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ADSORPTION ISOTHERMS OF DECOLOURISATION OF SHEA (*VITELLARIA PARADOXA* GAERTNER F) BUTTER

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ABSTRACT

The objective of this paper was to study the adsorption isotherms of decolourisation of shea butter. The adsorption of pigments from aqueous extracted shea butter using tonsil fuller earth was carried out. The absorbance of crude and decolourised black and yellow shea butter using 1, 2, 3, 4 and 5 mass % of the adsorbent at different temperatures (55, 65, 65, 75, 85 and 95°C) were measured. The experimental data obtained were analysed and fitted to Freundlich and Langmuir equations. Langmuir adsorption isotherm model fitted well the decolourisation of yellow shea butter at 95°C, while Freundlich model significantly fitted the decolourisation of black shea butter at 65°C. Gibbs free energy, enthalpy and entropy of adsorption were generated from the experimental data. The absolute value of enthalpy of adsorption showed that the decolourisation process of shea butter is a physical phenomenon, whereas the negative values of Gibbs free energy suggested that, the adsorption is spontaneous process.

Keywords: Shea butter, decolourisation, tonsil fuller earth, adsorption isotherm, Freundlich, Langmuir.

INTRODUCTION

Shea tree *(Vitellaria paradoxa* Gaertn), produces kernels which have an oil content of about 35-60% called shea butter (Kamga *et al*., 1999). Shea butter is used as cooking oil for some population of African Sahel region. It is used also in traditional medicines and as raw material for many industries such as soap, cosmetics, Pharmaceutics, chocolate, and confectionary (Booth and Wickens, 1988). The aqueous extraction of shea butter, though very tediousness, is still very predominant in the central African region and is the main source of supply of local markets with shea butter. The traditionally extracted butter has shown to be of an inferior quality, producers supply poor quality shea butter (yellow, brown and dark colored, poor hygienic conditions and with high acid and peroxide values). Refining is a step that may be included in the processing chain to improve the quality. Unfortunately only very few papers are found in the literature for the refining of shea butter (Bike Mbah *et al*., 2005). There are two types of shea butter in Chad, namely cosmetic (yellow) and edible (black). Their methods of preparation were described previously (Mohagir, 2003). To produce edible shea butter, shea kernels are roasted in red heated sand in a steel pot and then crushed with wooden mortar and finally grounds. The difference between the two methods is that the production of yellow shea butter not includes the roasting step. Bleaching of vegetable oils is performed for the removal of colour materials, phospholipids, soaps and oxidative products such as peroxides (Norris, 1982). Pigments have the state of a stable colloid in the oil. Their separation needs sufficient means to break the stability of the colloids and this is the essential role of adsorbent (Brimberg, 1982). Adsorption of pigments from vegetable oils with various types of adsorbents has been extremely reviewed (Norris, 1982; Brimberg, 1982; Achife and Ibemesi, 1989; Boki *et al*., 1992; Topallar, 1998). Isotherm plots represent the partition of pigments and other colouring materials between solid phase (adsorbent) and liquid phase (oil). It is a measure of the position of equilibrium in the adsorption process. The purpose of this study is to examine the applicability of Freundlich and Langmuir equations to the adsorption isotherms for the decolourisation of aqueous extracted shea butter using tonsil fuller earth.

MATERIALS AND METHODS

Materials

Aqueous black and yellow extracted shea butters were purchased from local Koumra market, Chad. Adsorbent used is tonsil fuller earth (240 FE, Olifants, Republic of South Africa). The absorbance of oil samples was measured using double beam UV-Visible Spectrophotometer model (SECOMAM, ISO 9001, France).

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Methods

Decolourisation procedure

The decolourisation apparatus was composed of 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 mass%, the mixture was continuously heated and stirred. The agitation rate used was that just enough to keep the clay dispersed (150rpm). After decolourisation (30min), the agitation was stopped and the mixture was filtered immediately by using Joseph filter paper (celite 545) and vacuum filtration pump (960101, Osi-DVD-Bolong, Italy).

Modelling of Isotherms

In this study, the adsorption data were analysed according to Freundlich and Langmuir isotherms (equation 1, 2) which are the most widely utilised models in this domain. Moreover, the correlation coefficient (R^2) was used to judge the applicability of the isotherms

$$\text{Freundlich model}: X/m = KX_e^{1/n} \quad (1)$$

$$\text{Langmuir model}: X_e/(X/m) = \frac{1}{X_{max} * b} + \frac{X_e}{X_{max}} \quad (2)$$

Where X is the relative amount of pigments adsorbed (mg/g), m is the mass of adsorbent (g), K and n are Freundlich constants; K is related to bonding energy, it can be defined as an adsorption or distribution coefficient which describes the amount of pigments adsorbed onto adsorbent agent for the unit equilibrium concentration. The Freundlich constant n is a measure of the adsorption intensity that ranges between 1 and 10 (Tsai *et al*., 2004). X_e is the residual relative amount of pigments at equilibrium (mg/g); X_{max} is the quantity of pigment adsorbed at monolayer or the maximum coverage (mg/g), b is Langmuir adsorption equilibrium constant (g/mg) that is related to direct measurement of the intensity of adsorption process.

The values of X and X_e were obtained from the absorbance of pigment at a wavelength in which the overall absorbance's curve in the selected zone shows maximum peak (Brimberg, 1982). These quantities were calculated using the relation (3)

$$X = \frac{A_0 - A_t}{A_0}, X_e = \frac{A_t}{A_0} \text{ or } = 1 - X \quad (3)$$

Where A_0 and A_t are the absorbance of crude and decolourised oil at equilibrium time t respectively.

Before measuring the absorbance, the black and yellow shea butter was diluted with petroleum ether (1:3 and 1:1) respectively and the absorbance of diluted samples was measured at the pre determined wave length (440 nm).

Freundlich isotherms were generated by plotting log (X/m) versus log (X_e) from the logarithm form of equation 1 and then K and n were determined from the intercept (log K) and slope (1/n). From equation 2, a plot of (X_e/(X/m)) against X_e represents Langmuir isotherms. Langmuir constants X_{max} and b were calculated from slope ($1/X_{max}$) and intercept ($1/ (X_{max}*b)$).

Determination of enthalpy, entropy and Gibbs free energy of adsorption

One of the more important applications of adsorption isotherms data is their utilisation is the determination of some thermodynamic properties such as enthalpy of adsorption ($\Delta H^o_{ad,}$) and the change in standard entropy ($\Delta S^o_{ad.}$). These parameters can be used to evaluate the mechanism of adsorption of pigments onto any adsorbent (Sabah and Celik, 2005; Sabah, 2007). The parameters were determined using Van't Hoff equation (4).

Where, R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$) and T is the temperature in Kelvin. The plot of Ln (X_e) versus (1/T) yields straight line with intercept ($\Delta S^o_{ad}/R$) and slope ($\Delta H^o_{ad}/R$).

$$Ln(X_e) = \frac{\Delta S^0 ad}{R} - \frac{\Delta H^0 ad}{RT} \quad (4)$$

Gibbs free energy of adsorption ΔG^o_{ad} was calculated from equation 5 as recommended by some authors (Sabah, 2007).

$$\Delta G^0_{ad} = -RTLn(X_e) \quad (5)$$

RESULTS AND DISCUSSION

The absorbance of crude black and yellow shea butter (A_0) was recorded as 1.72 and 2.10 (% light transmission) respectively. On the other hand, the absorbance of the two decolourised samples (A_t) using 1, 2, 3, 4 and 5 mass % of tonsil fuller earth at different temperatures (55, 65, 65, 75, 85 and 95°C) are presented in table 1 and 2.

The decrease in absorbance with increase in adsorbent mass % at constant temperature (Table 1and 2) could be attributed to the greater availability of exchangeable sites of adsorbent.

It is observed that at constant adsorbent mass % (Table 1), the absorbance increased as temperature increased. This means that either the relative amount of pigment adsorbed

Table 1. The absorbance of decolourised black shea butter (A_t) at different adsorbent dose and temperatures.

Adsorbent dose (mass %)					
Temperature (°C)	1	2	3	4	5
55	$0.597^{I}e \pm 0.01$	$0.568^{I}d \pm 0.02$	$0.526^{I}c \pm 0.01$	$0.512^{I}b \pm 0.04$	$0.430^{I}a \pm 0.02$
65	$0.627^{II}e \pm 0.02$	$0.584^{II}d \pm 0.02$	$0.534^{II}c \pm 0.02$	$0.523^{II}b \pm 0.03$	$0.460^{II}a \pm 0.01$
75	$0.703^{III}e \pm 0.04$	$0.658^{III}d \pm 0.01$	$0.538^{III}c \pm 0.03$	$0.529^{III}b \pm 0.01$	$0.468^{III}a \pm 0.04$
85	$0.817^{IV}e \pm 0.01$	$0,672^{IV}d \pm 0.04$	$0.556^{IV}c \pm 0.01$	$0.548^{IV}b \pm 0.02$	$0.491^{IV}a \pm 0.02$
95	$0.890^{V}e \pm 0.02$	$0.730^{V}d \pm 0.01$	$0.602^{V}c \pm 0.03$	$0.572^{V}b \pm 0.03$	$0.548^{V}a \pm 0.02$

Absorbances in the same row with different letters are significantly different ($P < 0.05$)
Absorbances in the same column with different superscripts are significantly different ($P < 0.05$)

Table 2. The absorbance of decolourised yellow shea butter (A_t) at different adsorbent dose and temperatures.

Adsorbent dose (mass %)					
Temperature (°C)	1	2	3	4	5
55	$0.582^{I}e \pm 0.03$	$0.477^{I}d \pm 0.01$	$0.456^{I}c \pm 0.02$	$0.445^{I}b \pm 0.03$	$0.377^{I}a \pm 0.01$
65	$0.535^{II}e \pm 0.01$	$0.460^{II}d \pm 0.02$	$0.446^{II}c \pm 0.01$	$0.418^{II}b \pm 0.01$	$0.363^{II}a \pm 0.03$
75	$0.458^{III}e \pm 0.04$	$0.442^{III}d \pm 0.03$	$0.427^{III}c \pm 0.04$	$0.395^{III}b \pm 0.01$	$0.355^{III}a \pm 0.02$
85	$0.453^{IV}e \pm 0.01$	$0.437^{IV}d \pm 0.02$	$0.413^{IV}c \pm 0.02$	$0.388^{IV}b \pm 0.04$	$0.338^{IV}a \pm 0.04$
95	$0.447^{V}e \pm 0.02$	$0.415^{V}d \pm 0.04$	$0.405^{V}c \pm 0.01$	$0.358^{V}b \pm 0.02$	$0.332^{V}a \pm 0.02$

Absorbances in the same row with different letters are significantly different ($P < 0.05$)
Absorbances in the same column with different superscripts are significantly different ($P < 0.05$)

Table 3. Model constants and coefficients of determination for decolourisation of black shea butter at different temperatures.

	Freundlich constants			Langmuir constants		
Temperature (°C)	n	K	R^2	X_{max}	b	R^2
55	4.09	34.44	0.76	0.13	2.41	0.75
65	4.67	57.02	0.97	0.14	2.41	0.90
75	3.11	7.76	0.90	0.12	1.93	0.85
85	2.52	3.38	0.91	0.12	1.58	0.86
95	2.42	2.38	0.90	0.11	1.42	0.83

Table 4. Model constants and coefficients of determination for decolourisation of yellow shea butter at different temperatures.

	Freundlich constants			Langmuir constants		
Temperature (°C)	n	K	R^2	X_{max}	b	R^2
55	3.62	70.80	0.91	0.10	3.10	0.90
65	4.05	166.73	0.91	0.11	3.38	0.96
75	4.54	180.02	0.79	0.10	4.04	0.93
85	4.67	683.91	0.78	0.10	4.00	0.91
95	4.74	916.22	0.86	0.11	4.13	0.97

X decreased and the residual relative amount of pigments at equilibrium X_e increased during the decolourisation of black shea butter or colour development might be occurring due to oxidation enhancement caused by the increase in temperature. Sabah and Çelik reported that peroxides act by reducing absorbance of chlorophyll and other pigments through their oxidation, and therefore decrease the bleaching performance of adsorbent (Sabah and Celik, 2005). On the other hand, during the decolourisation of yellow shea butter at constant adsorbent mass % as shown in table 2, it is observed that as temperature increased the absorbance decreased, which is the opposite of what was observed for the decolourisation of black shea butter. In this case, the amounts of pigment adsorbed X increased and the residual relative amount X_e in the liquid phase decreased.

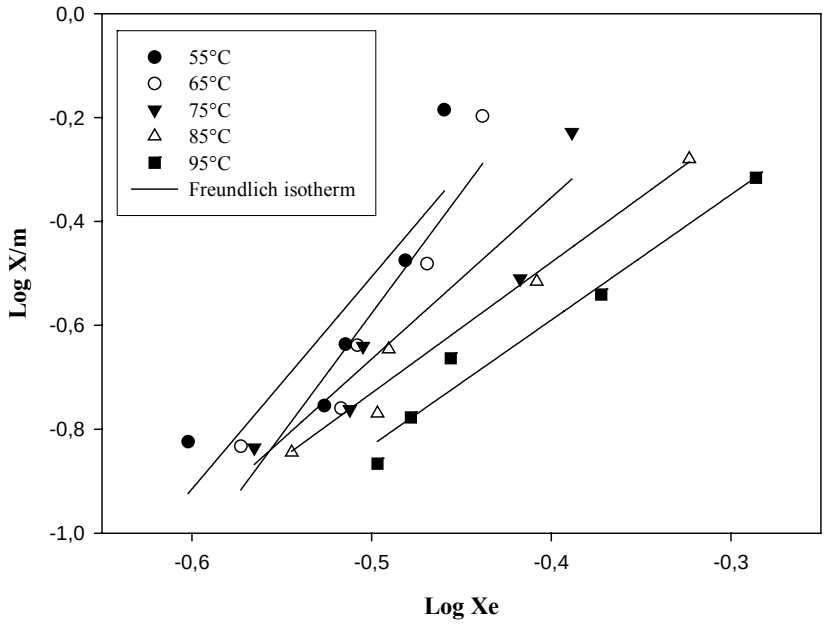

Fig. 1. Freundlich adsorption isotherms of black shea butter (stirred at 150 rpm, heated for 30min). X the relative amount of pigments adsorbed at adsorbent mass m; X_e the residual relative amount of pigments at equilibrium.

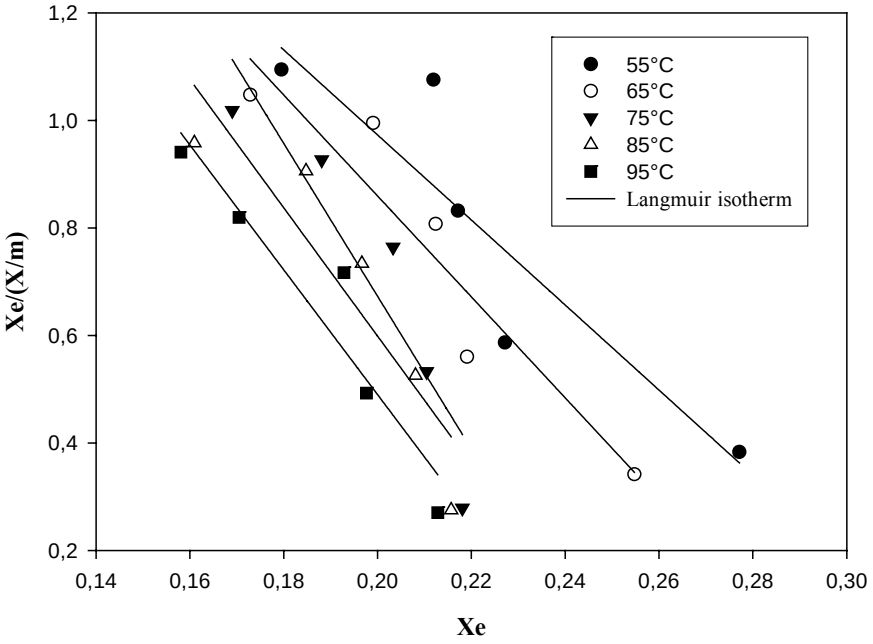

Fig. 2. Langmuir adsorption isotherms of black shea butter (stirred at 150rpm, heated for 30min). X the relative amount of pigments adsorbed at adsorbent mass m; X_e the residual relative amount of pigments at equilibrium.

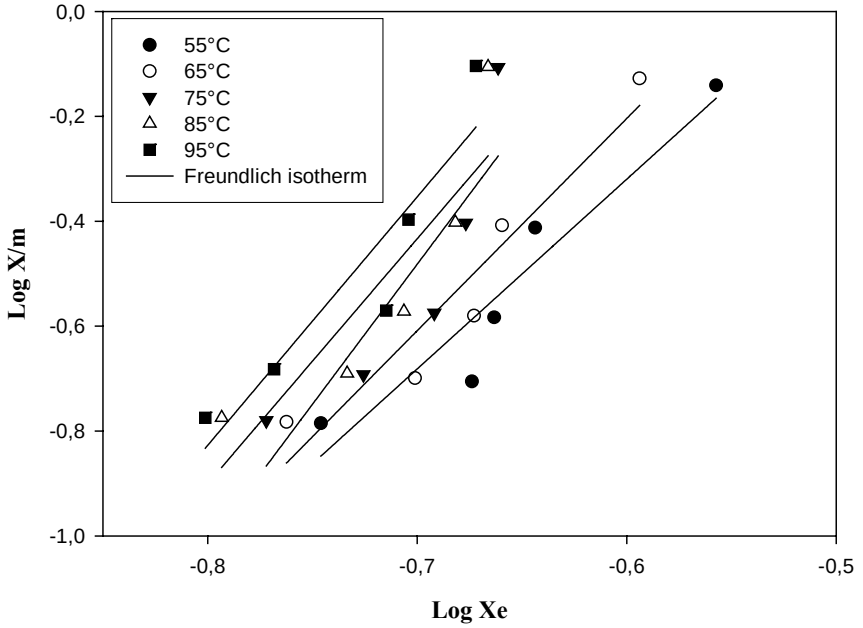

Fig. 3. Freundlich adsorption isotherms of yellow shea butter (stirred at 150 rpm, heated for 30min). X the relative amount of pigments adsorbed at adsorbent mass m; X_e the residual relative amount of pigments at equilibrium.

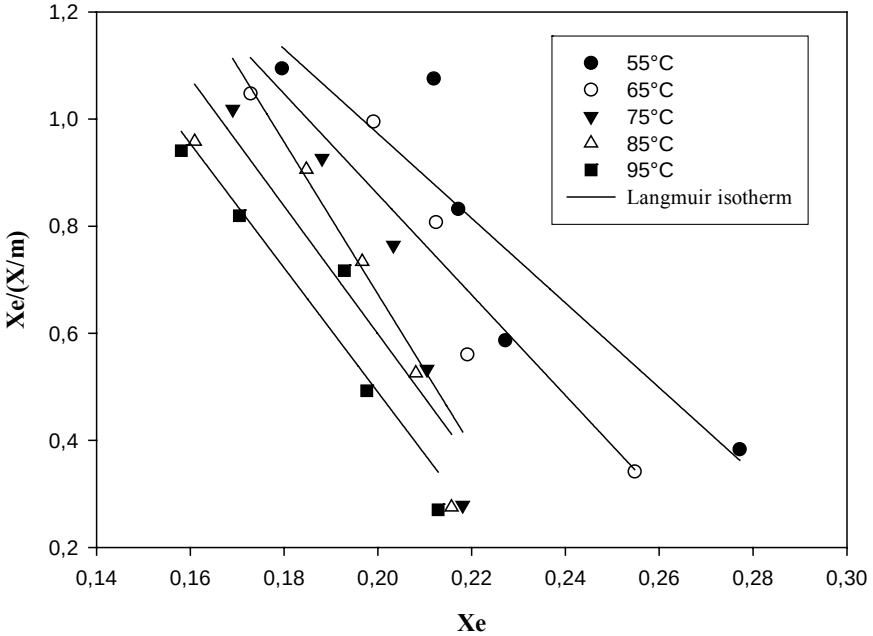

Fig. 4. Langmuir adsorption isotherms of yellow shea butter (stirred at 150 rpm, heated for 30min). X the relative amount of pigments adsorbed at adsorbent mass m; X_e the residual relative amount of pigments at equilibrium

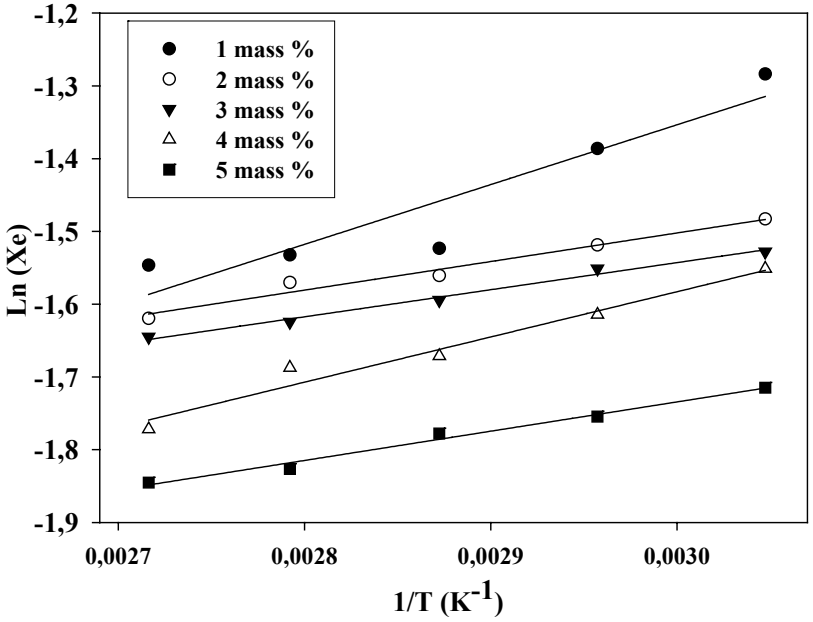

Fig. 5. Temperature dependence of the equilibrium at 1, 2, 3, 4 and 5 adsorbent mass %. Xe the residual relative amount of pigments at equilibrium; T temperature in Kelvin

These observations seem to support the assertion that higher temperatures create more adsorption sites in the adsorbent (Sabah *et al*., 2007).

Adsorption isotherms of black shea butter

The Freundlich and Langmuir adsorption isotherms of the decolourisation of black shea butter with tonsil fuller earth at various temperatures are presented in figure 1 and 2. The values of Freundlich and Langmuir constants in addition to the correlation coefficients are presented in table 3. Data presented in table 3, it is noticed that the adsorption intensity (n, b) reached a maximum at 65°C and then decreased along the range of temperature 65-95°C. Sabah (2007) reported that bleaching of some vegetable oils at high temperature (80-100ºC) and at even high dosages of adsorbent is ineffective in provoking pigment adsorption, because high temperatures encourage oxidation that produces peroxides. The peroxides act to oxidise the pigments and therefore decrease the bleaching performance of the adsorbent. From these results, it could be stated that for decolourisation of black shea butter using tonsil fuller earth, a better decolourising power attained at a temperature of 65°C (K= 57.02, n = 4.67) as indicated by the Freundlich model (R^2 = 97%). The values of n (2.42 - 4.67) appear to be in agreement with the usual range of 1 - 10 obtained for favourable adsorption. A similar trend was observed in the Langmuir model, i.e. highest value of adsorption capacity (X_{max}= 0.1) and intensity of adsorption (b = 2.41) attained at the same temperature (65°C) with R^2 = 90%. It was reported that a bleaching process where b from Langmuir equation is high implies that a small quantity of adsorbent would be consumed (Sabah, 2007). In other words, bleaching earth adsorbs much pigment during colour removal. From these results it might be reported that the adsorption of pigments in black shea butter using tonsil fuller earth obeys the Freundlich model at temperature of 65°C. Hence black shea butter should be decolourised at 65°C.

Adsorption isotherms of yellow shea butter

Figure 3 and 4 show Freundlich and Langmuir adsorption isotherms of the decolourisation of yellow shea butter using tonsil fuller earth at different temperatures. It is noticed that the application of the two models in decolourisation of yellow shea butter vary according to the data in table 4.

These data show that, for the decolourisation of yellow shea butter using tonsil fuller earth, the intensity of adsorption n of Freundlich model and b of Langmuir model increased with an increase in temperature (Table 4). Highest values were achieved at 95 °C for both cases. On the other hand, though the capacity of adsorption (X_{max}) of Langmuir model not followed a clear pattern, the capacity of adsorption K of Freundlich model increased with an increase of temperature and the highest value (916.22) attained at 95°C. Furthermore, the values of the coefficient of determination of the Freundlich and Langmuir isotherms at 95°C indicate that the Freundlich model explained only 86% of the adsorption process,

while Langmuir model explained 97%. Therefore, the Langmuir model better fitted the adsorption isotherm data of decolourisation of yellow shea butter.

Determination of the enthalpy of adsorption, change in entropy and Gibbs free energy

Temperature dependence of the residual relative amount of pigments at equilibrium (Xe) (Fig. 5) at 1, 2, 3, 4, and 5 adsorbent mass % provides the calculation of the heat of adsorption (ΔH^o_{ad}) and the change in standard entropy (ΔS^0_{ad}). From the data in table 5, it is observed that decolourisation of yellow shea butter using tonsil fuller earth is a physical phenomenon, since all the values of enthalpy of adsorption (ΔH^o_{ad}) were less than 20 kJ/mol (Sabah, 2007). The values of coefficients of determination (Table 5) suggested that the adsorption isotherm data were well fitted (R^2 = 0.97-0.99). The negative values of ΔH^0_{ad} (-3.03 -7.05) for the decolourisation of yellow shea butter indicated that the decolourisation is an exothermic process, while the negative values of ΔS^0_{ad} (-0.022 - 0.032 $kJmol^{-1}$) referred to a high binding strength between the colour material and the adsorbent (Liu *et al*., 2004). The negative values of ΔG^o_{ad} in table 6 suggesting that, the adsorption process is spontaneous and that the overall process is thermodynamically favourable. It is also shown that the magnitude of ΔG° generally increased as temperature increased, indicating a greater driving force to sorption, and subsequently leading to higher adsorption capacity at higher temperatures i.e. higher temperatures favour the removal of pigments.

CONCLUSION

Langmuir adsorption isotherm model fitted well the decolourisation of yellow shea butter at 95°C, while Freundlich model fitted well the decolourisation of black shea butter at 65°C. Moreover, the absolute value of enthalpy of adsorption showed that the decolourisation process of shea butter is a physical phenomenon, whereas the negative values of Gibbs free energy suggested that, the adsorption is spontaneous process. Also, the negative values of entropy referred to a high binding strength between the pigments and the adsorbent.

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Symbols used

A_0 Absorbance of crude shea butter
A_t Absorbance of decolourised shea butter at equilibrium time t
b Langmuir adsorption equilibrium constant (g/mg)
m Mass of adsorbent (g)
n, K Freundlich constants
R Universal gas constant (8.31414 $Jmol^{-1}K^{-1}$)
R^2 Correlation coefficient
T Temperature (Kelvin)
X Relative amount of pigments adsorbed (mg/g)
X_e Residual relative amount of pigments at equilibrium (mg/g)
X_{max} Quantity of pigment adsorbed at monolayer (mg)
ΔG^o_{ad} Gibbs free energy of adsorption ($kJmol^{-1}$)
ΔH_{ad} Enthalpy (heat) of adsorption ($kJmol^{-1}$)
ΔS^o_{ad} Change in standard entropy ($kJmol^{-1}$)

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