

Bleaching Potentials of Local, Foreign and Regenerated Bleaching Earth: Comparative Study

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Received: 27 November 2022/Accepted 28 December 2022/Published online: 30 December 2022

Abstract: *The deposition of spent earth causes environmental pollution, which affects the quality of life. In this work, the bleaching of vegetable oil was carried out using three different bentonite samples (foreign, local and regenerated bentonites), at varying temperatures. The optimum bleaching temperature was 90 °C with 90 %, 60 % and 63 % colour removal for 2 %(w/w) foreign, local and regenerated bleaching earth respectively. Therefore, local and regenerated bleaching earth that competes fairly well with foreign bentonite, has the potential to reduce environmental pollution from huge importation by industries. Most importantly, it is anticipated that the regeneration of spent bleaching clay in the edible oil refining industries would greatly contribute to reducing environmental pollution problems and saving costs.*

Keywords: *Regeneration, edible oil, spent bleaching earth, local bleaching and fresh bleaching earth*

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1.0 Introduction

Vegetable oils in their crude forms are deeply coloured. These coloured 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 and carotenoid (Al-Zahrani, and Alhamed, 1995). Other impurities are phosphatides, trace metals, traces of soap, peroxides and free fatty acids (Al-Zahrani and Alhamed, 1996). It is desirable to remove colour impurities from oil not only before use but also after use, thereby enabling the reusing or recycling of the oil. Processes involved in vegetable oil refining include; degumming, neutralization, bleaching, filtration, and deodorization. These processes are aimed at converting crude oil to more suitable oil for subsequent use. Degumming is the removal of phosphatides and mucilaginous material from crude oil by washing with hot water, dilute acid or sometimes dilute sodium hydroxide. The neutralization process involves the use of alkaline to produce soap is done to remove colour impurities and finally, deodorization is designed to produce oil of good flavour and shelf life.

Bleaching is the most important among the five stages of refining because it determines the appearance, flavour, taste and stability of the final product. This is achieved by using a surface-active solid to absorb the following matters. In the process of refining vegetable oil, bleaching clays have been used extensively as an adsorbent in vegetable oil refining (Alhamed and Al-Zahrani, 1998). The growing interest in using low-cost adsorbents in vegetable oil bleaching has brought about the use of carbonaceous materials as an alternative. In the vegetable oil industry, the use of clay and its minerals as an adsorbent in vegetable oil refining has been adopted on an industrial scale (Alhamed Y. A. and al-Zahrani, 2002). Natural clay

such as fuller's earth and clay can remove colour impurities from both edible and non-edible (Coulson and Richardson, 2002). The unique properties of bentonite clay materials make them valuable in so many important industrial applications. These properties include swelling and adsorption. Application areas include edible oils, fats, soaps, cosmetics, pharmaceuticals, catalysts, paints etc. In Nigeria, bentonite deposit has been found in different parts of the country especially the North Eastern part at an estimated reserve of about 700 million tons (Foletto *et al.*, 2002). This large bentonite reserve awaits commercial exploration for its various uses. The regenerated bleaching earth (RBE) contains up to 30% (w/w) of residual oil that rapidly oxidizes to the point of spontaneous auto ignition, and also produces unpleasant odours. The constant change in environmental legislation in the growing importance of safety in disposal techniques has led to many restrictions in solid waste management. To minimize the risk of pollution, many studies are devoted to the conversion of these wastes and their reuse in various applications. Regenerated spent bleaching earth has, notably, been used as a sorbent to remove pigments from oils. By recovering the oil, the cost of disposal will be reduced effectively and the recovered oil may be reused (Kheang *et al.*, 2006). Hence, the need to evaluate the bleaching performance of foreign bentonite clay (FBC), local bentonite clay (LBC) and regenerated bentonite clay (RBC).



Plate 1: Soybean

2.0 Materials and Method



The experimental procedure consists of three consecutive steps— extraction of oil from spent bleaching clay samples using n-Hexane, followed by calcination of the samples, and finally a bleaching test using these samples. Samples of foreign and spent (used) bleaching earth were collected in the refinery plant from Sunseed Nigeria Limited, while the local bentonite was collected at the chemical engineering department ABU Zaria while the spent (used) bleaching earth was regenerated in the chemistry laboratory, Federal University Dutsin-ma.

2.1 Extraction of oil from spent bleaching earth

Sample spent clay was extracted using n-hexane, to recover the oil. The clay sample was added to the solvent in the proportion of 10/100 (g/ml) and the mixture was stirred mechanically for 10 mins in a glass vessel at room temperature. Upon completion of the extraction step, the extracted oil and solvent were separated using a Soxhlet apparatus.

After the calculations (controlled burning) has taken place, about 0.25 g of the sample was lost. which the direct regeneration (without oil removal) of spent bleaching earth by calcination was carried out at temperatures ranging from 400 to 700 °C at a constant time of 1hr. The required number of crucibles each containing 10 g of the spent earth were placed in a furnace which has been heated previously to the desired temperature (100 °C). The crucible was then removed from the furnace at predetermined temperature intervals. The samples were allowed to cool down to room temperature in desiccators to be used later for the bleaching test.

2.2. Procedures for bleaching of edible oil

The bleaching attempts were performed in a beaker with a hot plate magnetic stirrer and a contact thermometer (used to regulate the temperature). 200 ml of the sample oil was heated under continuous stirring at 60 °C, for 30 mins. 2 g of foreign bentonite clay was added to the heated oil sample with continuous stirring. The contact time between oil and bleaching earth was within 30 mins to

avoid undesired side reactions. After oil treatment, the bleaching earth was removed by filtration using the Buchner funnel. An ultraviolet spectrophotometer was used to analyze the colour scale of the sample oil. Finally, the oil/clay slurry was transferred to a filtering flask equipped with double-layer filter paper. The procedure is repeated for 2 g at varying temperatures of 30, 60, 90, 120, 150, and 180 °C at a time interval of 30-150 mins.

1g of the refined oil was weighed using a weighing balance and transferred into a conical flask. 50ml each of neutral alcohol and chloroform was measured using a measuring cylinder and added to the oil in the

flask. The content of the flask was shaken well to dissolve the free fatty acids. This was immediately titrated with standard potassium hydroxide using phenolphthalein as an indicator. The end of the point was the appearance of a pale pink colour. The corresponding value gives the free fatty acid value.

UV spectroscopy was carried out on the crude soybean oil to test for colour removal. This was done using cyclohexane as blank between the wavelength of 400-500 nm where the peak (maximum wavelength) was determined at 450nm, and the absorbance at that point was found to be 3.800.

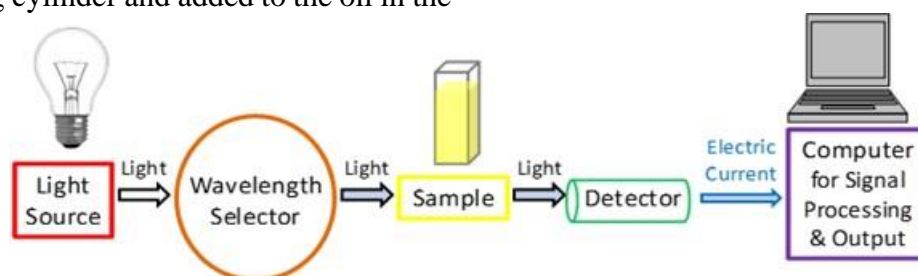


Fig. 1: Measuring Absorbance

3.0 Results and Discussion

A graph showing the percentage of colour removed (bleached) against time is plotted for local bleaching earth (LBE), regenerated

bleaching earth (RBE) and foreign bleaching earth (FBE). Detailed calculations and tables are shown in the appendix

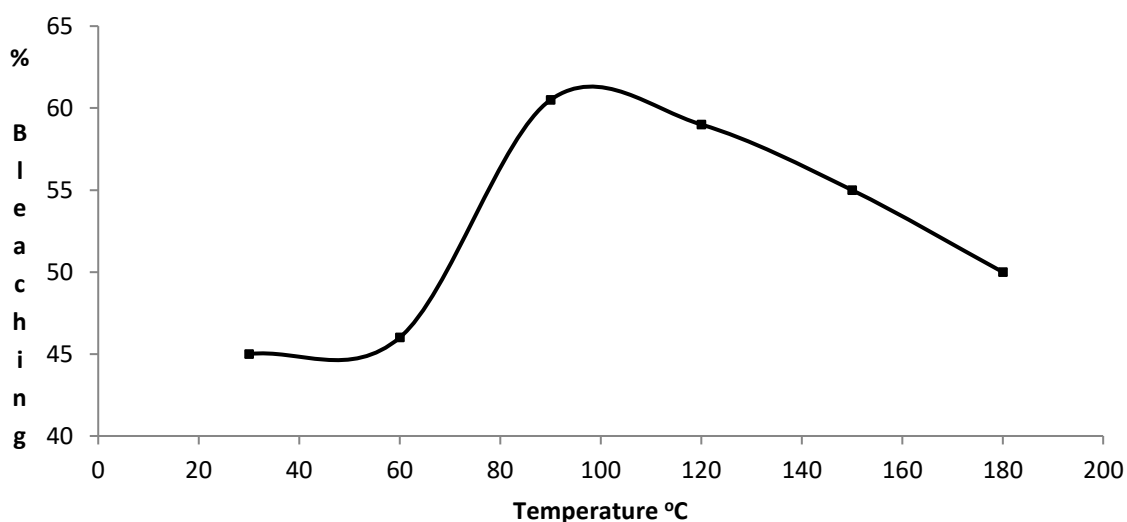


Fig. 4 : Bleaching performance of local bleaching earth



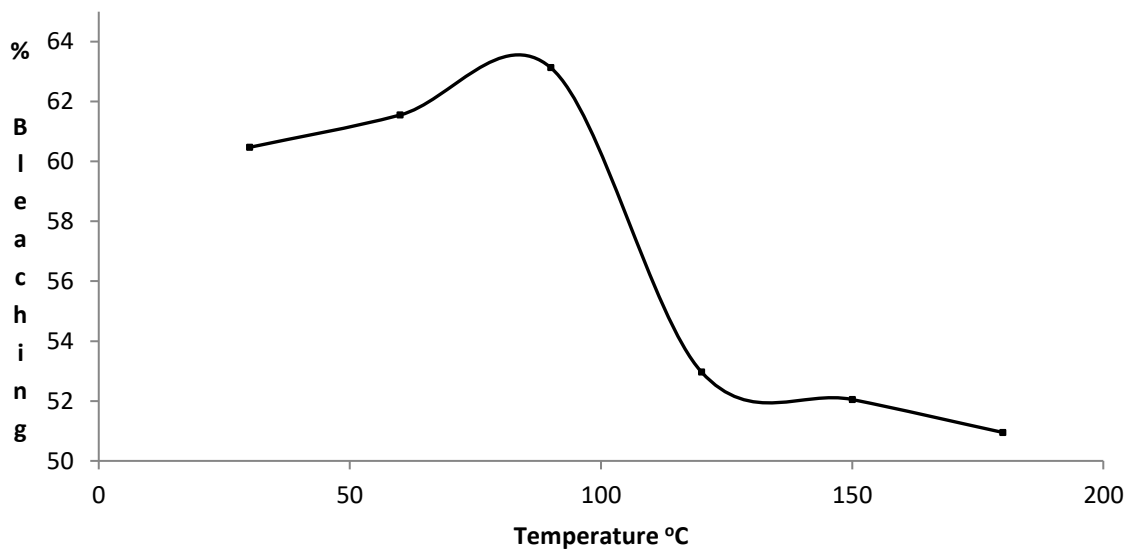


Fig. 5: Bleaching performance of regenerated bleaching earth

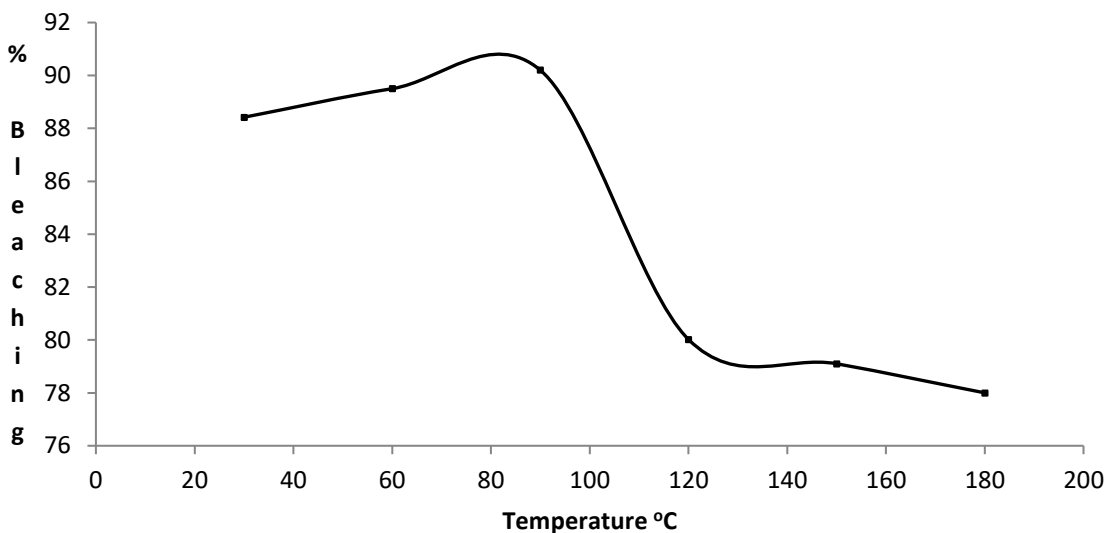


Fig. 6: Bleaching performance of fresh bleaching earth

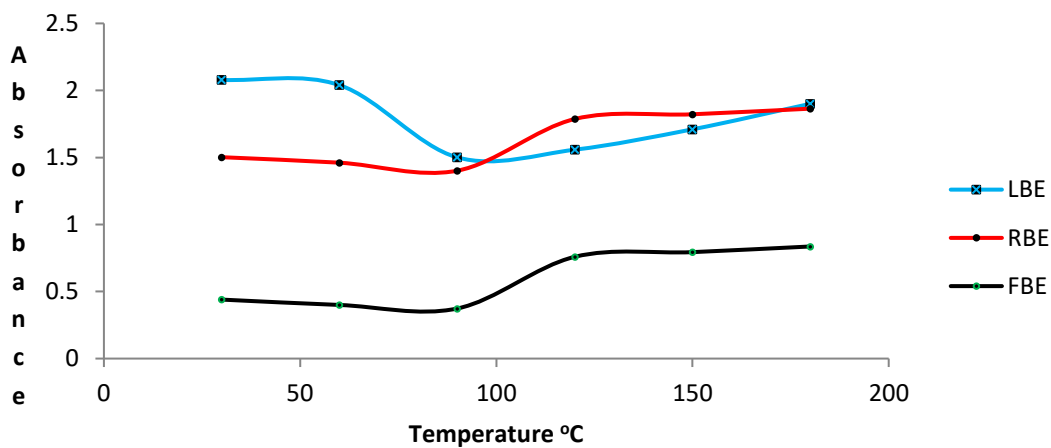


Fig. 7 : Absorbance for fresh, local and regenerated bleaching earth



Table 1 below shows the results of the corresponding tests run – free fatty acid and moisture tests.

Table 1: Moisture and free fatty acid tests

TESTS	LBE	RBE	FBE
Free Fatty Acid	0.33	0.23	0.18
Moisture Test	0.36	0.44	0.24

Carotenoids (mainly B-carotene) have been identified as the pigments in edible oils. They are soluble in non-polar solvents such as cyclohexane and have common absorption peaks at 444 – 448 nm, which obeys Beer-Lambert law. Bleaching in this context is equivalent to the removal of colour pigments. Hence, the bleaching performance was evaluated in terms of the percentage of carotenoids removed from the oil sample after bleaching (Lim *et al.*, 2006).

The experiment was conducted to determine the optimum bleaching performance of local bleaching earth, regenerated bleaching earth and fresh bleaching earth and their absorbance. The results obtained from the spectrophotometer (UV) analysis (absorbance) were used to determine the bleaching capacity of the local, regenerated and fresh bleaching clay. Moreover, from the UV analysis of unbleached soybean oil 3.800 was determined as the peak from the UV wavelengths of 450 nm and 3.800 was used as the reference absorbance for the unbleached soybeans oil and which agrees with the work reported by (Makhoukhi *et al.*, 2009). Tables 2 – 4 show results obtained from the calculations done for the determination of percentage bleaching for 2 (w/w)% using the absorbance obtained from the UV analysis. From the results, the percentages of bleaching were plotted against the temperature.

From the result obtained, there was an increase in bleaching capacity within the temperature range of 30-90 °C. It could be deduced that the optimum bleaching temperature to achieve maximum bleaching capacity is at 90 °C, which agrees with the

literature report by (Nursulhatimarsyila *et al.*, 2010). Beyond 90 °C, there was a general decrease in the bleaching capacity for the three bleaching earth samples. A

A sharp increase in bleaching capacity was noticed for local bleaching earth (LBE) used. From Fig. 4, it is evident that at varying temperatures, it was observed that an increase in temperature increases the percentage of oil bleached, suggestive of the fact that clay is more active within the range, and within this range, the oil has not reached its fire point (Oyem II and Henry, 2011). For the regenerated clay, the spent earth was calcined at various temperatures between 400-700 °C. Fig.5 shows an increase in bleaching capacity to the optimum temperature. The result shows that the calculation of the regenerated clay at optimum conditions can restore the bleaching power of the clay close to its fresh state (Wambu *et al.*, 2009), which is of acceptable quality. Fig. 6 showed the bleaching capacity of the fresh bleaching earth (industrial bleaching earth) which was achieved at the optimum temperature, it increases as temperature increases to the optimum temperature, 90 °C. Then a subsequent decrease as temperature increases due to evaporation as a result of an increase in the kinetic energy of oil (Zhanshenge *et al.*, 2006). The optimum bleaching percentage of the local, regenerated and fresh bentonite clay was observed to be 60 %, 63 % and 90 % respectively.

Alhamed and Al-Zahrani (2002) reported on the effect of both temperature and time of calcination on the percentage bleaching of the regenerated clay used in the bleaching of edible oil. At temperatures less than 90 °C, percentage bleaching initially increases with bleaching time then reaches a constant value for calcination time above 90 mins for temperatures above 120 °C. Percentage bleaching passes through a maximum at 90 °C then starts to fall gradually with increasing burning time. Fig. 7 shows that the value of absorbance decreases with an increase in temperature, reaches a maximum at a temperature of 90 °C, and then begins to decrease gradually. An increase in



temperature destroys the carotenoid (the precursor of vitamin A, which confers the oxidative property of oil) and chlorophyll (which makes the oil opaque and dark in colour), in turn, increases the absorbance (Yuanfa *et al.*, 2008).

Using the relationship;

$$BC \% = \frac{A_{\lambda}^o - A_{\lambda}}{A_{\lambda}^o} \times 100 \quad (1)$$

Where BC is the bleaching performance, A_{λ}^o is the optical density of neutralized oil at wavelength λ , and A_{λ} is the optical density of bleached oil at wavelength λ ,

For 2 g (w/w)% of bleaching earth used, the absorbance at 450 nm was found to be 3.800 from ultraviolet (UV) spectroscopy.

Table 2: Bleaching performance of local bleaching earth (LBE)

S/N	Temperature (°C)	Mass of Clay (g)	Absorbance	% Bleach
1.	30	2	2.079	45.00
2.	60	2	2.040	46.00
3.	90	2	1.501	60.50
4.	120	2	1.558	59.00
5.	150	2	1.710	55.00
6.	180	2	1.900	50.00

Table 3 : Bleaching performance of regenerated bleaching Earth

S/N	Temperature (°C)	Mass of Clay (g)	Absorbance	% Bleach
1.	30	2	1.502	60.47
2.	60	2	1.461	61.55
3.	90	2	1.401	63.13
4.	120	2	1.787	52.97
5.	150	2	1.822	52.05
6.	180	2	1.864	50.95

Table 4: Bleaching performance of fresh bleaching earth

S/N	Temperature (°C)	Mass of Clay (g)	Absorbance	% Bleach
1.	30	2.00	0.440	88.42
2.	60	2.00	0.400	89.50
3.	90	2.00	0.373	90.20
4.	120	2.00	0.759	80.02
5.	150	2.00	0.794	79.10
6.	180	2.00	0.836	78.00

4.0 Conclusion

In a nutshell, the comparative study of bentonites in the bleaching of vegetable oil shows that spent bleaching earth, a pollutant industrial waste can be regenerated and reused as a low-cost mineral adsorbent. By direct calcinations, it was possible to restore most of the clay activity for regenerated clay;

also the performance in terms of colour removal of local indigenous bentonite clay was studied with the fresh industrial bentonite clay used as standard. The absorbance of unbleached soybean oil was found to be 3.800 at a wavelength of 450 nm.

The optimum bleaching temperature to achieve maximum bleaching capacity for the three samples was found to be between 90 °C



with a bleaching performance of 90 %, 60 % and 63 % for fresh bleaching earth (FBE), local bleaching earth (LBE) and regenerated bleaching earth (RBE) respectively. Thus, percentage bleaching is directly proportional to the amount of adsorbent used at an optimum temperature.

Local and regenerated bleaching earth can be improved by activation with acid for higher bleaching performance. Also, further refining processes should be carried out to check for their effectiveness and improved refined oil good for consumption.

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Consent for publication

Not Applicable

Availability of data and materials



The publisher has the right to make the data public

Competing interests

The authors declared no conflict of interest.

Funding

There is no source of external funding

Authors' contributions

SAA designed the work. LE and AST did the experiment and the development of the manuscript under the supervision of SAA.

