Research Article

The UV-Vis spectrophotometric studies of natural dye absorption on a *Sida-rhombifolia*/Cotton blended fabric

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ABSTRACT

The environmental considerations in natural dye have gained prominence in the contemporary textile processing industry. Natural dyes have been exploited from a variety of plants. Some of these natural dyes have no substantive for cellulose fabrics so requires assistance of mordant during its application. Techniques were developed to extract dyes from red sandal wood (RSW) and avocado seed (AS) for the dyeing of *Sida-rhombifolia* blended fabric (SRBF). Solvent (ethanol and acetone) extraction method was found suitable for the dye extraction from red sandal wood and avocado seed. UV-Vis spectrophotometric studies were investigated on the dye absorption. Dyeing with RSW exhibited better rate of absorbance colour than AS dye. The concentration of each dye was determined using a calibration curve. The $R^2 = 0.9669$ for RSW and $R^2 = 0.9895$ for AS values accompanied the calibration curve and were considered good. Absorbance/exhaustion of dyes were determined and characterization was done by carrying out kinetic/equilibrium absorption and the thermodynamic absorption of isotherms. The kinetic and thermodynamic studies of red sandal wood dyes have higher rate of dyeing and higher affinity value of 28.3KJ/mol^{-1} at 80°C for SRBF than avocado seeds with affinity value of 14.09KJ/ mol^{-1} . The enthalpy and entropy of dyeing were also found to be positive for both dyes, hence confirming the increasing randomness at the solid/solution interface during the absorption of dyes. Washing and Rubbing Fastness properties were investigated according to the British Standard (EN BS 20105). The results ranged from 4-5 according to grey scale standard indicating that the colour on a dyed fabric can strongly resist fading out when washed or rubbed against a white fabric. It can be concluded that natural plants in Cameroon have considerable potentials as a source of natural dye.

Keywords: *Sida rhombifolia* blended fabric, dyes, red sandal wood, avocado, Mordant

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Resumé

Les considérations environnementales liées aux colorants naturels ont pris de l'importance dans l'industrie contemporaine de transformation des textiles. Des colorants naturels ont été exploités à partir d'une variété de plantes. Certains de ces colorants naturels n'ont aucun effet sur les tissus cellulosiques et nécessitent donc l'aide d'un mordant lors de leur application. Des techniques ont été développées pour extraire les colorants du bois de santal rouge (RSW) et des graines d'avocat (AS) pour la teinture du tissu mélangé Sida-rhombifolia (SRBF). La méthode d'extraction par solvant (éthanol et acétone) s'est avérée appropriée pour l'extraction du colorant du bois de santal rouge et des graines d'avocat. Des études spectrophotométriques UV-Vis ont été réalisées sur l'absorption du colorant. La teinture avec le RSW présentait un meilleur taux d'absorbance de la couleur que le colorant AS. La concentration de chaque colorant a été déterminée à l'aide d'une courbe d'étalonnage. Les valeurs R2 = 0,9669 pour RSW et R2 = 0,9895 pour AS accompagnaient la courbe d'étalonnage et ont été considérées comme bonnes. L'absorbance/épuisement des colorants a été déterminée et la caractérisation a été réalisée en effectuant une absorption cinétique/à l'équilibre et une absorption thermodynamique des isothermes. Les études cinétiques et thermodynamiques des colorants pour bois de santal rouge ont montré un taux de teinture plus élevé et une valeur d'affinité plus élevée de 28,3 KJ/mol-1 à 80 °C pour le SRBF que les graines d'avocat avec une valeur d'affinité de 14,09 KJ/mol-1. L'enthalpie et l'entropie de la teinture se sont également révélées positives pour les deux colorants, confirmant ainsi le caractère aléatoire croissant à l'interface solide/solution lors de l'absorption des colorants. Les propriétés de résistance au lavage et au frottement ont été étudiées conformément à la norme britannique (EN BS 20105). Les résultats allaient de 4 à 5 selon la norme d'échelle de gris, indiquant que la couleur d'un tissu teint peut fortement résister à la décoloration lorsqu'elle est lavée ou frottée contre un tissu blanc. On peut conclure que les plantes naturelles du Cameroun ont un potentiel considérable en tant que source de colorant naturel.

Mots clés : tissu mélangé Sida rhombifolia, colorants, bois de santal rouge, avocat, mordant
(google.com traslated)

Introduction

The word "dye" is employed in almost all disciplines of art and fashion. Dyes have been extracted from natural resources since ancient times: the use of natural colorants pose no problems in terms of waste disposal and can provide a natural finish to textiles. Defining a color and turning the tint are indeed of paramount importance in many areas such as dyeing, paintings, printings, clothing, pictures, and screens. Hundreds of investigations have been carried out over the years in order to elaborate dyes with specific properties for targeted applications.

A dye is generally described as a colored substance that has an affinity to the substrate to which it is being applied (Jadhav *et al,* 2012).

The release of harmful waste during the manufacturing of synthetic dyes and their utilization causes serious health issues due to the toxic chemicals associated to the dyeing process. These affluent do not turn out to damage only the environment but has a harmful effect on humans, causes water pollution, Eco-balance disturbance and even global warming. Some countries like Germany, USA and even UK have banned the use of azo dyes which produces 22 amines which are highly lethal. These affect most traders, consumers and suppliers who nowadays focus on the utilization of ecofriendly products with less waste effect on the environment and humans. The advantages and disadvantages associated with their production and usage has obliged dyers to search for alternative sources, particularly natural dyes. Wool fabric was mordanted with natural mordant agents extracted from the waste of three different plants. After the mordanting process, the samples were dyed with the natural dye extracted from the cone of *Chamaecyparis lawsoniana*.(Kilinc, M. *et al* 2015) Finally, the fastness properties, color strength (K/S) values and antimicrobial properties of samples were investigated in terms of the type of mordant. Dyes are generally applied in a solution that is aqueous and may require a mordant to improve the fastness of the dye on the material on which it is applied. Surface modification methods can improve the dyeing behaviour of natural dyes by increasing the surface roughness and/or by gaining new functional groups on the surface of the fibers.(Eyupoglu C. *et al* , 2023). Plasma, ultraviolet (UV) light, electron beam irradiation and laser treatment are examples of surface modification methods used for improving the dyeing properties of textile materials.

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Sida rhombifolia fibres which is used in making fishing lines in Niger, large hunting-nets in the Central African Republic, and ropes to lash firewood in Cameroon reveals its similarities with jute, hemp and kenaf fibers (stem fibers) but the difference lies in its medicinal value (Mejouyo *et al.*, 2020, Nkemaja *et al*, 2014). Attempts were made to soften the fiber using suitable enzymes in order for it to be used for fabrics. *Sida rhombifolia* blended fabric has under gone chemical processing such as dyeing with some synthetic dyes such as vat dyes and reactive dyes.

Sustainable dyeing with natural compounds has gained more attention for a wide range of functional properties and environmental benefits (Merdan, N. *et al*, 2017). The purpose of this study was to investigate aqueous and solvent technique of extraction of dyes from red sandal wood and avocado seed and then apply on *Sida rhombifolia* blended fabric. A blended fabric in this study is *Sida rhombifolia* fibres mixed or blended with cotton fibres. The literature survey indicates that no work has been reported in the field dyeing *of Sida rhombifolia* blended fabric with the use of natural dyes. It is then important to investigate the spectrophotometric studies on *Sida rhombifolia* blended fabric after dyeing it with natural dyes.

2. Material and Methods

2.1 Material

2.1.1 Chemicals and Plants

All the Chemical reagents used for this study were ethanol, acetone, aluminum sulphate, soda ash, vinegar, common salt, and sodium hydroxide.
Plant samples used were avocado seeds and red sandal wood powder extracted from red wood tree.

2.1.2 Equipment and the fabric

The main standard apparatus used for dyeing was RE300DB digital water bath and the apparatus used for analysis was UV-Vis spectrophotometer (UV-3600plus) (mark of UV-Vis spectrophotometer).

A blended fabric of weight 157g/m^2 warp density 403.73 and filling density 387.81. The warp and the weft yarn have the count of 40s and 38s respectively.

2.2 Methods

2.2.1 Preparation of avocado seed samples for dye extraction

As seen in figure 1, avocado seeds were separated from the fruits, washed and then crushed using a 3mm HAODA tabletop drum grater to reduce the sample sizes for easy drying. The 832 grams of crushed fresh avocado samples were spread on a tray and slotted in an oven for drying. The samples were dried in an oven for 24 hours at 70 ^{0}C with continuous checking and weighing until a standard weight of 306 grams was obtained. The dried avocado seed samples were then allowed to cool for 60mins and sieved using a locally made hand sieve.

a) Avocado Seeds b) Crushed seed C) Sieved avocado powder

Figure 1: Preparation of avocado seed dye extract

2.2.2 Extraction of avocado dye extract

Stages involved in the proper extraction of avocado extract are shown in figure 2. A set of 3 experiments each comprising of 30 g avocado seed blended paste with 300 ml of acetone was mixed in a 1000ml beaker using a spatula 3-4 times in an hour (60mins) at pH 7, ML:R 1:10 then later subjected to stirring in a RE300DB digital water bath for sonication and evaporation of acetone to take place for 60mins at 70 °C (Figure 2). An additional 2ml ? of acetone was added and the mixture centrifuged using TDL-50 ELECTRIC CENTRUFUGE. The supernatant was collected and filtered using grade 1 Whatman filter paper and the clear dye filtrate was obtained.

a) Powder Avocado seed b) TDL-50 Electric Centrifuge c) Avocado Seed Extract

Figure 2: Solvent (acetone) extraction of avocado seed

2.2.3 Preparation Sandal Wood

Figure 3 presents the Red sandal wood sawdust powder bought from wood merchandizers and obtained through sandpapering and drilling of holes from designed furniture were air-dried at room for one week, sieved and stored in a well closed container in preparation for dye extraction.

a) Block of red wood b) Plank from the wood c) Saw dust from the plank

Figure 3 Preparation for red sandal wood for extraction

2.2.4 Extraction of red sandal wood extract

The dried material wood powder was weighed and dissolved in ethanol solvent using a variety of extracted apparatus (Tablet Counter Soxhlet Extractor, RE300DB digital water bath and TDL-50 electric centrifuge) as seen in figure 4. The solvent evaporated at the temperature 70 °C and pH 7 in an evaporating dish (beaker) over a water bath to obtain dye extract

a) Powder Form b) TDL-50 electric centrifuge c) RE300DB digital water bath

Figure 4: Solvent (ethanol) extraction process of red sandal wood

2.3 MORDANTING PROCEDURES

Double pre-mordanting procedures were employed using aluminum sulphate (Al_2SO_4) and soda ash (Na_2CO_3), vinegar and common salt. In pre-mordanting, the mordant was added into the beaker containing ample amount of distilled water to dissolve then added to the mordanting bath and brought to a boil. The mordanting fabric was then submerged into the solution and the whole mixture left to boil for 30 mins at 90 ^oC. The solution was allowed to cool, and the fabric gently removed and air dried in preparation for second mordanting. This same procedure was repeated for the second mordanting and the fabric was then air dried to make them ready for subsequent dyeing. Post mordanting was performed on the samples during the last 30mins of the dyeing process by using aluminum sulphate and soda ash on both red sandal wood and avocado seed dye bath and also vinegar and common salts on different dye bath.

2.4 Dyeing procedures for *Sida-rhombifolia* blended fabric (SRBF)

In the dyeing process, 5% of dye extract was diluted with distilled water in 1:10 L/R. Dyeing process was carried out by immersing non-mordanted *Sida rhombifolia* blended fabric (SRBF) into 3 dyebaths of 60 °C, 70 °C and 80 °C for red sandal wood extract and same condition for avocado seeds extract. To achieve maximum dye absorbance/exhaustion of avocado seed dyes the extracts were buffered to pH 9 before dyeing by careful addition of diluted sodium carbonate solution (Kechi *et al.*, 2013).

Pre-mordanted SRBF were later separately dyed with red sandal wood and avocado seeds under the same conditions previously described. The samples were dyed for 180 mins at the pH of 9-10, MR of 1:10 and at different temperature ranges. After dyeing, the dyed fabrics were removed from the dye bath, left to cool, washed gently using laundry soap to remove loose dyes.

2.5 UV-VIS spectrophotometric study

The ultraviolet visible spectrophotometric study which is a spectral scan use to determine the hue and absorbance of aqueous or non-aqueous extracted solution of purified natural dye whose UV-zone and the visible ranges from 190 to 700nm or higher indicating the peak and troughs in different wavelength. The peak and troughs in visible zone indicate the main colour and absorption while the ultraviolet zone with or without peaks showed the property of dye under light which may be correlated with fastness properties.

2.5.1 Calibration curve

The amount of dye adsorbed onto a fabric was calculated using equation 1. Where q_e is the amount of dye adsorbed at equilibrium, C_o is the initial concentration of dye in the solution, C_e is the final concentration of dye at equilibrium, M is the mass of adsorbent (g) and V is the volume of solution (ml). Concentration of dye was calculated by plotting a calibration curve at wavelength 504 nm for RSW and 480 nm for AS dyes.

$$q_e = \left(\frac{C_o - C_e}{M}\right) \times V \qquad \text{Eq1}$$

In line with the objectives of this study, the initial and equilibrium dye concentrations were determined using a calibration curve figure 3.6. The amounts of RSW and AS dye adsorbed onto SRBF were calculated using equation 1. Concentration of dye 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 were calculated by plotting a calibration curve at wavelength 504 nm for RSW and 480 nm for AS respectively using a beer lambert plot.

2.5.2 Selection of suitable wave length:

A wave length of 288 nm to 504 nm for peak and trough was found to give maximum optical density for red sandal wood and 380nm to 480nm was found to give maximum optical density for avocado seeds. These said peak and troughs figures adopted for this study were that of (Gulrajani *et al.,* 2002) for and (Dabas *et al.*, 2011) for some natural dyes.

2.5.3 Absorbance/ Exhaustion study

After obtaining the dye bath ratio, 2ml of the prepared aqueous dye solution was filled in a spectrophotometer glass cuvette and the solution subjected to a wavelength scan in V1000 spectrophotometer at a wavelength range from 288 to 504nm for red sandal wood and 380 to 480nm for avocado seed. These wavelengths were taken at the initial stage of dyeing then continued at 30, 60, 90, 120, 150, and 180 minutes respectively for each dyeing temperature 60°C, 70°C and 80°C for both red sandalwood and avocado seed dyes. The corresponding absorbance wavelength values were then recorded and further used for the plotting of absorbance against wavelength graph.

2.6 Kinetic/equilibrium studies

For the rate of dyeing measurement (dyeing Kinetics), an aqueous dispersion of avocado dye was prepared, and the bath buffered with sodium carbonate to give an alkaline constant pH of 9. Studies of dyeing kinetics were carried out on a *Sida rhombifolia* blended fabric dyed for the varying period between 30mins to 180minutes at 60°C, 70°C and 80°C respectively on a RE300DB digital water bath. The dye uptake was measured at different intervals by evaluating the extinction value at 504nm ëmax for red sandal wood and 480nm ëmax for avocado seed on a V1000 UV-Vis spectrophotometer. The initial and equilibrium dye concentrations were determined using a calibration curve based on absorbance at $ë_{max}$ (504 nm) versus dye concentration 0.05, 0.1, .02, 0.3, 0.4, and 0.5 in standard dye solution. The amount of dye adsorbed per gram of SRBF (mg/g) at time (q_t) and the equilibrium (q_e) was calculated by mass-balance equations as follows, where C_o is the initial dye concentration (mg/l), C_t is dye concentration (ml/l) at time t and C_e is the dye concentration (ml/l) at equilibrium. V is the volume of dye solution (ml) and W is weight of SRBF (g) used. All experiments were carried in triplicate and the average values were taken to minimize random error (Chandravanshi & Upadhyay, 2014).

$$q_t = (C_o - C_t) \times \frac{V}{W} \qquad \text{Eq 2}$$

$$q_e = (C_o - C_e) \times \frac{V}{W} \qquad \text{Eq 3}$$

Pseudo first and second-order kinetics models were used to analyze experimental data of absorption kinetics of RSW and AS dyes on *Sida rhombifolia* fabric.

$$\frac{dq_t}{dt} = k_1\,(q_e - q_t) \qquad Eq\ 4$$

K_1 is the pseudo first-order rate constant and q_e and q_t are amount of dye absorbed in mg/g of SRBF at equilibrium and at time t respectively. After applying the initial concentration, we had the following equation,

$$\ln(q_e - q_t) = \ ln q_e - k^1 t \qquad Eq\ 4.$$

2.6 Thermodynamic studies

For thermodynamic studies, dyeing was carried out using a range of dye concentrations over a period of 180 minutes at 60 °C 70 °C and 80 °C keeping the MLR and pH same as that of kinetics. The avocado seed dye liquor was buffered in all cases to obtain an alkaline pH and the amount of dye in fabric estimated using the same procedure as described in kinetics.

2.6.1 Adsorption Isotherm

The quantitative estimation of the dye in the fabric and that left in the dye bath was done with results plotted as adsorption isotherms. In order to predict the nature of the best fit isotherm two models of dye sorption were utilized; the Langmuir and Freundlich isotherms which defined the theoretical model for a particular design system which was to serve as a basis for calculation of thermodynamic parameters.

2.6.2 Dye affinity

Dye affinity or chemical affinity was calculated using equation 5

$$-\Delta\mu = R\,T \ln \{[D]\}_f / V[D]_s\} \qquad \text{Eq 5.}$$

Where R is the universal gas constant (8.317JK^{-1}) (?? Give the value of R in kjkj), T is the temperature of dyeing in kelvin, $[D]_f$ the dye absorbed by the fabric (g/kg), $[D]_s$ dye in solution (ml/l) and V the volume of internal Phase of the fabric (l/kg?? what is this unit?). The value of V of a particular fabric taken is equal to the moisture regain of that fabric at 100% RH which was reported by (Moshi *et al.*, 2019).

2.6.3 Enthalpy of dyeing

Heat or enthalpy (ÄH) of dyeing was calculated using equation 6;

$$[D]_f = \frac{T_2\,\Delta\mu_1 1 - T_1 \Delta\mu_2}{T_1 - T_2} \qquad \text{Eq 6.}$$

Where T_1 is the initial dyeing temperature, T_2 is the final dyeing temperature, $Äì_1$ is affinity for T_1 °C and $Äì_2$ is affinity for T_2 °C.

2.6.4 Entropy and Gibb's free energy

The entropy or ÄS and Gibb's free energy has the following equation (Eq 7)

$$-\Delta\mu = \Delta G = \Delta H - T\Delta S \qquad \text{Eq 7}$$

Where –Äì is the dye affinity, ÄH is the heat or enthalpy of dyeing, T is the temperature, ÄS the entropy of dyeing and ÄG is the Gibb's free energy.

2.7 FASTNESS PROPERTIES

Colour fastness is the resistance of a material to change in any of its colour characteristics or extent of transfer of its colorants to adjacent white material in touch. The resistance of a material to change its colour can also be due to different environmental conditions or treatments like washing, dry cleaning and exposure to different agencies like heat, light etc.(breakdown the sentence too long and limit the use of "and so on" and "etc" The colour fastness is usually rated either by loss of depth of colour or colour change in original sample, or its often expressed by staining scale which means the accompanying material gets tinted (stained) by the colour of the original fabric when made to touch by means of text procedures (A. K. Samanta & Agarwal, 2009).

2.7.1 Colour fastness to wash

1-gram dyed sample was placed between two pieces of non-dyed sample and these three pieces were held together by stitching the edges round. These set of three fabrics were submerged into a washing bath in the ratio 1:40 containing soap. The sample was treated at the temperature of 40 °C for 1 hour and then removed, rinsed in cold water and dried.

2.7.2 Colour fastness to rubbing

The rubbing fastness was carried out with the use of a crock meter. A white piece of cotton fabric was rubbed 10 times according to the British standard (BS EN 20105) against the dyed fabric. The white fabric was then removed and compared to the standard samples for subjective evaluation.

3 RESULTS AND DISCUSSION

3.1 Avocado and Red Sandal dyes extracted

The avocado seed and red sandal dyes were extracted using acetone and ethanol as solvents. Figure 5 shows the extracted samples.

a) avocado dye extract

b) red sandal wood extract

3.2 Dyed samples of the blended fabric

The dyed samples are: non mordanted fabric, mordanted fabric with $Al_2(SO_4)_3$ + Na_2CO_3 and mordanted fabric with $C_2H_4O_2$ +NaCl dyed separately with red sandal wood and avocado seeds extract. One can notice an identical shades of colour on the 9 samples (figure 7 and 8). These samples were further analyzed with spectrophotometer.

It is reported that the pre-mordanting of cellulose fabrics with the use of 20% alum and 5% sodium carbonate is the most suitable system for dyeing bast fibers fabrics with red sandal wood (A. K. Samanta *et al*., 2008a). Hence the same system has been used for this study with evident outcome.

3.2.1 Dyed samples with red sandal wood

Figure 6 presents samples of *Sida rhombifolia* blended fabrics dyed with red sandal wood extract

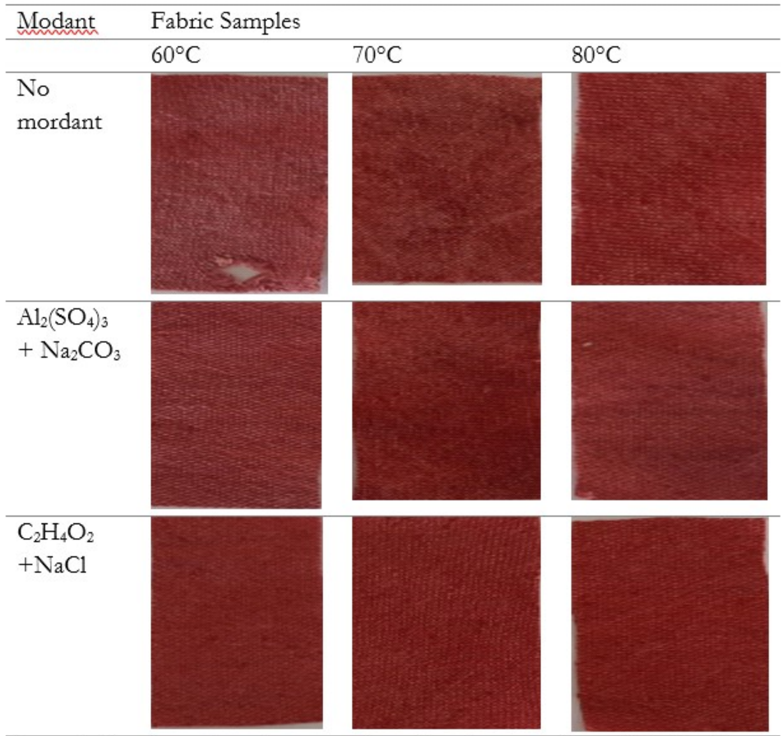

Figure 6: Dyed samples of non-mordanted and pre-mordanted SRBF with red sandal wood extract

3.2.2 Dyed samples with avocado seed extract.

Figure 7 presents photos of samples of *Sida rhombifolia* blended fabrics dyed with avocado seeds extract.

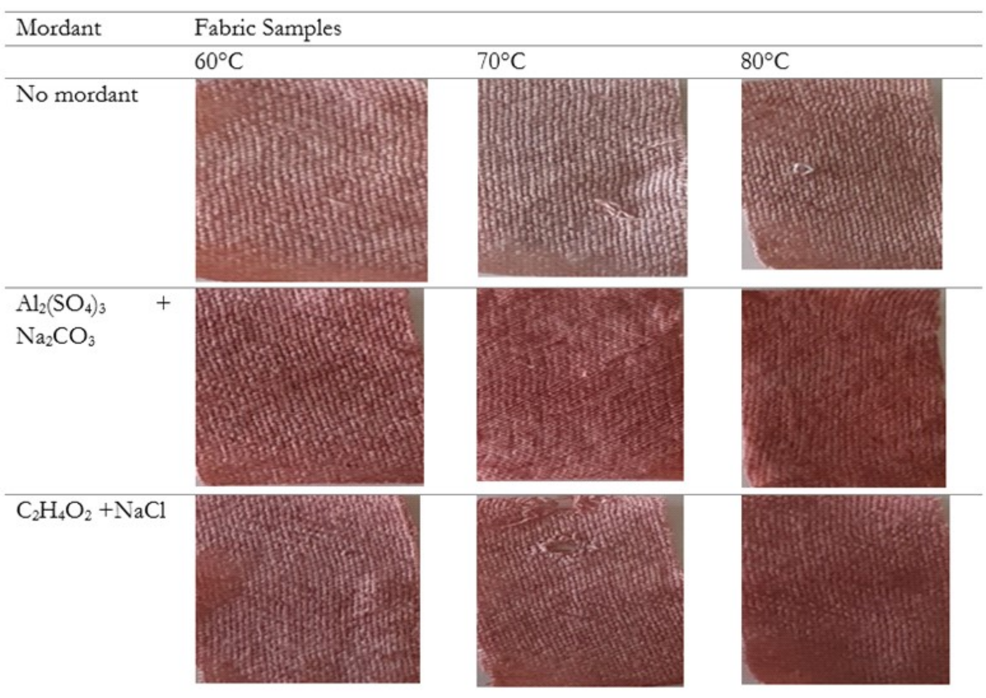

Figure 7: Dyed samples of non-mordanted and pre-mordanted SRBF with avocado seeds extract

3.3 UV-Vis spectrophotometric analysis

3.3.1 Calibration curve

The $R^2 = 0.9669$ values for RSW and $R^2 = 0.9895$ for AS (Figure 8) were considered 'good' because the R^2 values that accompanied our calibration curve are measurements of how closely our curve matches the data we generated from the initial and equilibrium dye concentration and the closer the values are to 1.00, the more accurately our curves represent our detector response (Dolan, 2009).

3.3.2 Absorbance/Exhaustion of RSW and AS dyes on SRBF

Figures 9 -14 present dye absorbance/exhaustion curves obtained from dyeing the SRBF with RSW and AS with and without the aid of mordant. The non mordanted fabric, the $Al_2(SO_4)_3$ + Na_2CO_3 mordanted fabric and the $C_2H_4O_2$ +NaCl mordanted fabric were dyed in different dyebath to obtain independent shades. The uniform shade physically observed on the sample dyed with RSW dye extracted and the higher rate of absorbance as seen on figure b with a unified red colour formation. This is an indication that RSW is better compared to AS dye extracted which produced a tone of peach colour palette with slightly lower absorbance rate as seen on figure d. This is in line with the ethanol extract of RSW for the dyeing of nylon and wool which showed a higher absorption rate and good affinity for nylon (Gulrajani *et al*., 2002), and avocado seed giving a higher absorbance rate on cotton and silk fabric treated with alum mordant due to the flavonoids responsible for colour found in avocado seed (BAI, 2017). Comparing the absorbance/ exhaustion curve of non-mordanted SRBF (Figure a and c) one can clearly notice the effects of mordants in the dyeing of SRBF with RSW and AS. Dyeing temperature ranges from 60^0C to 8^0C do not have any significant effects on the rate of absorbance.

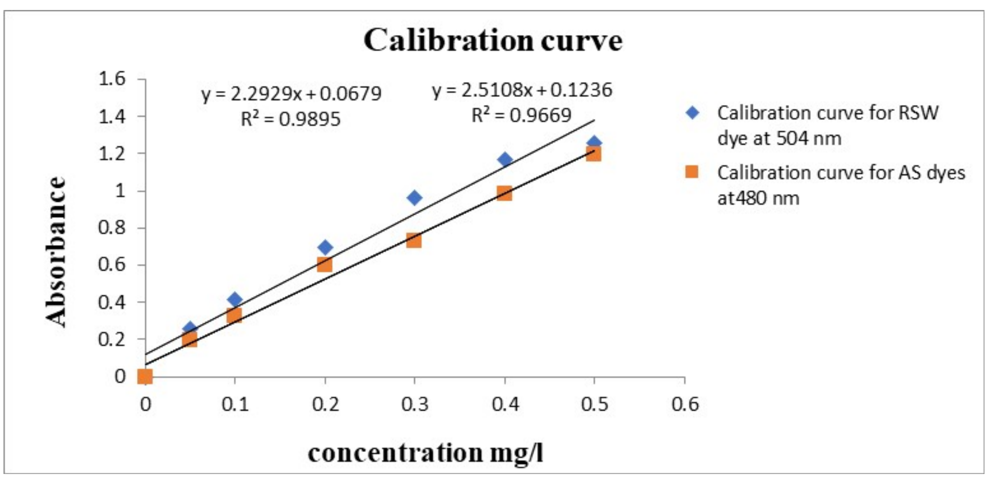

Figure 8: Calibration curve for RSW at wavelength of 504 nm and 480 nm for AS

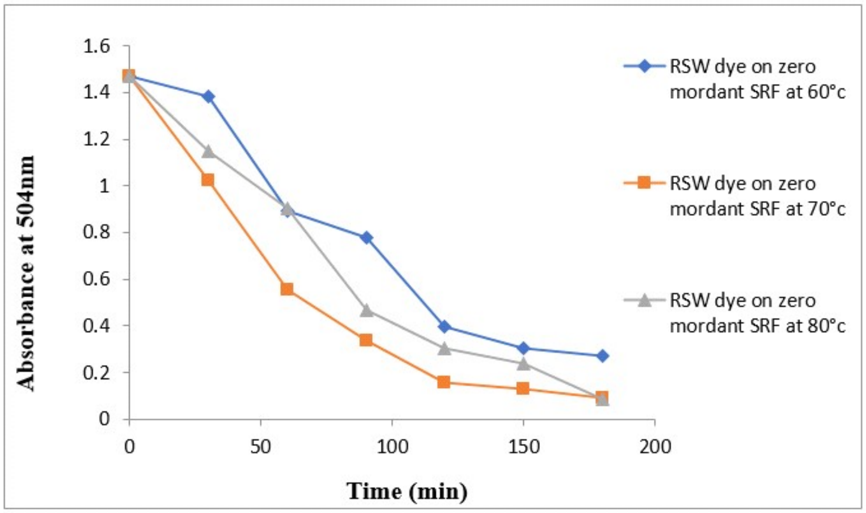

Figure 9: RSW dye absorbance/exhaustion curve on non-mordanted SRBF.

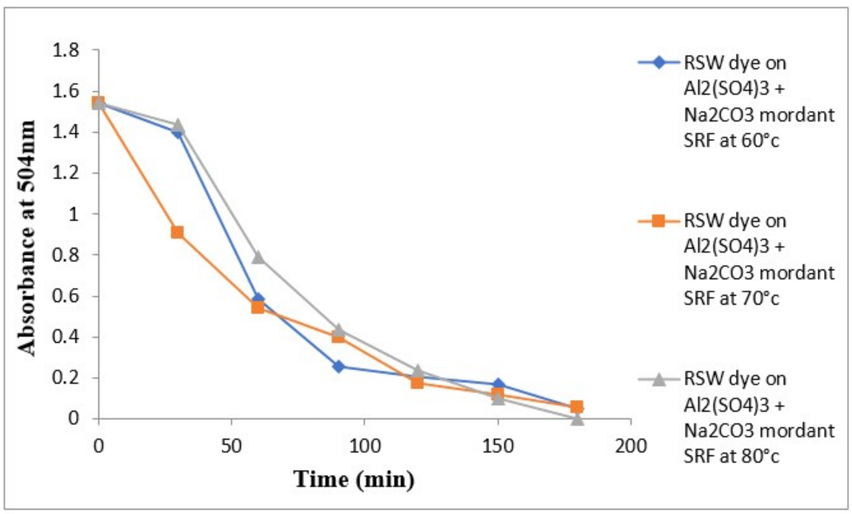

Figure 10: RSW dye absorbance/exhaustion curve on $Al_2(SO_4)_3 + Na_2CO_3$ mordanted SRBF.

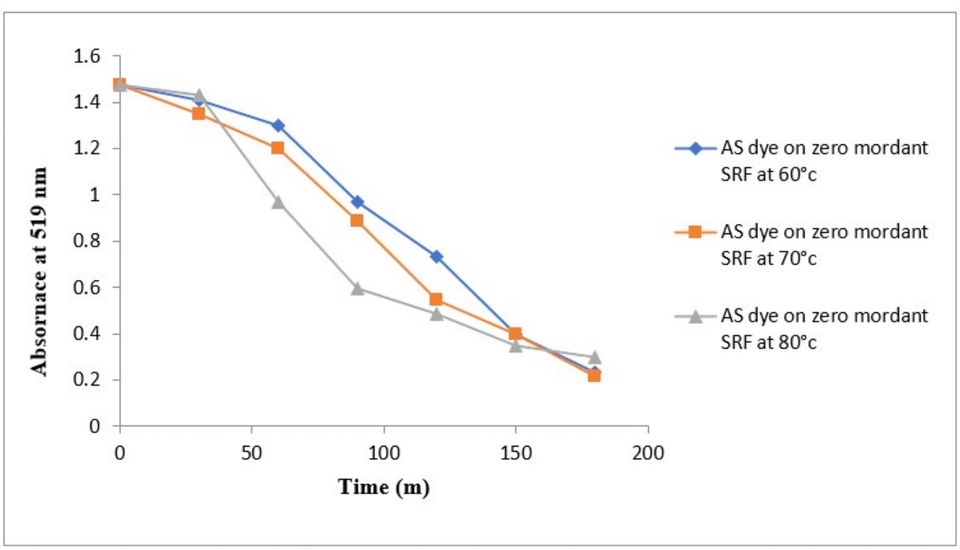

Figure 11: AS dye absorbance/exhaustion curve for non-mordanted SRBF.

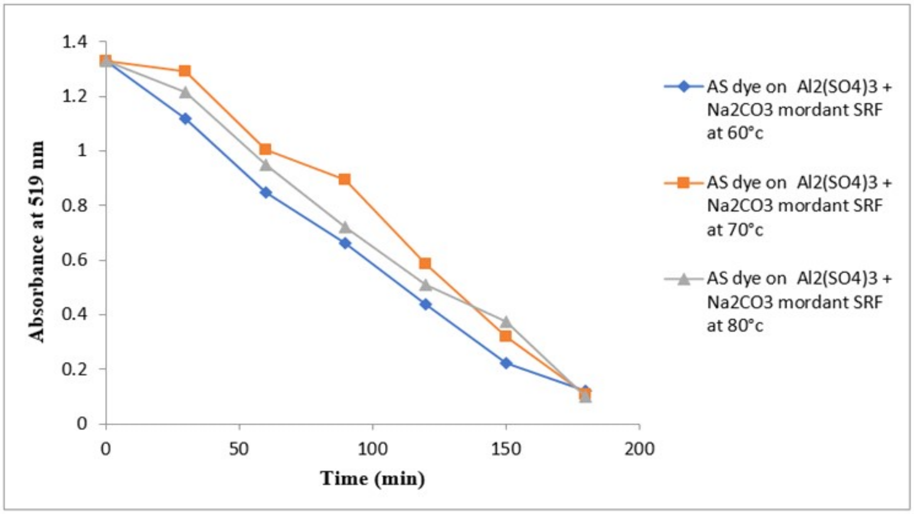

Figure 12 : AS dye absorbance/exhaustion curve for $Al_2(SO_4)_3 + Na_2CO_3$ mordant SRBF.

It is also noticed that similar results to that of mordanted SRBF are obtained in dyeing of mordanted SRBF with RSW and As. However, RSW continues to give a better absorbance rate (Figure e) compared to AS (figure f)

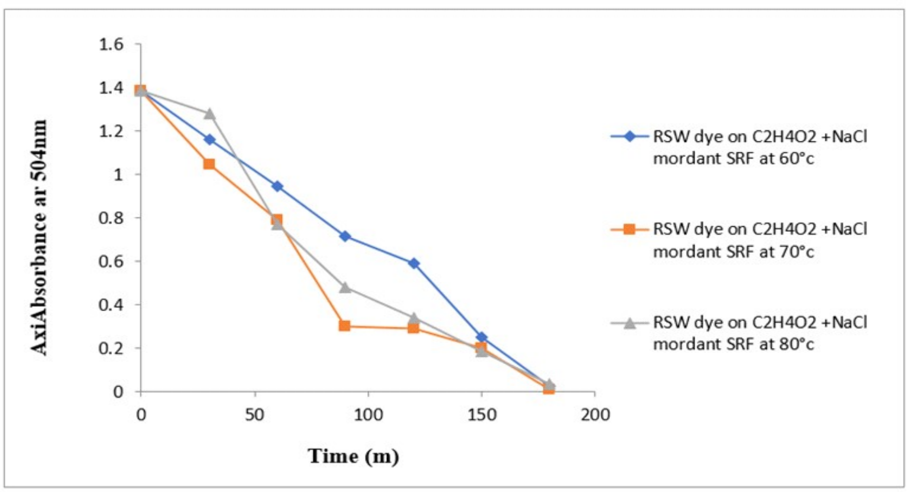

Figure 13: RSW dye absorbance/exhaustion curve for $C_2H_4O_2$ + NaCl mordant SRBF

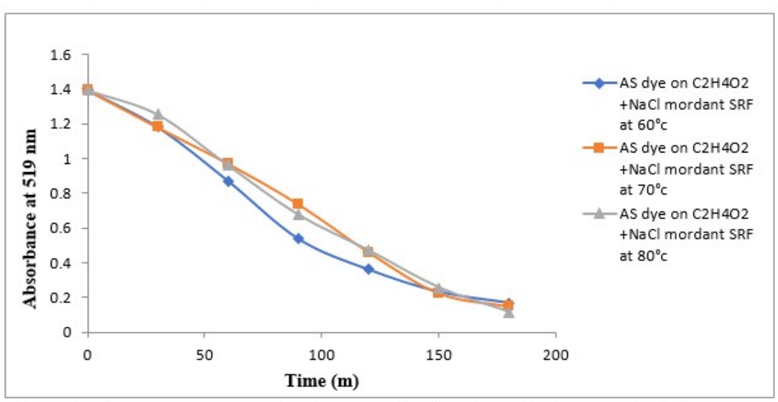

Figure 14 : AS dye absorbance/exhaustion curve for $C_2H_4O_2$ + NaCl mordant SRBF.

3.4 Kinetic/equilibrium studies

The exhausted dye bath was estimated by evaluating the extinction value at 504 nm ëmax and 519 nm ëmax for red sandal wood and avocado seed, respectively. From the results of dye concentrations in the liquor or solution (D_s) before and after dyeing for specific time of dyeing and the corresponding amount of dye exhausted in the fabric (D_f) were estimated by subtraction method. These results of pair of D_s and D_f for different cases were used for calculation of thermodynamic parameters of dyeing namely – $\Delta\mu$(dye affinity), rate of dyeing, ΔH (heat of dyeing), ΔS (entropy of dyeing) and ΔG (Gibb's free energy).

It was noticed that the adsorption uptake of dye increased in dye bath with the contact time and subsequently balanced at 150 minutes for both red sandal wood and avocado seed. Once this equilibrium was attained, all the active sites on the adsorbent surface were saturated but further adsorption occurred. The mordant substances ($Al_2(SO_4)_3 + Na_2CO_3$ and $C_2H_4O_2 + NaCl$)) have a significant effects on RSW as seen on Figure 10 and 13. On the other hand, there is no significant effects on avocado seeds (AS) on addition of mordants (as seen on Figure 12 and 14. The results is in line with a that of (Zuber, M. *et al* 2019) in the study of the Influence of microwave radiation on dyeing of bio-mordanted silk fabric using neem bark (*Azadirachta indica*)-based tannin natural dye

3.5 Degree of Exhaustion

Table 1 and 2 summarize the experimental values of the degree of dye absorbance/exhaustion obtained from dyeing of mordanted and non-mordanted *Sida rhombifolia* blended fabric (SRBF) with red sandal wood (RSW) and avocado seed (AS).

Table 1: The value of degree of exhaustion of dye bath for RSW dyes on SRBF

RED SANDAL WOOD DYE

SRBF	Temp	PH	Time (m)	Absorbance q_e	q_t	q_e-q_t	Exhaustion % dye bath
No mordant	60°C	10	180	1.471	0.27	1.201	81.64
	70°C	10	180	1.471	0.094	1.377	93.60
	80°C	10	180	1.471	0.089	1.382	93.94
$Al_2(SO_4)_3$ + Na_2CO_3 Mordanted SRBF	60°C	10	180	1.539	0.05	1.489	96.75
	70°C	10	180	1.539	0.056	1.483	96.36
	80°C	10	180	1.539	0.001	1.538	99.93
$C_2H_4O_2$ + NaCl mordanted SRBF	60°C	10	180	1.385	0.025	1.36	98.19
	70°C	10	180	1.385	0.011	1.374	99.20
	80°C	10	180	1.385	0.037	1.348	97.32

As noticed on Table 1, the percentage of exhaustion of RSW (ranges from 81.64% to 99.93%) is a clear indication that RSW is generally suitable for the dyeing of SRBF. Dyeing quality can be improved with the use of mordant as dyeing assistants in the dyeing process,

Table 2 The value of degree of exhaustion of dye bath for AS dyes on SRBF
AVOCADO SEED DYE

SRBF	Temp	PH	Time (mins)	Absorbance q_e	q_t	q_e-q_t	Exhaustion % dye bath
No mordant	60°C	9	180	1.475	0.231	1.244	84.33
	70°C	9	180	1.475	0.217	1.258	85.28
	80°C	9	180	1.475	0.298	1.177	79.79
$Al_2(SO_4)_3$ + Na_2CO_3 mordant	60°C	9	180	1.327	0.121	1.206	90.88
	70°C	9	180	1.327	0.111	1.216	91.63
	80°C	9	180	1.327	0.101	1.226	92.38
$C_2H_4O_2$ + NaCl mordanted SRBF	60°C	9	180	1.395	0.168	1.227	87.95
	70°C	9	180	1.395	0.148	1.247	89.39
	80°C	9	180	1.395	0.115	1.28	91.75

Avocado Seed dyes are equally good for the SRBF with and without mordant. However, the dyeing quality can also be improved by adding mordant as dyeing assistants.

3.6 Thermodynamic analysis

3.6.1 Absorption isotherm

Results obtained from the experiment of dye uptake measurements of RSW and AS dyes on SRBF at 60 °C, 70 °C and 80 °C are presented in table 3a and b with isotherm. The most widely used two parameters equation describing the adsorption process is the Langmuir equation (Eq 8) showing the linearity form of the equation

$$\frac{C_e}{q_e} = \frac{1}{Q \times b} + \frac{1}{Q} C_e \qquad \text{Eq 8}$$

Where Q is the maximum amount of dye absorbed per unit weight of fabric on high equilibrium dye concentration C_e, q_e is the amount of dye absorbed per unit weight of the fabric at equilibrium and b is Langmuir constant related to the affinity of bonding. The value of Q indicated a practical limiting adsorption capacity when the surface is fully covered with the dye molecule. The best fit isotherm indicates the partition mechanism of dyeing corresponding to the linear model with correlation coefficient R^2 = 0.9895 for RSW and R^2 = 0.9669 for AS of hydrophobic and hydrophilic fabrics with non-ionic dyes. The slope of the isotherm increases with increase in temperature for both RSW and AS dyes into SRBF. The applicability of adsorption isotherm were also observed by (Gulrajani et al., 2002) in dyeing nylon and wool and also by (A. K. Samanta et al., 2008b) in dyeing cotton and jute. This observation confirms that the mechanism of dyeing using non-polar natural dyes is like that of disperse dyes on synthetic fabrics. The slope and statistical analysis for best fit isotherm are presented in figs a and b.

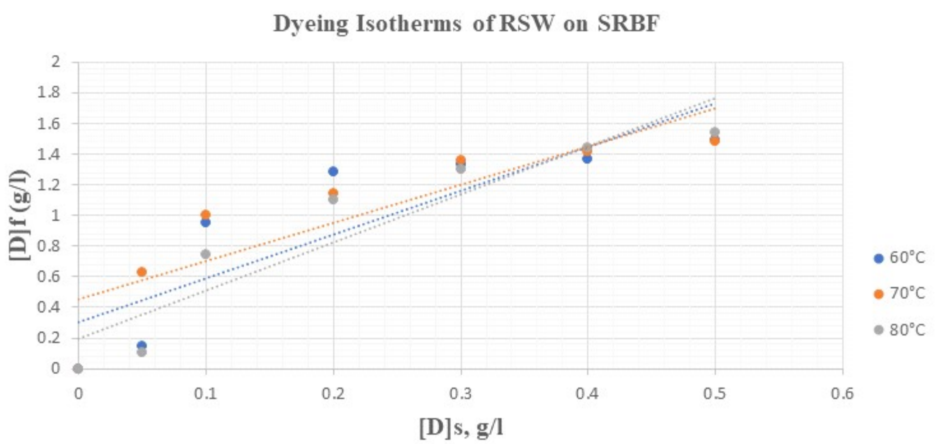

Figure 15: Dyeing isotherms for RSW dyes on SRBF

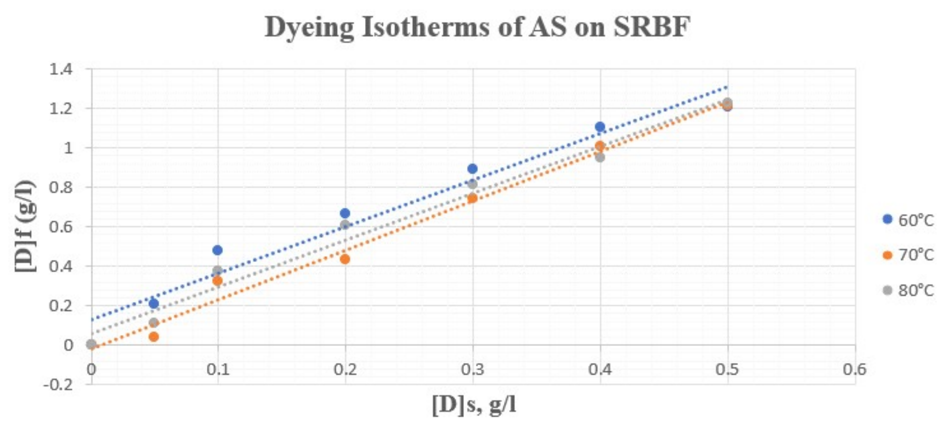

Figure 16: Dyeing isotherms for AS dyes on SRBF

The dye affinity $(-\Delta\mu)$ was calculated using Eq (5) above for mordanted SRBF dyed with the use of both RSW and AS dyes at 60 °C, 70 °C and 80 °C as presented in table 3. It was observed that the standard affinity in both dyes increased with increased temperature (from 60 °C to 80 °C) as indicated in the isotherm. Moreover, the affinity values for RSW were higher than that of AS dyes with the highest value at 28.3 KJ/mol^{-1} at 80 °C.(Table 3). Dye affinity studies have been carried out on fabric like nylon dyed with RSW at varying temperature between 70 °C and 100 °C with 27. 57 KJ/mol^{-1} as values obtained, wool dyed using *arnebia nobilis* at 70-90 °C with 7-29 KJ/mol^{-1} and cotton and jute using jackfruit with 7.57 KJ/mol^{-1} and 9.75 KJ/mol^{-1} respectively (Gulrajani et al., 2002), (Arora et al., 2012), (A. K. Samanta et al., 2008b). Based on these studies, it has been observed that the red sandal wood has a higher affinity on cellulosic fabrics than other natural dyes.

Table 3: Calculated values of thermodynamics parameters for SRBF

$[D]_f$, g/kg			$[D]_s$, g/l			$-\Delta\mu$, kJ/mol						ΔH kJ/mol	ΔS kJ/mol
						With V			Without V				
333.15	343.15	353.15	333.15	343.15	353.15	333.15	343.15	353.15	333.15	343.15	353.15		
SRBF with RSW dye													
1.201	1.377	1.382	0.27	0.094	0.089	10.51	14.22	14.81	9.4	12.36	12.5	11.45	105.27
1.489	1.483	1.538	0.05	0.056	0.001	15.77	15.91	28.3	14.12	13.82	23.89	21.89	201.16
1.36	1.374	1.348	0.025	0.011	0.037	17.44	20.34	17.31	15.61	17.67	14.62	13.39	123.07
SRBF with AS dye													
1.244	1.258	1.177	0.231	0.217	0.298	11.04	11.58	10.79	9.88	10.06	9.11	8.34	76.7
1.206	1.216	1.226	0.121	0.111	0.101	12.74	13.39	14.09	11.4	11.64	11.89	10.89	100.13
1.227	1.247	1.28	0.168	0.148	0.115	11.88	12.64	13.83	10.63	10.99	11.68	10.7	98.32

$[D]_f$ – conc. of dye in fabric, $[D]_s$ – conc. of dye in solution, $-\Delta\mu$ – dye affinity, ΔH- Heat of dyeing, ΔS – entropy of dyeing and V- internal volume of fabric.

3.6.2 Enthalpy (ΔH) and Entropy (ΔS)

The results of ΔS on table 3 were calculated using Eq 7. The entropy for dyes in the fabric is positive though higher with 21.89 KJ/mol^{-1} for RSW than AS dyes. Again, the entropy values for dyeing nylon and wool using RSW were found to be positive (Gulrajani et al., 2002), whereas that of *nobilis* on wool were negative -22.05 KJ/mol^{-1} (Arora et al., 2012). It can be concluded that the positive values of entropy confirm the increasing randomness at the solid/solution interface during the absorption since the positive values of enthalpy also confirms that the adsorption is endothermic in nature.

3.7 Fastness Properties due to washing and rubbing

Results of wash fastness previously carried out showed on table 5 that non-mordanted SRBF dyed with AS presents very good fastness property for both staining and colour change (4-4), whereas SRBF dyed with RSW present a deep red colour slightly different from its original dyed colour on colour change and excellent fastness property on colour staining (4-5). This implies that the dyes have substantive and affinity for SRBF which enable the auxochromes to properly diffuse and desorb into the fabric.

Table 4: Slope and statistical parameters of isotherms

Parameters	SRBF with RSW dye			SRBF with AS dye		
	60°C	70°C	80°C	60°C	70°C	80°C
Slope	0.008	0.007	0.009	0.006	0.007	0.006
SD	0.616	0.531	0.628	0.45	0.468	0.449
R	0.913	0.927	0.985	0.995	0.988	0.996
Intercept	0.156	0.32	0.051	0.028	-0.106	-0.037

SD - Standard deviation and R - Correlation coefficient

3.7 Fastness Properties due to washing and rubbing

Results of wash fastness previously carried out showed on table 5 that non-mordanted SRBF dyed with AS presents very good fastness property for both staining and colour change (4-4), whereas SRBF dyed with RSW present a deep red colour slightly different from its original dyed colour on colour change and excellent fastness property on colour staining (4-5). This implies that the dyes have substantive and affinity for SRBF which enable the auxochromes to properly diffuse and desorb into the fabric.

Table 5: Colour fastness of SRBF for RSW and AS

SRBF	RSW Dye				AS Dye			
	Washing fastness		Rubing fastness		Washing fastness		Rubing fastness	
	CS	CC	wet	dry	CS	CC	wet	dry
Unmordanted	4	4	3/4	4	4	4	4	5
$Al_2(SO_4)_3$ + Na_2CO_3 mordanted	4/5	5	4	5	3/4	5	4/5	5
$C_2H_4O_2$ +NaCl mordanted	4/5	5	4/5	5	4	5	5	5

Results of rub fastness showed that non-mordanted SRBF dyed with AS presented very good rubbing fastness ranging from (4-5) for wet rubbing (Table 5) whereas all pre/post mordanted fabric presented excellent fastness (5) for both wet and dry rubbing. For SRBF dyed using RSW dyes, all the 3 samples of the fabrics showed acceptable fastness rating from very good to excellent (4-5) for wet rubbing and excellent for dry rubbing (5).

3.8 Conclusion

Solvent method is successfully used for the dye extraction of dyes from red sandal wood (RSW) and avocado seed (AS). Dyeing with RSW exhibited better rate of absorbance colour than AS dye. Absorbance/exhaustion of AS and RSW dyes give good results which indicates that the dyes are suitable for dyeing. However, it is noticed that in the thermodynamic kinetic studies, RSW has higher rate of dyeing and higher degree of affinity for the blended fabric than avocado seeds. The fastness properties (washing, rubbing and light) of RSW and AS dyes show that the colour can resist on the fabric during usage. It can be concluded that natural plants in Cameroon have considerable potentials as a source of natural dye. The perspectives of this study is to optimize the method of extraction of dyes and application of mordants during dyeing process.

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