

Bleaching of crude marula oil using activated bentonite and activated marula shells: A comparative analysis

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ABSTRACT


Refining of edible and cosmetic oil consists of various steps which include bleaching process. Bleaching is an important step as it removes colour pigments resulting in improvement of taste of oil and appearance. In this work, activated bentonite and activated marula shells were used to refine crude marula oil. Fresh bentonite was activated using H₂SO₄ whilst marula shells were activated using both H₂SO₄ and KOH. Vacuum bleaching of crude marula oil was performed using both the activated bentonite and activated marula shells. Fresh, activated, spent bentonites and marula shells were analysed using X-ray Diffraction (XRD), Fourier transform infrared (FTIR), X-ray Florescence (XRF), Thermal gravimetric analysis (TGA) for phase identification, elemental composition of crystalline material, functional groups present and thermal decomposition of the materials. Analysis of β-carotene and chlorophyll was done using UV–visible spectrophotometer on bleached and crude marula oils. Acid values (AV) and free fatty acids (FFA) values in the oil were calculated using standard procedures. The effects of acid activation parameters were investigated namely, acid concentration and activation time. Acid and alkali activation improved the adsorption properties of fresh bentonite and fresh marula to remove colour pigments. Increase in acid concentration and activation time resulted in increase in bleaching capacity of adsorbent. Optimum acid concentrations for activation were 2 N and 15 N for bentonite and marula shells respectively and optimum activation times were 7 and 1.5 h for bentonite and marula shells respectively. The study indicated that activated bentonite and activated marula shells are effective and were successful in improving the appearance of crude marula oil to the required quality standards. Marula shells are a by-product waste in cosmetic oil processing and its use assists in waste utilization in-line with circular economy principles.

Keywords: Activated bentonite, Activated marula shells, Bleaching, Marula oil.

OPEN ACCESS

Received: February 7, 2022
Revised: September 26, 2022
Accepted: November 21, 2022

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Publisher:
[Chaoyang University of Technology](https://www.chaoyang.edu.cn/)
 ISSN: 1727-2394 (Print)
 ISSN: 1727-7841 (Online)

1. INTRODUCTION

It is very important to have a quality oil with the appropriate colour so that it attracts customers. Coloured compounds in some oils are not favoured by the customers and should be bleached. The colour of oil is mostly as a result of α and β-carotene which can be removed through adsorption using activated bentonite and this is termed bleaching. Bleaching involves mixing oil with clay under specific conditions to eliminate colour components and other impurities. It is usually carried out under vacuum at contact temperatures (90–100°C) and contact time (20–30 min) where bleaching earth used depends on oil type and oil quality with about 1% of bleaching material being commonly used during refining of the oil Erten et al (2004). This process involves decomposition of colouring organic pigments, ion exchange, physical adsorption, chemical adsorption

on the bleaching earth with the power to remove impurities of an acid-activated bentonite commonly measured on adsorption capacities of chlorophyll and the β -carotene. Bleaching increases the shelf life of the oil by removing gums, soaps, odour and metal components, and its success is linked to crude oil quality to be refined and bentonite composition Didi et al (2009). It addresses aspects during oil refining which include colour pigments removal, trace metals, phosphatides, odour, remaining soap that are important to oil quality, and materials with good adsorption strength remove colouring pigments from crude oil Kaynak et al (2004). Vacuum bleaching is carried out to minimize oxidation and for better stability Tai et al (2007).

During commercial bleaching, the oil is first neutralised before bleaching then it is mixed in a bleaching tank with the adsorbent to form a slurry. The slurry is transferred to the bleaching filter tank where steam is applied followed by filtration process to separate the oil from the bleaching agent Deniz (2020). Bleaching process is done before the final process of refining called deodorization Shin et al (2020).

1.1 Bentonite

Bentonite is an abundant, clay-based mineral which is mainly composed of the smectite clay mineral montmorillonite Gates et al (2009). The structure is made up of two tetrahedral silicon ions sheets surrounding an octahedral co-ordinated aluminum ion sheet Eren et al (2009). Bentonite belong to the smectite group which is a 2:1 silicate layer with slight negative charge attributed to ionic substitutions in the octahedral and tetrahedral sheets because of replacement of trivalent aluminium ions with Mg^{2+} and Fe^{+} and they shrink upon drying and swell upon wetting. Bentonites exhibit high surface area, good adsorptive properties and can absorb water in the interlayer site Christidis et al (1997).

In oil refining, Tonsil (acid activated bentonite) adsorbs impurities in crude oil during bleaching process such as fatty acids, gums, phosphatides, and trace metals. Several methods have been carefully reported to activate bentonites. These include photonic, electric and biological processes Zhou (2011), activation by acid Steudel et al (2009), thermal activation Toor et al (2012), interparticle polymerization by polymer addition Betega et al (2008), chemical grafting of organic compounds Liu (2007). Among the methods, thermal treatment and acid activation processes are widely used to improve the adsorptive properties of the clay owing to their simplicity and low-cost. In acid activation, inorganic acids such as H_2SO_4 and HNO_3 are usually used to treat bentonite to improve its adsorptive capacity by removing some impurities. In addition, the adsorptive performance of the clay mainly depends on the activation procedures.

Activated bentonite has been useful in producing sulphur, conservation of water, for protection of the environment, adsorption in the paper industry as well as in the chemical industry. Applications of acid-activated bentonite powders include carbonless copy paper preparations, as catalysts, adsorbents, electrodes, bleaching earth, pillared clay,

nanocomposites and organoclay. Moreover, activated bentonite can also be used to remove oil coloured pigments, metal oxides from edible and cosmetic oils. To get maximum bleaching performance, there is need to control preparation of acid-activated bentonite.

1.2 Marula Shells

Marula tree is part of mango trees with a fruit that contains a hard shell with 2–4 seeds and the tree grows mostly in Southern African countries Moyo et al (2015). The valuable oil extracted from the seeds can be used as cooking oil (Mamvura et al., 2018; Edokpayi et al., 2019) and it is used in cosmetics as well. Marula fruit is juicy and may be eaten fresh. Marula shells are disposed as agricultural waste after use of marula seed and fruit resulting in environmental pollution. Marula products can be used for many applications Francis et al (2016) and marula shells are not measured as valuable because of less available processes to convert them to products that are useful Molelekoa et al (2018).

1.3 Adsorption in Oils

Biosorption has gained more research interests because it is renewable and cheap and marula shells have gained interest in reducing quantity of Pb (II) and Cu (II) Moyo et al (2015), methylene blue in aqueous solution (Mathew et al., 2017; Edokpayi et al., 2019), adsorption of methyl orange and zinc Lotfy et al (2012), removal of parasites Misihairabgwi et al (2014). Marula shells can be acid activated resulting in increase in acidic functional groups. These shells can also be alkali activated resulting in expansion of the carbon lattice which then improves porosity and increase in surface area due to metallic potassium (K) intercalation as well as enhancing uptake of organics Foo et al (2010). Previous studies reported the use of activated groundnut hulls, snail shells and rice husks in bleaching crude palm oil Ojewumi et al (2021), activated carbon in refining sunflower oil Guliyev et al (2018), activated carbon in refining carp oil Monte et al (2015), activated carbon in removing glycidyl ester from palm oil Restiawaty et al (2021), use of activated carbon from African teak wood and coconut shell in bleaching palm oil Onwumelu (2021). In literature, there is no report on the use of marula shells for bleaching of crude marula oil. This work is an extensive study with the objective to determine activation effects on marula shells and bentonite and to remove colour pigments in crude marula oil using activated marula shells and activated bentonite with potential developments in the cosmetics and food industry. Thus, it is best to understand the behaviour of the adsorbent during activation treatment and since the production rate of marula shells is approximately one tonne per tree Rakereng et al (2019), this results in a potential supply to meet the bleaching process needs of an oil refining company as a result promoting recycling of agricultural waste for a clean environment.

2. MATERIALS AND METHODS

2.1 Materials

Fresh bentonite (FB) was bought locally in Botswana, fresh marula shells (FM) and Tonsil (T) were collected from one of the marula oil processing companies in Botswana. Tonsil was used as a reference adsorbent since it is used as a commercial bleaching earth in oil production industries.

2.2 Acid Activation of Bentonite

Fresh bentonite (ECCABOND-N Bentonite) was mixed in 2 N 98% pure H_2SO_4 at a temperature of $90^\circ C$ in a round bottomed flask for 7 h in an ESCO Perchloric acid fume hood using an electric heater (Medline Scientific Limited MS-E electric heater). The whole process is shown in Fig. 1. After activation process, 125 mm Whatman filter paper was used to filter the solid residue followed by continuous washing of the residue with distilled water to remove excess acid then drying was done at $105^\circ C$ in TTM-J4 oven for 4 h Önal et al (2007). Dried bentonite was pulverized to size of particle that infiltrated $75 \mu m$ sieve. Storage for the activated bentonite was done in polythene bags which were tightly closed and denoted AB.

Activation of bentonite was repeated in 1, 3, 5, 7, 10, 15 and 20 N acid concentrations at a fixed temperature of $90^\circ C$ for 7 h. To determine effect of activation time, the slurry was activated at various contact times (0.5, 1, 1.5, 2, 3, 8 h) in a 2 N acid concentration solution at $90^\circ C$.

2.3 Acid Activation of Marula Shells

Acid activated marula shells were prepared through two step chemical activation process. Marula shells were carbonized first at $500^\circ C$ then mixed with 2 N 98% H_2SO_4 in a beaker and heated for 1.5 h at $90^\circ C$ with continuous stirring. The mixture was cooled to room temperature. The solid residue was filtered followed by continuous washing with distilled water then drying was done at $105^\circ C$ for 6 h and heated in the furnace for 30 min at a temperature of

$450^\circ C$.

The same procedure was repeated at concentrations of 1, 3, 5, 7, 10, 15 and 20 N at $90^\circ C$ for 1.5 h. To determine effect of activation time, the same procedure was repeated for 0.5, 1, 2, 3, 7 and 8 h in 15 N acid concentration at $90^\circ C$. Acid activated marula shells (ACM) were stored in sealed tubes.

2.4 Alkali Activation of Marula Shells

Activated carbon from marula shells were prepared through one step chemical activation process. At first, fresh marula (FM) shells were washed with distilled water, then drying at $100^\circ C$ overnight in an oven. The dried marula shells were then pulverized using ball mill (size 1–2 mm). The crushed marula shells were mixed with KOH (ratio 1:1) mechanically using mortar and pestle and the mixture was activated using an electric resistance tube furnace Model OTF 1200 X at $700^\circ C$ for 1h (heating rate: $10^\circ C$ per min) under an atmosphere of nitrogen (flow rate: 20.0 std. cubic centimetres per minute). After cooling to room temperature, the resulting activated sample was soaked in 1M HCl to remove intercalated K on the carbon pores and inorganic particles before being washed with deionized water several times. Finally, the wet alkali activated marula (AM) was oven dried at $100^\circ C$ overnight. Dried activated carbon sample was cooled to room temperature before being stored in a separate sealed tube for further use.

2.5 Characterization of Bentonite and Marula Shells

X-ray diffraction (XRD) spectra of FB, AB, spent bentonite (after bleaching) (SB), FM, AM, spent marula (SM) and Tonsil (T) samples were generated from a Bruker D8 Advance powder diffractometer. The radiation used was $Cu-K\alpha$ with a wavelength of 1.5418 Angstroms Dinh et al (2022). The data collection was for 2θ , ranged between 5- and 90° degrees ant steps of 0.02 degrees with a time of 0.2500 s/step.

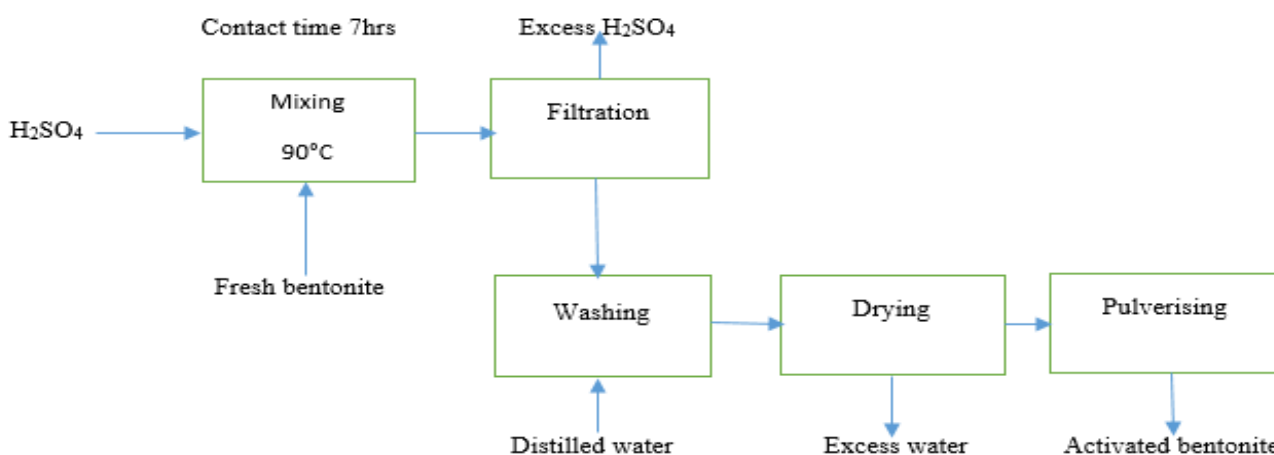


Fig. 1. Acid activation of bentonite process flow

The machine was run at 40 mA and 40 kV. pH was measured using Orion Star A111 Thermo Scientific pH meter by dispersing 1.43 g sample in 14.3 mL of deionized water. Chemical composition of FB, AB and SB was determined by use of Olympus DELTA Portable X-ray fluorescence (XRF). Thermal decomposition of adsorption material was analysed using Mettler Toledo TGA/DSC3+ model. Functional groups of adsorption material were determined using Vertex 70 v vacuum FTIR spectrometer. Proximate analysis for all adsorbents was done using Leo TGA 701. Filtration rate of different adsorbents was also observed by passing slurry through a permeable material.

2.6 Bleaching of Marula Oil

Vacuum bleaching was conducted by connecting a 500 ml flat bottomed flask to MRC vacuum pump (model CVP-13). 140 g crude marula oil was placed into flat-bottomed flask and then heated to 90°C as well as subjected to a vacuum whilst stirring at 240 rpm using Camlab MS-H280-Pro electric heater. The vacuum was then released intermittently, and 1.4 g of activated bentonite was added. The bleaching apparatus were re-subjected to a vacuum pump and heated further to 100°C for 20 min. After 20 min, vacuum was broken followed by filtering the clay and oil mixture using Whatman 125 mm filter paper through vacuum filtration to separate the oil from the clay Kaynak et al (2004). This same procedure was performed using FB, AM, ACM and T.

2.7 Characterization of Marula Oil after Bleaching

Chlorophyll pigment content was calculated using an AOCS Official Method Topkafa et al (2013) for both crude and bleached marula oil. Chlorophyll content was determined at wavelengths of 710 and 630 nm on a UV-Vis spectrophotometer (Model Evolution 201) using equation 1:

$$C_{\text{chlorophyll}} = \frac{[A_{630}(A_{630}+A_{710})]/2}{0.0964 \times L} \quad (1)$$

where: C is the chlorophyll pigments (ppm), L is the cell length (cm) and A is the absorbance.

Carotenoid content was measured spectrophotometrically as chlorophyll content. Specific absorbance measurements were conducted. Oil (1 g) was put in a 25 mL volumetric flask followed by adding isoctane to the mark (40 g / 1 L). Maximum absorbance was monitored (region 440–455 nm) then carotenoid concentration calculation was done using equation 2:

$$C_{\beta\text{carotene}} = \frac{AV}{W \times 0.261} \quad (2)$$

where: C is the β -carotene pigment (ppb), A is the absorbance, W is the sample weight (g), and V is the volume of the solution (mL). Acid value was determined according to AOAC 940.28 & ISO 660.2009 Standard procedure.

2.8 Bleaching Capacity

Fresh bentonite, activated bentonite and activated marula shells were tested to determine their bleaching capacity on marula oil. Bleaching capacity (BC) or fractional degree of bleaching (FDB) was calculated using equation 3:

$$BC (\%) = \left[\frac{A_0 - A}{A_0} \right] \times 100\% \quad (3)$$

where: A_0 is the crude oil absorbance and A is the bleached oil absorbance at the maximum absorbance wavelength (362 nm) of crude oil.

2.9 Effect of Acid Concentration and Activation Time

Effect of acid concentration and activation time was investigated for acid activated bentonite and acid activated marula shells.

3. RESULTS AND DISCUSSION

3.1 Adsorption Material Characterization

Adsorption material properties were examined using XRD, XRF, TGA and FTIR.

3.1.1 XRD

The crystallinity of fresh, activated and spent bentonite is shown in Fig. 2. Fresh, activated and spent bentonite reflect the same peaks with the presence of cristobalite (C), montmorillonite (M), willemite (W) and quartz impurities (Q) which indicates the presence of smectite phase Maged et al (2020). The montmorillonite, cristobalite, quartz and willemite peaks are positioned at 6.498°, 22.181°, 26.507° and 31.753°, respectively. Quartz (SiO₂) and cristobalite (SiO₂) have the same chemical formula but differ in their crystal structure. The sample shows more of cristobalite than the other silica phases. This observation is in agreement with previous studies showing that the treatment undergone by the material physiochemically does not affect the clay principle structure Meziti et al (2011). The quality of bentonite depends on crystal chemistry as well as size and shape of montmorillonites Kaufhold et al (2002). Other crystals like cristobalite play an important role on adsorption capacity Salem et al (2015) because of the loose bonds that exist on the surface of a minute grain of it than on montmorillonite Fuller et al (1940). From this observation, the primary structure of bentonite did not change because of the activation process. Only some small changes are noted in the region of 5° < 2θ < 13° and 21° < 2θ < 24° with peaks which corresponds to diffraction angles 6.498 and 22.181 and the inter-lamellar distance was 13.5918 Å and 4.0043 Å, respectively. Montmorillonite and cristobalite peak intensity decreased and width increased slightly due to acid activation by H₂SO₄. This can be due to replacement of cations (Ca²⁺, Fe²⁺, Al³⁺) with H⁺ ions. However, the differences between the XRD profiles are minimum.

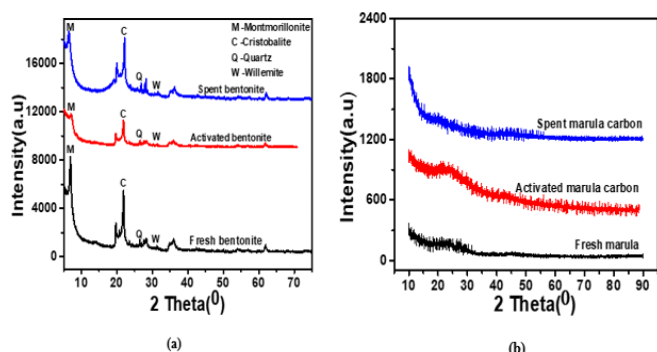


Fig. 2. XRD patterns for adsorption material (a) bentonite clay (b) marula shells

Acid activation did not affect the crystallinity of clay mineral Önal et al (2007) but surface properties were affected by improvement of adsorption capacity. This is as a result of replacement of cations in the bentonite structure by hydrogen ions as well as impurities being removed from the clay material, followed by leaching of ions from the octahedral and tetrahedral positions in the clay material resulting in the exposure of the edges of platelets Toor et al (2015). Activation results in H⁺ ions replacing cations thereby breaking up octahedral and tetrahedral sheets which results in the change in properties of the clay such as an increase in its adsorption capacity Foletto et al (2011).

The diffraction pattern of FM, AMC and SMC showed uncrystallized nature of the adsorbent since no peaks were detected which were prominent as shown by Fig. 2. The absence of sharp peaks is a typical characteristic of activated carbon. After adsorption process, the diffraction peaks did not change showing that adsorption using marula shells do not lead to bulk phase changes of activated carbon prepared.

3.1.2 XRF

Chemical composition of FB, AB and SB is shown in Fig. 3 with the chemical composition showing presence of Al, Ca, Cr, Fe, K, Mn, P, Si and Zn for all the three samples which was similar to those previously recorded (Patel et al., 2007; Tabak et al., 2007; Changchaivong et al., 2009; Abdallah et al., 2011; Nweke et al., 2015; Abdullahi et al., 2017). The anions of the bentonite interlayer are not included.

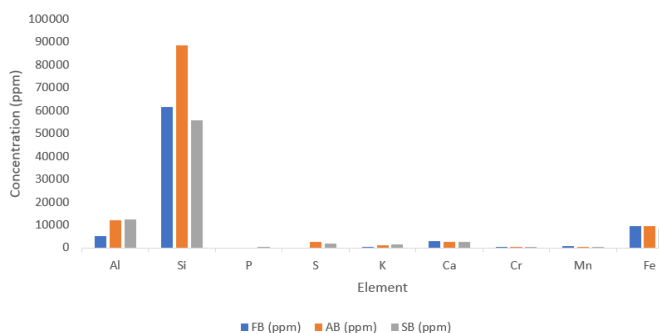


Fig. 3. Elemental analysis for FB, AB and SB

There are noted changes in the chemical composition for fresh and activated bentonite. The amount of silicon increased from 61700 ppm to 88500 ppm showing an increase of 43%, most likely due to acid activation Didi et al (2009) whereby protons penetrate into the mineral layers resulting in exchange of hydrated interlayer charge which contributes to movement of cations in the tetrahedral or octahedral sites (Venaruzzo et al., 2002; Maged et al., 2020) and release of cations into solution as a result of dissolution of clay mineral layers but silicate groups remains intact and the final product constitute hydrated, protonated, amorphous silica with cross-linked structure which is three dimensional. Sulphur was detected after acid activation which meant its source is sulphuric acid. This showed that acid treatment for bentonite caused changes in some features for the physical structure. Bleaching process did not change the structure significantly. As previously mentioned, Al, S, Ca and Fe remained relatively constant while Si was reduced significantly (37%). Phosphorus was only detected for the first time after bleaching process and this means it was introduced from marula oil.

3.1.3 pH and Filtration Rate

Addition of sulphuric acid during activation process resulted in a lower pH for AB (Table 1) with hydrogen ions replacing cations within the lattice and at the edges during activation process thereby making it acidic Salem et al (2015). The spent bentonite is also acidic due to the same process, however, the change in the pH value maybe due to some H⁺ ions neutralized during bleaching process. Pores start to develop within the bentonite structure when it is mixed with an acid solution which increases its specific surface area compared to its original state. Al³⁺, Fe²⁺ and Mg²⁺ move from the octahedral layers resulting in emptiness in the cationic spaces Salem et al (2015).

Table 1. pH values and filtration rate for bentonite and marula material

Adsorbent	pH	Filtration Rate (g/h)
FB	9.39	4.352
AB	3.21	2.279
SB	4.10	-
AMC	9.26	4.261
SMC	7.54	-

Octahedral layers of bentonite are altered during acid treatment whilst tetrahedral layers are altered during alkali treatment Soetaredjo et al (2021). Treatment of bentonite with acids may collapse the clay framework under severe activation conditions.

Activated marula carbon is basic because of KOH added during activation process. Activation of biochar leads to increase in surface area and porosity driven by metallic potassium intercalation which expands the carbon lattice (Hui et al., 2015). Filtration is important in oil refining because it is essential for separation of adsorbent and oil

after bleaching. Filtration rate will then determine the extent of flow rate of oil being filtered using different adsorbents.

3.1.4 Thermal Gravimetric Analysis (TGA)

Figs. 4 (a), (b) and (c) show the TGA curve of bentonite, marula shells and tonsil respectively. Thermogravimetric analysis of (a) was conducted to find out effects of activating fresh bentonite on degradation of fresh bentonite. From the analysis, two levels of degradation are noted for fresh and activated bentonite Galamboš et al (2021). For fresh and activated bentonite, there was mass loss at first degradation of 7% and 9%, respectively which was as a result of water loss from the interlayer of mineral Jlassi et al (2021).

Weight loss also appeared at second degradation with mass losses of 5% and 2% for FB and AB, respectively and this was attributed by hydroxylation which is desorption of -OH groups from the surface of bentonite material in water form Martín et al (2021). The second decomposition occurred at 597°C for both FB and AB and from the graphs after decomposition, fresh bentonite sample remains with a higher residue compared to acid activated bentonite Amalanathan et al (2021).

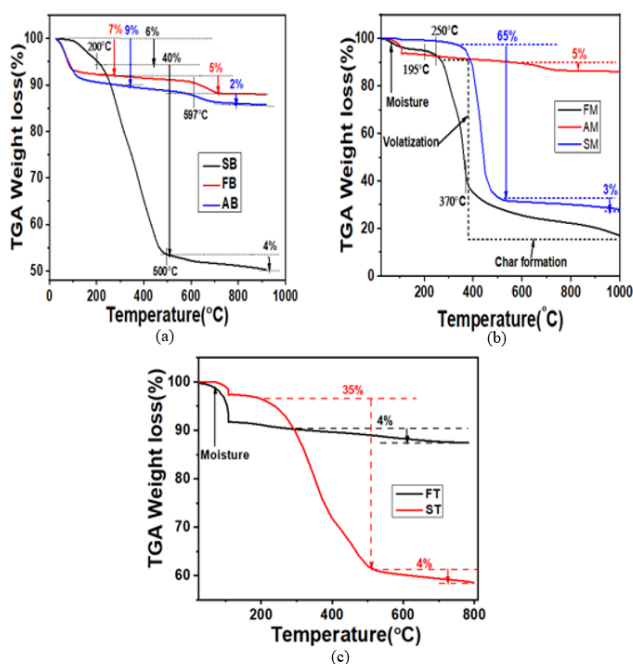


Fig. 4. TGA for fresh, activated and spent (a) bentonite (b) marula shells and (c) tonsil

This is because hydroxyl groups and interlayer water become less due to activation process thereby easy decomposition of AB Mao et al (2020) resulting in less residue. Thermogravimetric analysis for spent bentonite indicated three levels of degradation. Generally, the change in decomposition of spent bentonite involves removal of adsorbed water molecules at temperatures below 200°C,

hydroxylation and degradation of organic material at temperatures above 200°C Naser et al (2021). There was a sharp weight drop for spent bentonite sample from 200°C to 500°C. This is because of evaporation of marula oil which is a volatile matter and has a flash point of 250°C. This remarkably high flash point makes marula oil less flammable and enables safer handling as a cosmetic and edible oil. Total weight loss for spent bentonite and activated bentonite was approximately 49% and 14% respectively. This can be attributed to the fact that residual oil adsorbed during bleaching process was 35% of total weight of the spent bentonite which is in line with literature (Huang et al., 2010; Eliche-quesada et al., 2014; Liu et al., 2020).

Initial weight loss of marula shells from Fig. 4(b) was recorded at approximately 195°C (1–4%) because of evaporation of water bound by the raw material as well as moisture content in the adsorbent and water on the surface of marula shell plant material as reported by different authors (Edokpayi et al., 2015; Pathak et al., 2017; Joshua et al., 2019; Salman et al., 2019). There was a subsequent weight loss at 250°C which is due to decomposition of hemicellulose and cellulose and thermal degradation at 370°C which can be related to lignin degradation. Hemicellulose and cellulose polymers have a lower stability than lignin (Yang et al., 2007; Postai et al., 2016). Weight loss for activated marula carbon and spent marula carbon summed up to 14% and 72%, respectively giving a range of 58% and this is the residual oil left after bleaching process in activated carbon. For Tonsil the total weight loss was 14% and 49% for fresh and spent tonsil respectively, resulting in 35% residual oil in spent tonsil. The proximate analysis for the materials after thermogravimetric analysis are summarised in Table 2. Table 2 shows percentage content of volatile solids, moisture, ash and fixed carbon for the adsorbents. These results correspond to TGA graphs in Fig. 4.

Table 2. Proximate Analysis for Adsorption material

Adsorbent	Moisture %	Volatile %	Fixed carbon %	Ash %
FB	5.98	4.38	0.06	89.57
AB	5.90	8.47	0.11	85.52
SB	0.25	60.21	0.31	39.24
FM	3.54	71.43	22.4	2.63
AM	5.90	8.47	0.11	85.52

3.1.5 FTIR Analysis

FTIR results are shown in Fig. 5 and Table 3 with FM, AM and SM showing visible differences in their spectra. Reduction in intensity and disappearance of a number of peaks after activation of marula shells is noted with some peaks emerging after adsorption process which relate to residual oil attached to the biosorbent. Spectra of SM showed very intense peaks compared to AM and FM suggesting that adsorption process has taken place. Spectra for spent biosorbents (SM, SB, ST) showed new peaks

which were absent from the other spectra. The same functional groups must have been involved in adsorption process since new peaks which emerged were similar.

From Fig.5 (a), peak at 612/cm shifted to 619/cm after activation and adsorption process. A new peak emerged at 2169/cm after activation which relates to weak $-C\equiv C-$ stretch vibrations and can be assigned to alkynes. The band at 2169/cm moved to 2155/cm after adsorption. Peaks at 2853/cm and 2930/cm emerged after adsorption and are attributed to medium C-H stretch vibrations of alkanes. The presence of aliphatic compounds suggests that these compounds contain C-H bonds and are organic compounds and these IR bands are similar to those of other plant materials (Moyo et al., 2015; Edokpayi et al., 2015; Mathew et al., 2017).

FTIR spectra for bentonite shows the same number of vibration and OH stretching bands for FB and AB. Band positions deviated slightly due to replacement of cations (Ca^{2+} , Fe^{2+} , Al^{3+}) with H^+ during activation. There was an intensity decrease and shift in the band at 1625/cm for AB and FB 1632/cm. This is due to loss of water during activation process and is associated with high temperatures. The stretching vibration band of Si-O group at 1012/cm; after activation with acid, had a slight shift with a higher

frequency at 1019/cm attributing to dissolution because of activation process.

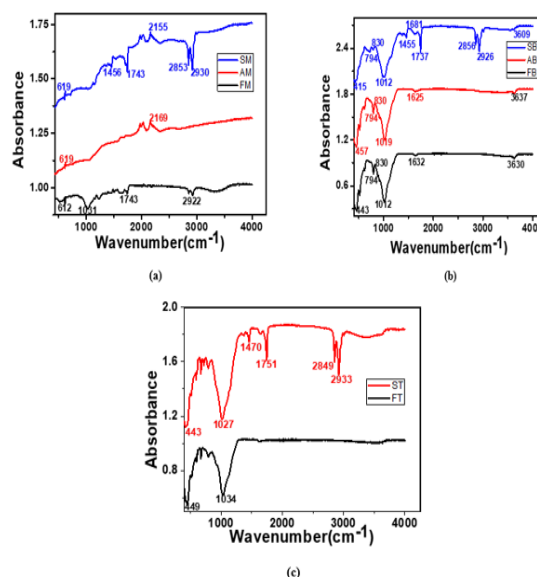


Fig. 5. FTIR analysis for (a) marula shells, (b) bentonite and (c) tansil

Table 3. Compounds represented by marula shells, bentonite and tansil

FM	AM	SM	FB	AB	SB	FT	ST	Possible compounds/Chains Rationale	Type of vibration causing IR Absorption	Sources
			443	457	415	449	443	Amorphous silica	OH vibrations or Si-O bending vibrations	(Christidis et al., 1997; Eren et al., 2009)
612	619	619						Alcohol	OH out of plane bending vibrations	(Pathak et al., 2017)
			794	794	794			Quartz	OH bending vibrations	(Maged et al., 2020; Petit et al., 2013)
			830	830	830			Aluminium magnesium hydroxide	OH bending vibrations	(Maged et al., 2020; Petit et al., 2013)
			1012	1019	1012	1034	1027	Amorphous silica	Si-O stretching (in-plane) vibrations in the tetrahedral sheet.	(Toor et al., 2015; Christidis et al., 1997; Eren et al., 2009)
1031								Aliphatic amine	C-N stretch	(Edokpayi et al., 2015; Pathak et al., 2017)
		1456			1455	1470		Alkanes	C-H bend	(Charis et al., 2020)
		1632	1625	1681				Silica	H-O-H bond	(Maged et al., 2020)
1743	1743				1737	1751		Aldehydes	C=O stretch	(Pathak et al., 2017; Edokpayi et al., 2019; Moyo et al., 2015)
	2169	2155						Alkynes	$-C\equiv C-$ stretch	https://ih.pmf.ukim.edu.mk 18/03/22
		2853			2856	2849		Alkanes	C-H vibrations	(Edokpayi et al., 2019)
2922	2930				2926	2933				(Edokpayi et al., 2015; Mkungunugwa et al., 2021; Jegede et al., 2021)
			3630	3637	3609			Montmorillonite	O-H stretching vibrations	(Eren et al., 2009; Maged et al., 2020)

Like XRD, FTIR bands did not show significant change of AB compared to FB meaning activation with acid did not destroy the parent bentonite. The use of Fourier transform infrared was able to distinguish the chemical structure of the adsorbents before and after activation and adsorption. It also helped in identifying the type and extent of adsorption as it occurs at the surface of the adsorbent.

3.2 Bleaching of Marula Oil

The following parameters were measured on the filtered oil samples; chlorophyll, β -carotene, acid value, FFA value and bleaching capacity. Crude oil before refining was also analyzed to ascertain any differences. The results are summarised in Table 4.

3.2.1 Bleaching Capacity

From Table 4, activated bentonite has four times better adsorption capacity when compared to unmodified bentonite (fresh bentonite). Impurities and colour pigments in the oil were adsorbed onto the activated bentonite at above half capacity. Raw bentonite was less effective for bleaching process using heat because of lower surface area per unit volume for adsorption Shin (2020). Results from literature corresponds to this information (Christidis et al., 1997; Makhoukhi et al., 2009; Foletto et al., 2011) where the bleaching capacities of activated bentonite were above 50% depending on the type of oil bleached, activation time, acid concentration and the type of acid used.

Activated carbon and Tonsil had bleaching capacities of 52% and 40% respectively signifying the use of activated carbon instead of commercial bleaching earth. Activation using KOH produces activated carbon with good pore development and a greater surface area because of potassium intercalation onto the carbon network during activation process. This shows the importance of the activation step and the benefits it brings to the process.

3.2.2 Chlorophyll and β -Carotene Content

More than 50% decrease in chlorophyll and β -carotene content after the bleaching process with activated bentonite and activated marula shells was noted, removing most of the colour pigments (Table 4) compared to raw bentonite. More than half of the chlorophyll present was adsorbed by raw bentonite and activated bentonite removed almost all chlorophyll present in crude oil. The presence of high levels

of chlorophyll results in serious problems for the refiner. There was a small range on the amount of β -carotene removed by FB and AB. 63%, 52% and 12% of β -carotene was removed by AB, AM and FB, respectively showing effectiveness of activation. Results showed that some β -carotene is left after bleaching process which may suggest that the final refining process, deodorization is and should be responsible for removal of the remaining β -carotene.

3.2.3 Acid Value and FFA Value

The acid value and FFA value reduced upon addition of adsorbent and generally free fatty acids in cooking oil range from 0%–3% Ojewumi et al (2021). The shelf life of oil is linked to amount of free fatty acids with low values indicating that the oil will be prolonged. Lowest value for FFA was obtained for AB followed by T, then AM and lastly FB.

3.2.4 Colour Appearance of Marula Oil after Bleaching Process

Two types of natural pigments, carotenoids and chlorophylls determine the colour of edible and cosmetic oils. AB and AM were found capable to improve the colour of oil by removing these pigments after the bleaching process (Fig. 6). It also removed smell compounds to make the oil smell better, but these were not tested in this study. Oil exposed to AB also exhibited a more transparent appearance showing that more impurities were adsorbed. AB and AM improved the colour of marula oil by removing the cloudy appearance in crude oil leaving the oil with a clear appearance (Fig. 6).

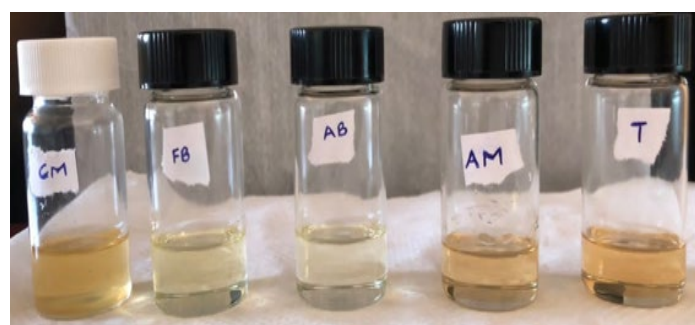


Fig. 6. Colour appearance of oil; crude marula (CM), bleached using fresh bentonite (FB), activated bentonite (AB), activated marula (AM) and tonsil (T)

Table 4. Crude and bleached marula oil parameters

Marula oil samples	Crude marula	Bleached oil (FB)	Bleached oil (AB)	Bleached oil (AM)	Bleached oil (T)
Chlorophyll (ppm)	$8.617 \times 1/10$	$2.971 \times 1/10$	$8.64 \times 1/10^5$	$2.94 \times 1/10^2$	$5 \times 1/10^2$
B-carotene (ppb)	$2.923 \times 1/10$	$2.563 \times 1/10$	$1.080 \times 1/10$	$1.404 \times 1/10$	$2.391 \times 1/10$
AV	1.64	0.82	0.64	0.75	0.71
FFA value (%)	1.16	0.58	0.45	0.53	0.50
BC (%)		13%	56%	52%	40%

BC: Bleaching capacity AV: Acid value (mgKOH/gmol) FFA: Free fatty acids

3.2.5 Effect of Acid Concentration on Activation of Adsorbent

Bleaching capacities of the samples after varying acid concentrations were obtained (Fig. 7). Bleaching capacity increased with increase in acid concentration for both bentonite and marula shells. Optimum acid concentrations were 2 N and 15 N for bentonite and marula shells respectively. Activated bentonite has higher bleaching capacity over acid activated marula shells.

Increase in acid concentration improves bleaching capacity and beyond 2 N for bentonite and 15 N for marula shells, significant reduction in bleaching capacity was observed due to collapse of material structure. Further increase in acid concentration results in destruction of crystal structure because of leaching of Al^{3+} , Mg^{2+} and Fe^{3+} from the octahedral sites hence decrease in surface area. Carbon lattice collapse with further increase in acid concentration hence reduction in bleaching capacity after 15 N acid concentration for marula shells.

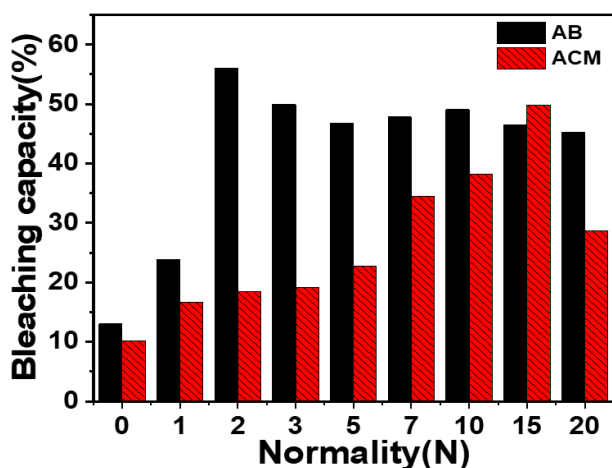


Fig. 7. Effect of acid concentration on activation of bentonite and marula shells

3.2.6 Effect of Activation Time on Activation of Adsorbent

Bleaching capacity results of activated adsorbents with varying activation times are shown in Fig. 8. Maximum bleaching capacity was for activation time of 1.5 and 7 h for marula shells and bentonite respectively. This difference in contact times is as a result of differences in material properties. Prolonged contact time reduces bleaching capacity because of pore enlargement and collapse of material.

4. CONCLUSIONS

FB, AB, FM and AM were characterized to a great extent to bring out changes before and after activation of the adsorbent. Crystallinity of bentonite material was not affected by acid activation but affected surface properties.

Alkali activation also showed changes in surface properties and this study has demonstrated that sulphuric acid and KOH form activated bentonite and activated carbon which were effective in reducing the amount of chlorophyll, carotenoids and free fatty acids in crude marula oil with a huge difference in terms of colour intensities as observed by the naked eye for crude and bleached marula oil. Activation using 2 N acid concentration (bentonite), 15 N acid concentration (marula shells) and KOH 1:1 (marula shells) yields adsorbent materials that effectively removes colour pigments from marula oil and their bleaching capacity performance were three times better than fresh bentonite. Bleaching capacity increases with increase in acid concentration and activation time. Bentonite and marula shells were able to refine marula oil effectively therefore there is no need to dispose marula shells as agricultural waste since valuable products can be produced from marula shells which can be used in oil refining and are biodegradable. Marula shells can be blended with bleaching earth found in the domestic market to improve adsorption. Future studies in addition to analyzing the effects of activating agent, temperature and bleaching time using marula shells also focus on finding sustainable technologies for treating the spent marula carbon and spent bentonite after the bleaching process.

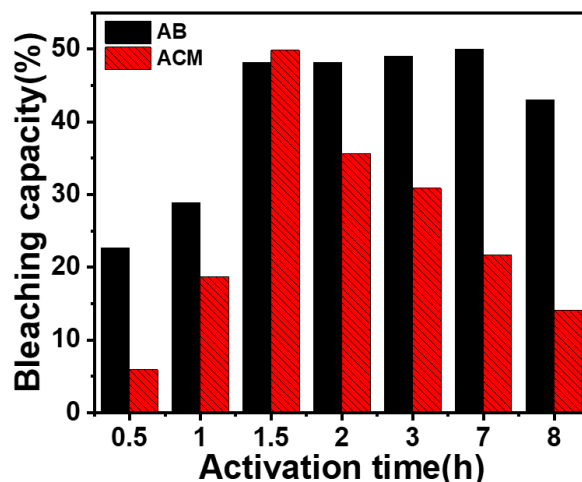


Fig. 8. Effect of activation time on activation of bentonite and marula shells

ACKNOWLEDGEMENT

The authors are thankful to Botswana International University of Science and Technology for providing financial and technical support.

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