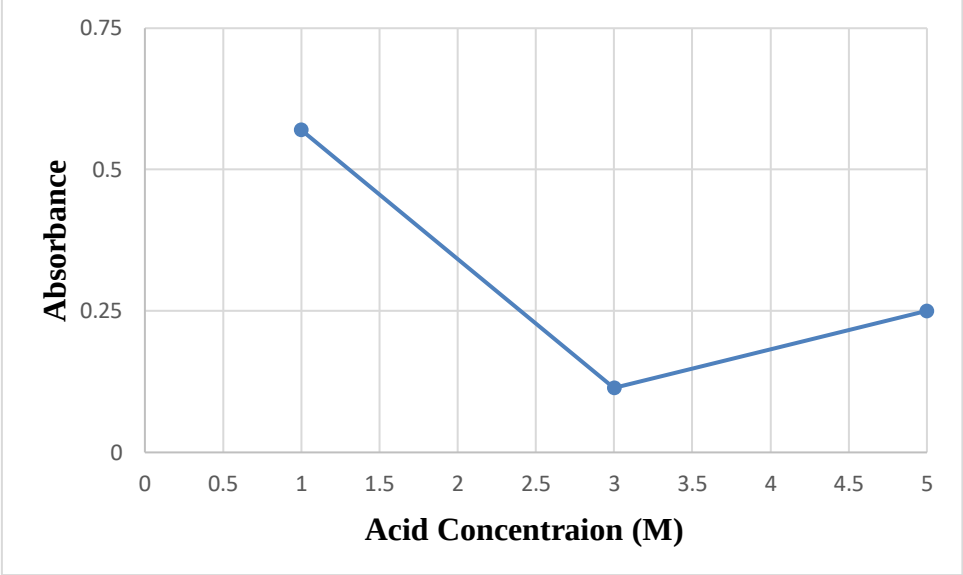

Fig 5. Concentration vs. Absorbance graph

As shown in the above graph, the absorbance of oil first decreases as the acid concentration increases, indicating the existence of a lower contaminant level in the oil. However, when the acid concentration used for the activation process increased further, the absorbance of bleached oil measured did not show a greater difference from the absorbance of unbleached oil. this is because greater acid concentration applies more acid power that results in undesirable porosity in the clay structure and high moisture content also the bentonite clay became hydrated and swelled, causing them to be negatively charged and repel rather than attracting impurities (Alamery & Ahmed, 2021)

The minimum absorbance (0.114) gained at 3M acid concentration is consistent with the Lambert-Beers law, in which the absorbance range of edible oils is between (0.05-0.8).

1.8. Effect of bleaching time

The effect of bleaching time was investigated by considering other things constant and by taking the same sample such as 30 ml oil with 4.5g acid-activated bleaching earth gained from 3M concentration of sulfuric acid activation. Three samples were taken at bleaching times of 25, 40, and 60 min, and the results are shown below.

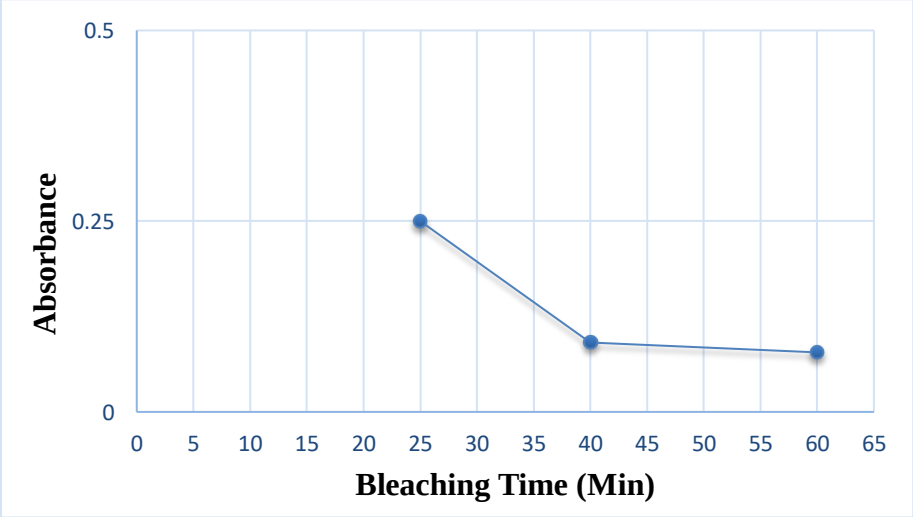

Fig 6. Bleaching time versus absorbance graph

As the time went from 25 to 40 min, the absorbance of the bleached oil was reduced. Due to the sufficient contact time of acid-activated bleaching earth with impure oil. However, further increasing the time of bleaching gave very close absorbance values. The minimum absorbance (0.091) gained at the 40-min bleaching time is consistent with the Lambert-Beers law, in which the absorbance range of edible oils is between (0.05-0.8).

1.9. Effect of acid-activated bleaching earth dosage

The effect of acid-activated bleaching earth on bleaching efficiency by considering other factors constant and varying dosage of acid-activated bleaching earth form 1.5, 4.5, 6g per 30 ml of impure oil(Hada & Goitomgebreyohannesmueduet, 2023).As shown in the graph below, the absorbance of oil reduced when the dosage of acid-activated bleaching earth was increased from 1.5g to 4.5g per 30 ml of impure oil. However, the absorbance of bleached oil was stopped from further reduction as the dosage of acid-activated bleaching earth per 30 ml of impure oil increased by more than 4.5g. This is because the excessive amount of acid-activated bleaching earth causes difficulty in separation.

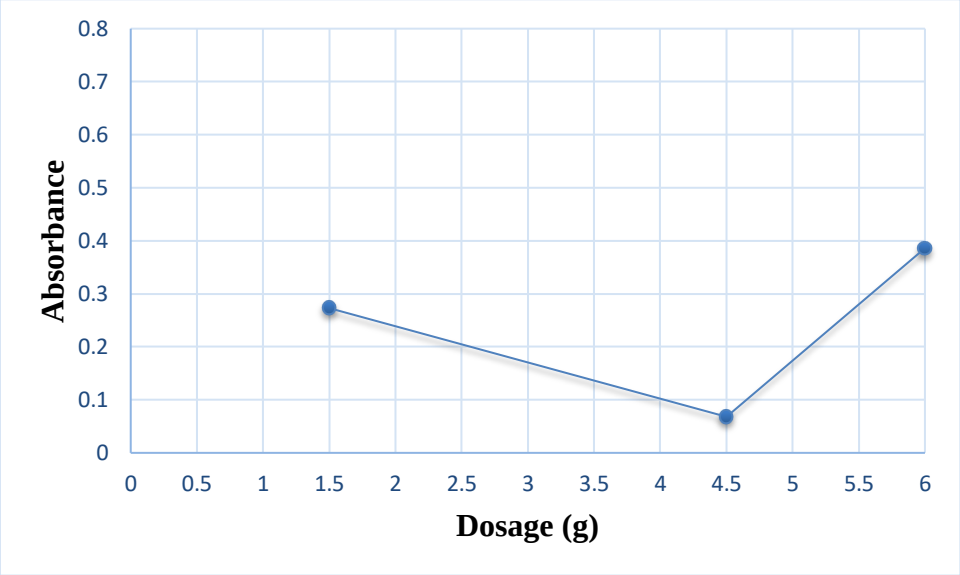

Fig 7. Dosage vs. Absorbance graph

1.10. Percentage colour reduction

1.10.1. Percentage of colour reduction at different acid concentrations

The percentage colour reduction of the oil after bleaching was determined using a UV-visible spectrophotometer at different acid concentrations used for the activation process. The maximum absorbance of the samples was observed at a maximum wavelength of 450 nm using distilled water as a reference.

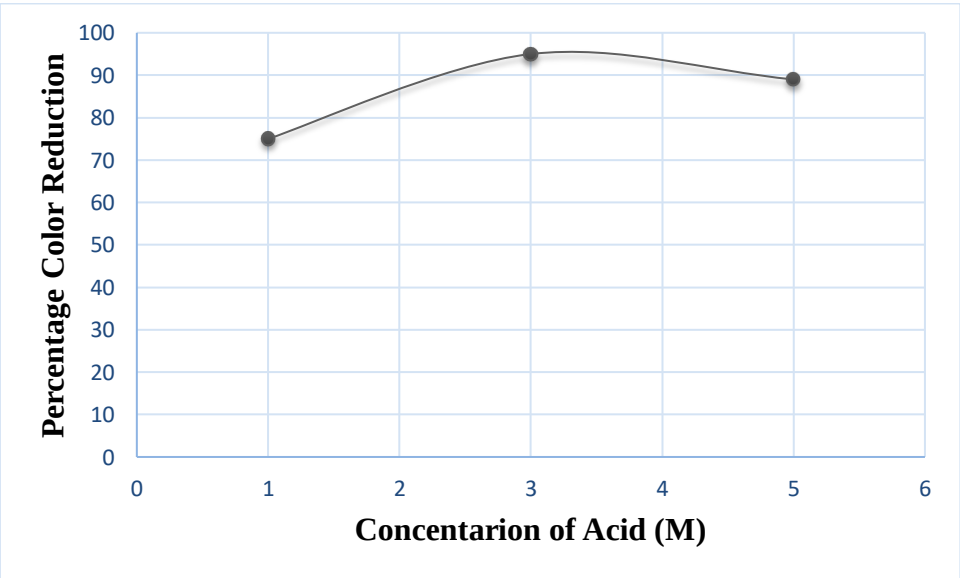

Fig 8. Effect of acid concentration on percentage colour reduction

With an increase in acid concentration from 1M to 3M sulfuric acid, the percentage colour reduction first increased. Above this concentration, it decreased. These findings show that at a concentration of 3M acid, the highest percentage of colour reduction of 95% was achieved. The bleaching efficiency of AABE generally increases with acid concentration because acid treatment increases the area and porosity of the bentonite clay. When the acid concentration in the solution increases cat ion exchange by exchanging calcium and magnesium ions in the interlayer space with hydrogen ions, the acid causes structural opening and creates a more active site for the adsorption of impurities. The initial increase in bleaching performance with increasing sulfuric acid concentration was due to the formation of active sites on the bentonite surface, but further increasing the acid concentration led to the collapse of the clay, which resulted in low bleaching performance.Industrial studies indicate that the maximum percentage colour reduction of acid-activated bleaching earth for the bleaching of edible oils ranges from 80-98%. In this study, accepted results were obtained at 3 and 5M acid concentrations, which are 95 % and 89% colour reduction, respectively. This is consistent (Usman et al., 2012) with the effect of acid concentration on the percentage colour reduction of sunflower oil using activated bentonite.

1.10.2. Percentage colour reduction at different bleaching times

Bleaching time was directly related to bleaching performance. As the time of bleaching increased, the percentage of colour reduction increased to 96.57%. A longer activation time provides more opportunity for acid-activated bleaching earth to adsorb the impurities. Meanwhile, the percentage colour reduction observed at bleaching times of 40 and 60 min was not significantly different because the adsorption sites in acid-activated bleaching earth became saturated to absorb colours and impurities.

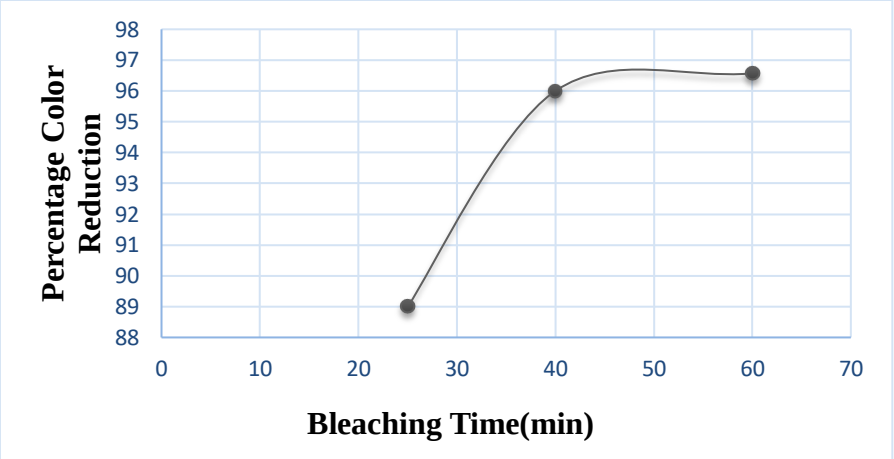

Fig 9. Effect of bleaching time on percentage colour reduction

1.10.3. Percentage colour reduction at different AABE Dosage

The acid-activated bleaching earth dosage was varied from 1.5 to 6g AABE in 30 ml of oil. It was observed that increasing the clay dosage increased the percentage of colour reduction.

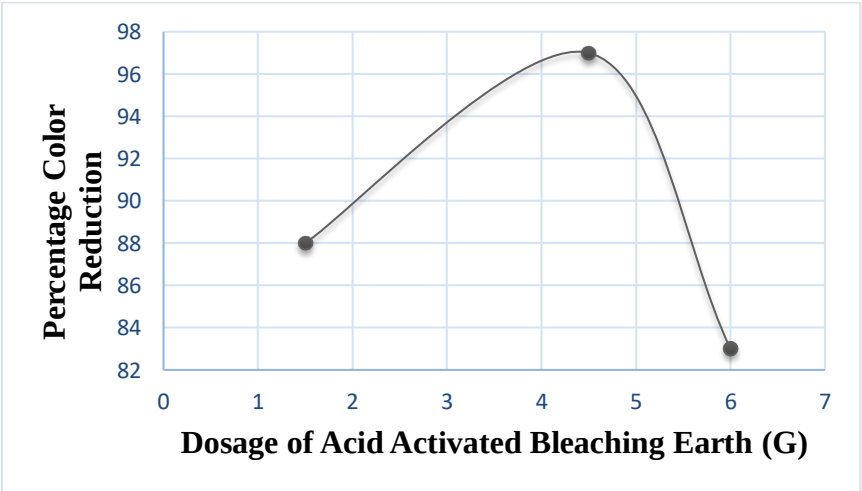

Fig 10. Effect of AABE dosage on percentage colour reduction

Acid-activated bleaching earth, which was used as an adsorbent to remove impurities from oil, showed that its percentage colour reduction increased with the dosage of acid-activated bleaching earth because of the availability of more surface area of the adsorbent. In addition, a very high dosage of AABE per volume of oil made the centrifugation process difficult. The percentage colour reduction increased to a maximum of 97% with increasing clay dosage at 4.5g. This can be attributed to the increase in active sites available for adsorption. This is consistent with (Helwig et al., n.d.) which stated that increasing AABE dosage enhances the removal of impurities in edible oil. In contrast, when the amount of acid-activated bleaching earth increased significantly, the amount of purified oil decreased because the amount of sludge increased. In addition, it was observed that by increasing the dosage of AABE by more than 4.5g per 30 ml, the percentage colour reduction was reduced because of the formation of a gel-like structure in the oil. Therefore, to obtain the appropriate amount of purified oil, the optimum amount of acid-activated bleaching earth per volume of impure oil should be used. Generally, all percentage colour reduction results were within the standard, and the produced acid-activated bleaching earth was effective for the bleaching of impure edible oil at 3M acid concentration, 40 min bleaching time, and 4.5g dosage.

IV. CONCLUSION

This research presents a study on the production of acid-activated bleaching earth (AABE) from bentonite clay for edible oil bleaching. This study involved characterization, activation, and bleaching experiments using different parameters such as acid concentration, bleaching time, and AABE dosage. The study finds that the optimal conditions for producing AABE are 3M sulfuric acid concentration, 40 min bleaching time, and 4.5g AABE per 30 ml of impure oil. These conditions result in a 97% colour reduction of the oil.In addition, this study proposes and designs a plant for producing AABE from bentonite clay, based on the projected demand and economic evaluation. The plant has a high rate of return and a short payback period. The study concludes that bentonite clay is an effective adsorbent for edible oil bleaching and that acid activation enhances its performance. The study also suggests that AABE can reduce the health impact of unqualified edible oil products.

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