

Research Article

Influence of Decolourisation Condition on the Physicochemical Properties of Shea (*Vitellaria paradoxa* Gaertner F) Butter

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Abstract: In this investigation, kinetics studies of adsorption of colour material of shea butter showed a peak at the wavelength 440 nm and the equilibrium time was found to be 30 min. Response surface methodology applying Doehlert experimental design was used to investigate decolourisation parameters of crude shea butter. The decolourisation process was significantly influenced by three independent parameters: contact time, decolourisation temperature and adsorbent dose. The responses of the process were oil loss, acid value, peroxide value and colour index. Response surface plots were successfully made to visualise the effect of the independent parameters on the responses of the process.

Keywords: Decolourisation, doehlert experimental design, physicochemical characterisation, RSM, shea butter

INTRODUCTION

Crude vegetable oils contain impurities like free fatty acids, phospholipids, traces of metals and pigments like carotenoids, chlorophyll and tocopherols (Boki *et al.*, 1992; Sabah *et al.*, 2007). These impurities limit the preservation and uses of the oils. It is thus imperative to refine the crude oils to extend its preservation period and increase its price. Decolourisation is one of the most significant steps of any vegetable oil refining process. In this step pigments and other unwanted compounds are adsorbed on solid material. The efficiency of decolourisation process depends on many parameters like temperature, contact time, agitation rate, adsorbent dosage, adsorbent particle size, variety of oils (Brimberg, 1982; Kamga *et al.*, 2000; Sabah and Çelik, 2005). The evaluation of influence of these parameters on the efficiency of decolourisation process is required for any optimisation procedure. Although there are many works realised on the decolourisation of vegetable oils using different types of adsorbent such as charcoal, clay materials and aluminium and silicon oxides, very few studies had been carried out on the decolourisation of shea butter.

Shea butter obtained from kernels of shea (*Vitellaria paradoxa* Gaertner F.) tree fruit is highly appreciated as cooking and frying fat, as cocoa butter substitute in chocolate and confectionary products and as cosmetic moisturizing cream (Krist *et al.*, 2006).

Mbah *et al.* (2005) studied the decolourisation of shea butter using activated clay and reported that pigments and free fatty acids decreased and peroxides

compounds were destroyed with the increase in decolourisation time. Since elimination of free fatty acids, oxidative products and other impurities of crude oils is the main function of neutralisation process, this work was focused on the decolourisation of shea butter to improve its physicochemical properties. Hence the main objective of this investigation was to study the kinetics of the adsorption of pigment of shea butter.

MATERIALS AND METHODS

The materials used were: Crude black and yellow traditionally aqueous extracted shea butter was purchased from Penie village-South of Chad in January 2008. The method of extraction was described by Adoum (1996). Adsorbent: Tonsil fuller earth (240 FE, Olifants, Republic of South Africa), supplied by Cotton Chad company. Spectrophotometer: Double beam UV-Visible Spectrophotometer of model (SECOMAM, ISO 9001, France). Lovibond Tintometer: Model (F 292, Tintometer Ltd., U.K, with tungsten halogen lamp as source of light).

Visible spectrum of shea butter: The purpose of this part of the study was to determine the wavelength at which the spectrum curve showed a peak. This wavelength was then used to study the kinetic of adsorption of pigment and the adsorption isotherms of shea butter. Samples of crude black and yellow shea butter were decolourised using 2 weight percentage of adsorbent and 20 min contact time. Samples of crude and decolourised black and yellow shea butter were

diluted with petroleum ether (1:5 and 1:1 v/v, respectively). Then the spectrum was recorded between 400-700 nm using a UV-visible spectrophotometer of model (SECOMAM, ISO 9001-France).

Kinetics of the adsorption of pigments: The aim of kinetics study was to determine an equilibrium time that could be used in the optimisation of decolourisation parameters of shea butter. For each experiment, 60 g of crude shea butter was placed in a conical flask held in water bath, thermostated at a predetermined temperature that is 55, 75 or 95±2°C. When the required temperature was attained (around 15 min), 2 mass% of adsorbent was added to the flask which was then agitated for the desired length of time. The contact time was varied between 5-90 min. After each residence time, 5 g of the decolourised oil was filtered and diluted. Before measuring the absorbance, the spectrophotometer was standardised by filling the glass cell with a reference solvent (petroleum ether), put in the spectrophotometer and zero absorbance was recorded. Then using similar glass cell the absorbance of the diluted sample was measured at the predetermined wave length (440 nm) and then curves of decolourisation temperature versus contact time were plotted. Each experiment was repeated twice and the average value was used.

SigmaPlot®, (2004) version 9.01 was used for statistical Analysis (ANOVA). The significances of all terms in the polynomial of Doehlert experimental design were judged statistically by the probabilities of 0.001, 0.01 or 0.05.

Procedure of decolourisation: The decolourisation apparatus was composed of a 250 mL conical flask equipped with a mechanical agitator of model (Heidolph, RZR1, Germany). The flask was immersed in a thermostated water bath. In each experiment, 30 g of crude shea butter was heated and maintained at the desired temperature for 15 min before adding the adsorbent. After the addition of adsorbent dosage, the mixture was continuously heated and stirred. The agitation rate used was that just enough to keep the clay dispersed (150 rpm). After decolourisation, the agitation was stopped and the mixture was immediately filtered using Whatman no 1 filter paper on a layer of celite 545 and a vacuum pump of model (960101, Osi-DVD-Bolong, Italy). Each experiment was repeated twice and the results reported are the means of three measurements. The response surface methodology using Doehlert experimental matrix as mentioned previously was used to optimize the decolourisation process (Mohagir *et al.*, 2009). Contact time, decolourisation temperature and adsorbent dose were the major independent parameters investigated in this study.

Responses of the decolourisation process: The physicochemical analysis which were done are acid value, peroxide value and colour index. Acid and peroxide values were evaluated using the method

described in AFNOR (1981), while the colour index was determined as Lovibond red and yellow colour.

Lovibond colour: This technique as described by (ISO 15305, 1998) involves matching the colour of light transmitted through a specified depth of oil with the colour of light transmitted from the same light source through a set of coloured glass slides called Lovibond colour glasses. For vegetable oils frequently it requires fixing the yellow numeral in some functional relation to the red or vice versa. The colour of shea butter was measured using Lovibond Tintometer of model (F292, Tintometer Ltd. UK). All the test samples were homogenised to clear liquids by heating them in an oven set at 50±2°C. In our measurement the yellow unit was fixed at 20 for black sample, while the red units were independently varied. Similarly the red unit was fixed at 10 for yellow shea butter and the yellow units were independently varied. The measurements were all carried out using 1 inch glass cells.

RESULTS AND DISCUSSION

Absorption spectra of shea butter in the visible band:

The absorption spectra of the crude (black, yellow) and decolourised shea butter are shown in Fig. 1. This spectrum was carried out in order to determine the wave length at which the absorption curve showed a peak.

From Fig. 1, it is observed that the wavelength at which shea butter presented a maximum absorption is 440 nm. For both types of shea butter the absorbance for the decolourised type was lower than that of the crude butter. The reduction of absorbance of decolourised shea butter at this wave length was used to study the kinetic of adsorption of pigment and the fitting of adsorption isotherms data of shea butter. The thermal stability of shea butter pigments was tested. For this purpose, crude shea butter was heated at 75 and 95°C for 60 min and the absorbance of the final product was read at 440 nm. It appears that there was no major change in the pigment concentration, since the absorbance remained constant throughout the heating process. This result is in accordance with that obtained by Mbah *et al.* (2005), who observed the thermal stability of shea butter pigment over heating between 65 and 90°C.

Kinetics of the adsorption of pigments: The results of the kinetics of the adsorption of pigment are presented in Fig. 2. The kinetic curves of adsorption of pigments were found to follow an exponential equation rise to maximum:

$$y = a(1 - e^{-bt})$$

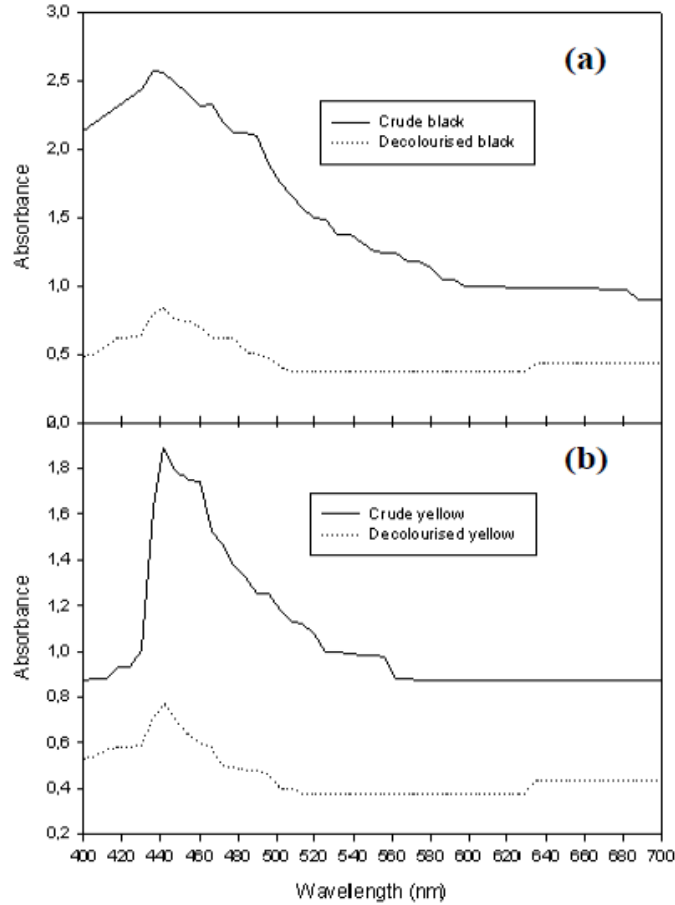


Fig. 1: Spectra of absorption of crude (—) and decolourised (···) black (a) and yellow (b) shea butter

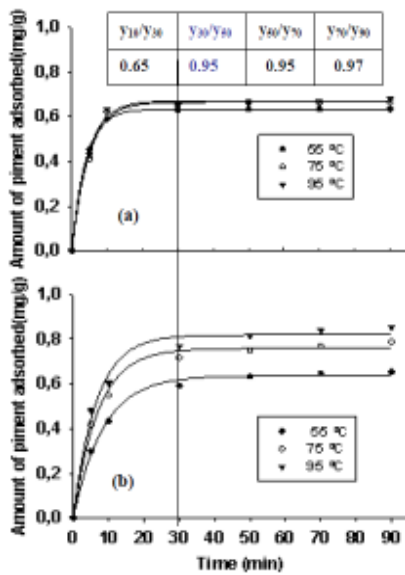


Fig. 2: Kinetics of the adsorption of pigment of black (a) and yellow (b) shea butter on tonsil fuller earth at different temperatures

where,
 y : The yield (g/g)

t : Extraction time (min)

a and b : Constants

From Fig. 2, it is observed that the amount of pigment adsorbed increased as decolourisation temperature increased especially in the case of yellow shea butter. In the first 10 min the uptake of pigment was very rapid with increase in decolourisation temperature and then followed by a moderate increment. Steady state was reached after 30 min for black and yellow shea butter, regardless of the decolourisation temperature used. The results of y_{30}/y_{50} appeared over the figure gave 95% of decolourisation efficiency for both yellow and black shea butter.

The overall feature of the kinetic of the adsorption of shea pigments observed herein is in agreement to what was proposed by Chritidis and Kosiari (2003) for the adsorption of β -carotene on bentonite clay. The authors reported two steps in the kinetic of the adsorption of vegetable oil pigment on the clay. The first one was a sharp increase which is due to the diffusion of pigment molecules toward the surface of the adsorbent or to a more significant activation of the site of adsorption by the heat. The second step which was a low adsorption rate is attributed to the interaction of pigment and clay surface.

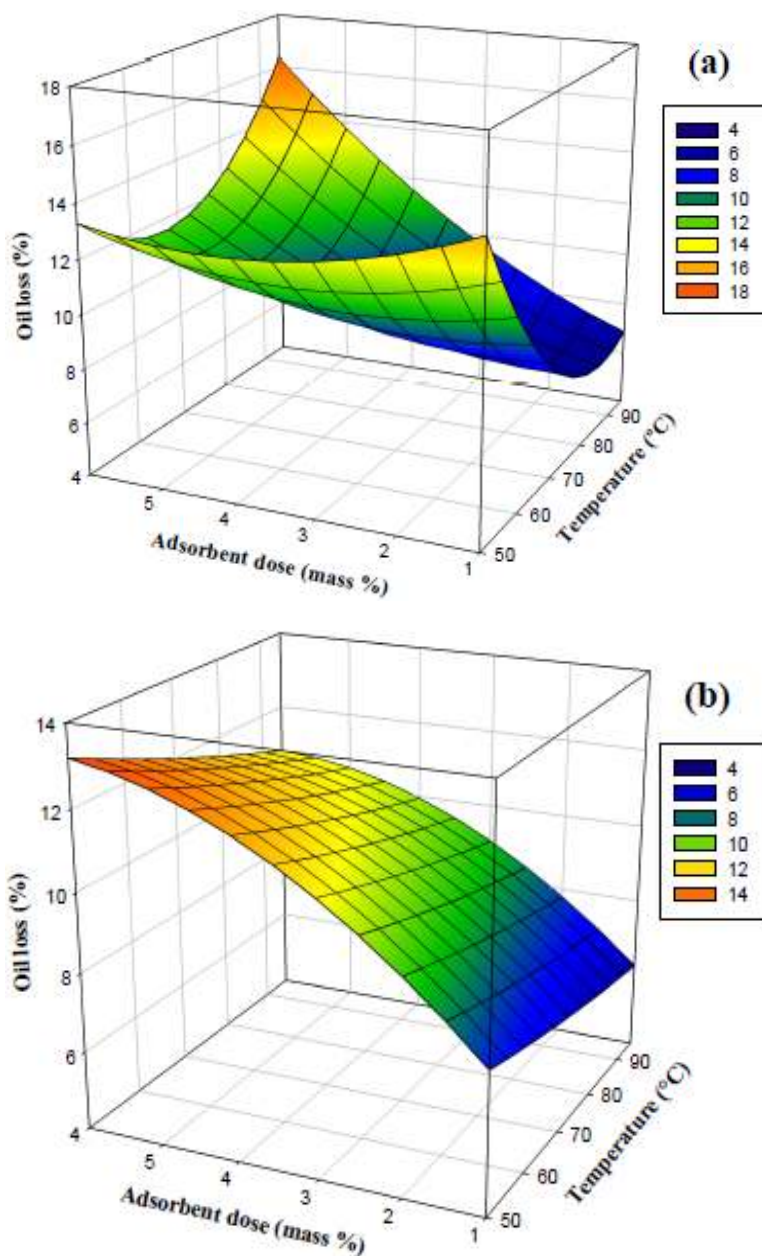


Fig. 3: The variation of oil loss (%) of decolourised black (a) and yellow (b) aqueous extracted shea butter as a function of decolourisation temperature and adsorbent dose (mass%); (contact time 65.5 min)

Influence of independent parameters on the responses of the decolourisation process: The influence of decolourisation conditions on the oil loss (%), acid value, peroxide value and the colour of decolourised shea butter is reported in Fig. 3 to 6 using response surfaces plot.

Oil loss (%): Figure 3, is an aid to visualise the effect of decolourisation temperature and adsorbent dose on the oil loss (%) of black and yellow shea butter. The oil loss was expressed as a mass ratio of decolourised oil to that of crude one. From Fig. 3a and b), it was observed

that, the oil loss decreased with an increase in decolourisation temperature until 80°C, then remained constant afterwards.

The decrease in oil loss with the increase of decolourisation temperature is due to the decrease of viscosity of shea butter with the increase of temperature and the decrease of viscosity enhanced the efficiency of filtration of shea butter. From Fig. 3b), it was observed that the oil loss increased marginally as the adsorbent dose increased during the decolourisation of yellow shea butter. The increase in oil loss with an increase in adsorbent dose could be attributed to the retention of oil

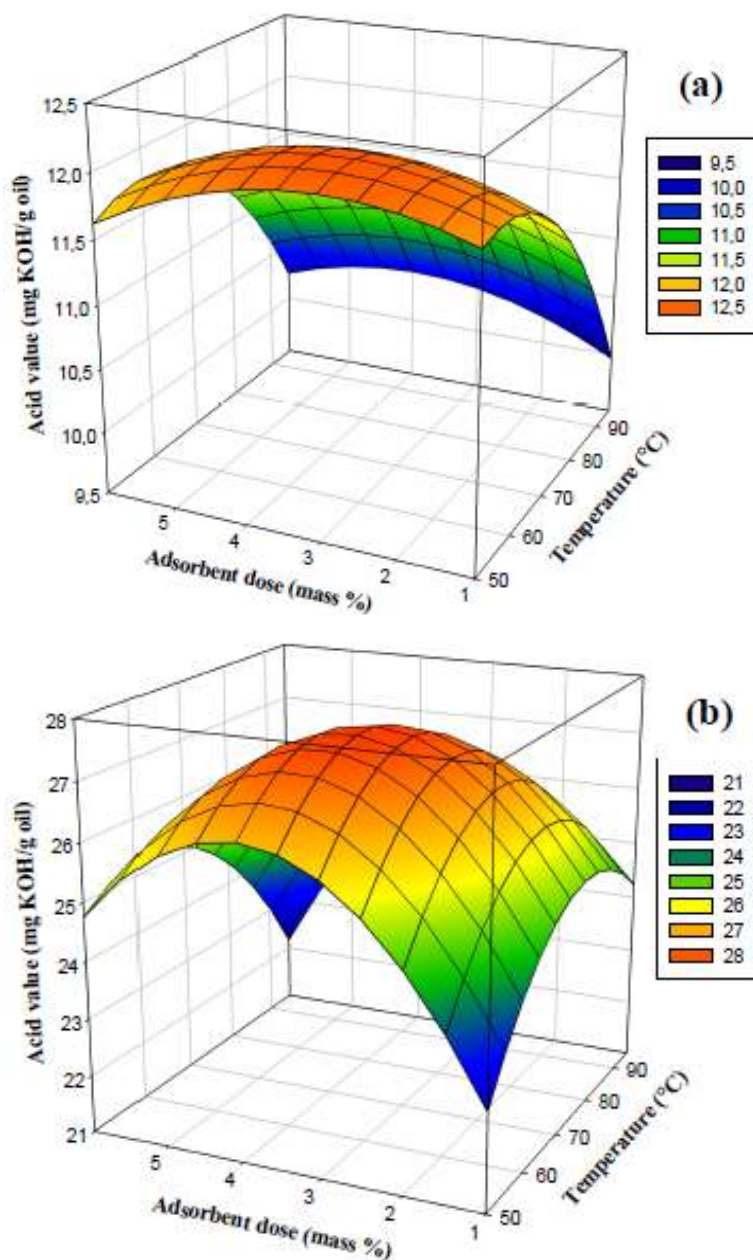


Fig. 4: Influence of decolourisation temperature and adsorbent mass% on acid value, for the decolourisation of black (a) and yellow (b) aqueous extracted shea butter

by tonsil fuller earth. Chritidis and Kosiari (2003) reported that during bleaching process, fuller earth retains up to 9 of its mass percentage of the oil.

Acid value: Figure 4a and b show the surface plots for the effect of the independent parameters on the acid value of shea butter.

From Fig. 4a it is observed that, when the contact time was kept constant at the central point, the acid value of black shea butter remained fairly constant as decolourisation temperature increased from 50 to 70°C and then decreased marginally afterwards. For yellow

shea butter, the acid value increased with an increase in decolourisation temperature from 50 to 80°C and then decreased steadily with decolourisation temperature (Fig. 4b). The increase in acid value with the increase in decolourisation temperature could be attributed to the hydrolysis of fat catalysed by lipase enzymes that were naturally found in shea kernels. On the other hand, the decrease in acid value with decolourisation temperature might be due to deactivation of lipase at elevated temperature. Ladurelle (1984) reported that the deactivation of lipase usually begins at 80°C when oilseeds are boiled in water.

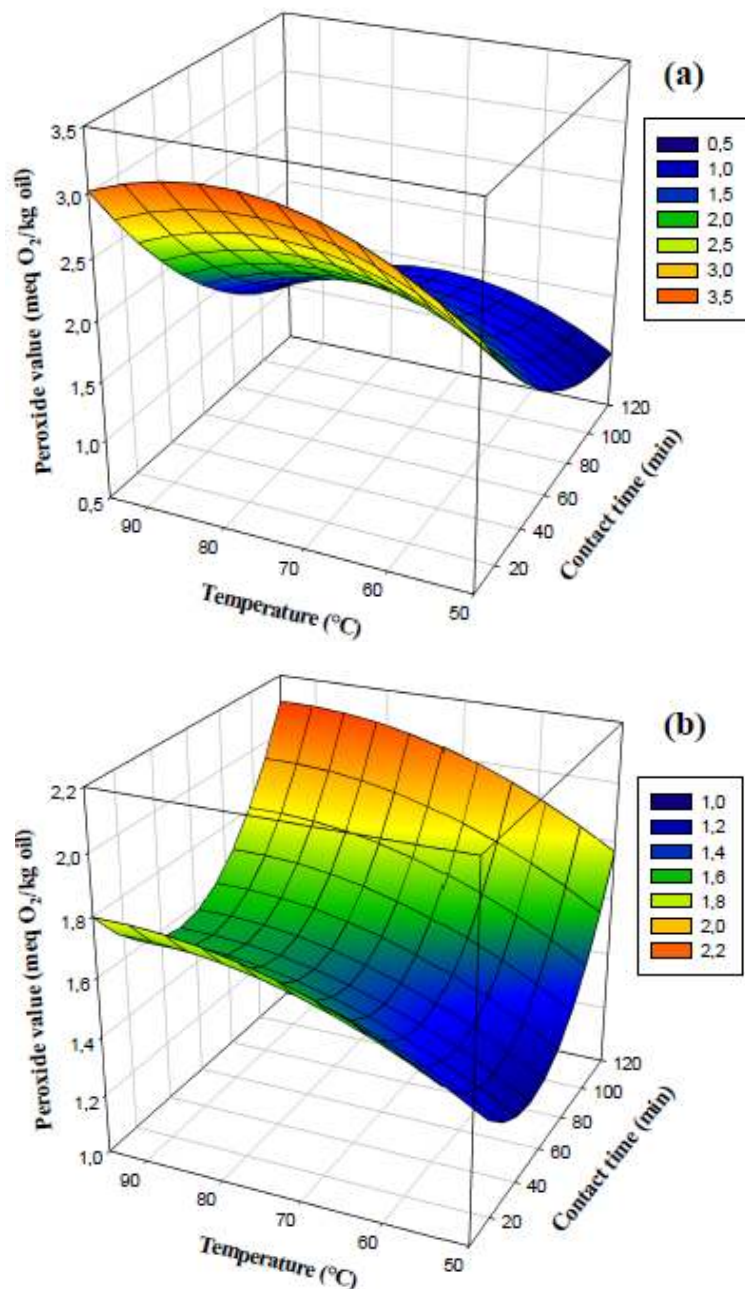


Fig. 5: Influence of decolourisation temperature and contact time on the peroxide value of decolourised black (a) and yellow (b) aqueous extracted shea butter

Also from Fig. 4a, it is observed that at constant contact time, the increase in adsorbent dose had no influence on the acid value of black shea butter, whereas for yellow shea butter (Fig. 4b) the increase in adsorbent dose was accompanied with an increase in acid value up to 4 mass % and then decreased marginally. El Warraki (1995) reported that the presence of Al₂O₃ and SiO₂ in adsorbent and the presence of moisture in the oil (0.5-1% in shea butter), catalyse the hydrolysis of oils and fats during bleaching, leading to an increase in the acid value of the bleached oil. This result is in agreement with those

reported by Nnandozie *et al.* (1989) during bleaching of palm oil.

On the other hand the decrease in acid value with an increase in adsorbent dose (mass %) could be attributed to the adsorption of free fatty acids by adsorbent. Similar observation was reported by Kheok and Lim (1982).

Peroxide value: Figure 5a and b show the surface plots for the effect of the independent parameters on the peroxide value of shea butter.

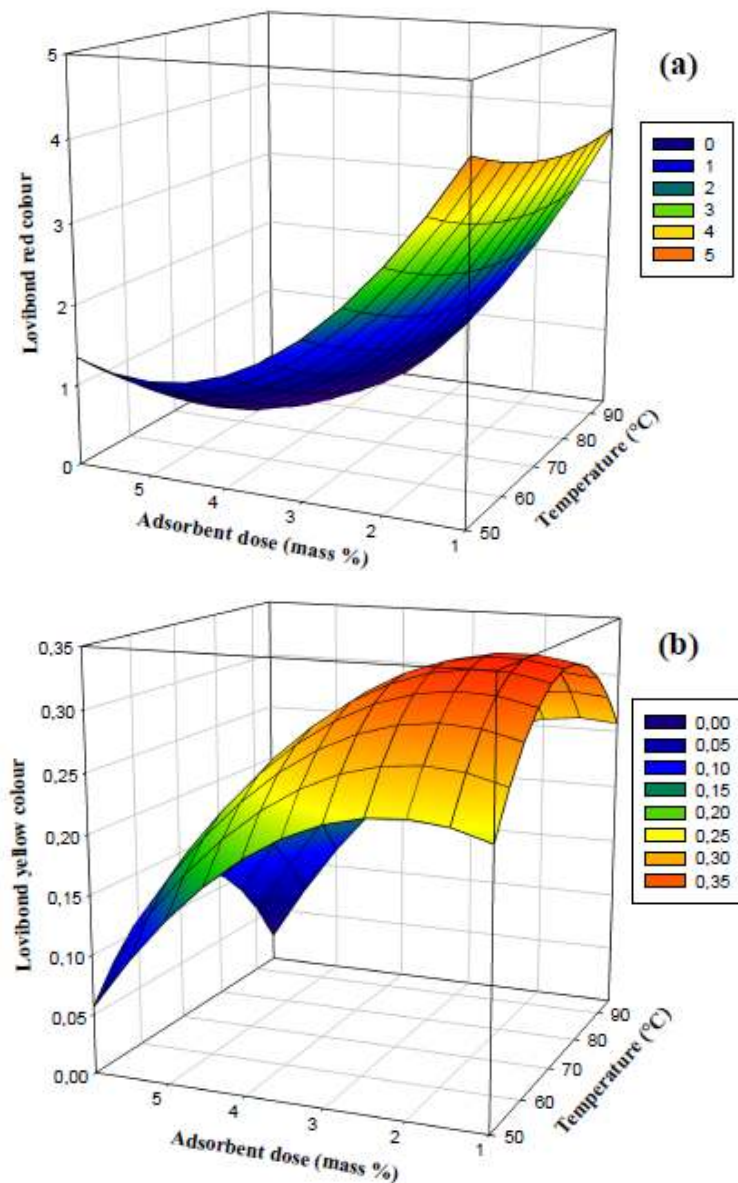


Fig. 6: Influence of decolourisation temperature and adsorbent dose on Lovibond colour scale, for the decolourisation of black (a) and yellow (b) aqueous extracted shea butter

At constant adsorbent dose (2.5 mass %) the peroxide value increased non-linearly with an increase in decolourisation temperature for both black and yellow shea butter Fig. 5a and b. Under the same conditions, the peroxide value of black shea butter decreased as the contact time increased up to 80 min, after which it remained almost constant (Fig. 5a). For yellow shea butter, the peroxide value decreased as contact time increased up to 30 min and then increased gradually throughout the process (Fig. 5b).

The decrease in peroxide value with the increase in contact time could be attributed to the adsorption of hydroperoxides and other oxidants by the adsorbent (2.5 mass %). The adsorption of free fatty acids and destruction of peroxides during bleaching process were

also noted by Mbah *et al.* (2005) and Nde-Aga *et al.* (2007). On the other hand, the increase in peroxide value with the increase in decolourisation temperature was probably due to oxidation of shea butter by atmospheric oxygen, since decolourisation process was carried out in an opened environment.

Lovibond colour: Figure 6 is response surface plot explains 97 and 75% of colour variations of black and yellow shea butter, respectively.

When the contact time was held constant at the central point, the colour of black shea butter decreased rapidly as the adsorbent dose increased until it reached a minimum at about 4 mass %, then remained constant for the rest of the adsorbent dosages (Fig. 6a). For

yellow shea butter under the same conditions, it is observed that at low adsorbent dose (about 3 mass %) the colour remained constant. However, at high adsorbent dose, the colour decreased considerably to a minimum value (Fig. 6b). When the contact time was held constant at 65.5 min, the colour of black shea butter remained constant with the increase of decolourisation temperature (Fig. 6a), while that of yellow shea butter increased with the decolourisation temperature until it reached a maximum at about 75°C and then decreased (Fig. 6a).

The decrease in colour with the increase in adsorbent dose could be attributed to the adsorption of colour material by the adsorbent. In fact, the bleaching process with acid-activated clays such as fuller earth is generally a combination of catalytic action "peroxide destruction" and equilibrium adsorption "pigment removal from the oil" (Henderson, 1993). Impurities in the oil, such as carotenes and chlorophyll, can rapidly diffuse through the sample and adhere to most of the active acid sites on the clay surface. Improved adsorptive properties for the removal of chlorophyll from edible oils were observed by Sabah (2007). He reported that acidic OH groups of tonsil fuller earth can directly exchange protons with chlorophyll molecules. In addition, the protonated $AlOH_2^+$ structure can serve as an effective binding site to permit the attachment of pigments and other colouring material contained in oils. Furthermore, Morgan *et al.* (1985) and Sabah *et al.* (2007) reported that pigments such as β -carotene can either be adsorbed directly onto a cation to form a chemisorbed complex or react with the protonic centers present on the adsorbent surface.

CONCLUSION

Absorption spectra of shea butter in the visible region were carried out. The kinetic curves of adsorption of pigments were found to follow an exponential equation rise to maximum. The decolourisation time was found to be 30 min. The response surface graphs were plotted and successfully explained the influence of the independent parameters on the responses of the decolourisation of shea butter.

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