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COST EFFECTIVE STRATEGY FOR THE SYNTHESIS OF AZO DYES BY USING CASHEW NUT SHELL LIQUID (CNSL)

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ABSTRACT

The synthesis and dyeing properties of two types of azo dyes are reported in this paper. The two types of dyes were obtained from coupling of amino cardanol with unsaturated anacardic acid [ACUSA (Aminocardanol unsaturated anacardic acid)] and saturated anacardic acid [ACSA (Aminocardanol saturated anacardic acid)] separately. Both, anacardic acid and aminocardanol were obtained from CNSL as their source material. ACSA dyes were solid and dark brown while ACUSA were gelatinous and dark red. The performance of both ACUSA and ACSA dyes was moderate on textile fabrics with varying cotton content. The dyeing efficiency of the ACUSA was better than that of ACSA. ACUSA dyes had 33% total extent of fixation on the 100% cotton fabrics and 27% for 35% cotton and 65% polyester content fabrics. Likewise, 13% total extent of fixation was observed for ACSA on 100% cotton fabrics and 12% on 35% cotton and 65% polyester fabrics. While ACUSA had a fair fastness to washing on 100% cotton fabrics, the rest had poor fastness. Successful synthesis of azo dyes starting from CNSL as the only carbon source demonstrates further the versatility of this renewable resource as an industrial raw material.

Key words: Azo dyes, Anacardicacid, Aminocardanol and Cashew Nut Shell Liquid.

INTRODUCTION

Of all commercially produced dyes, azo dyes form the largest class,this is however, due to their multipurpose applications such as in textile industries, printing industries and pharmacology. The dyes are characterized by the presence of azo group, a chromophoric group (Karci et al. 2006, Sharma et al. 2004). The color exhibited by azo dyes is a result of the conjugated bond system which allows them to exhibit absorption in the visible light ranging from 400-750 nm (Pereira and Alves 2012, Sudha et al. 2014). The compounds are not easily biodegradable under natural conditions and they resist chemical and microbial attacks as well as stable to light and washing (Okoro et al. 2008, Furry and Viemont 1935). Their stability in light and washing make them a good choice for textile fabrics dyeing (Furry and Viemont 1935).

Various synthetic methods towards azo dyes have been described, including the earliest where diazotized aromatic amine were coupled with activated aromatic compounds, whereby, the conversion to diazonium salts was achieved at 0-5 °C in $NaNO_2$ and mineral acid (Mirjalili et al. 2012).Some synthetic methods utilize reagents/chemicals that are environmentally unfriendly; this include, the use of lead tetraacetate for oxidation of aromatic amines, and use of lead metal for nitroaromatics reduction (Clark 1995,Firouzabadi and Mostafavippor 1983,Ohe et al. 1989,Osuka et al. 1983).

CNSL is a renewable material which is cheap and easily available in huge amounts in form of thick reddish brown oil contained in the interior sponge part of the Cashew Nut Shell (CNS)fromthe cashew plant

Anacardiumoccidentale (Vanker 2008,Senger et al. 2012,Sornprom 2007).The CNSL is characterized by specific gravity, moisture content, iodine value, total volatile content, viscosity, and polymerization hardening time.These properties makes CNSL important in various applications in industrial processes (Chaudhar et al. 2012, Rodrigues et al. 2011). Important broad applications of the versatile CNSL include; break lining, paints, primers, foundry chemicals, lacquers, cements and coatings (Sibbarao et al. 2011,Akinhanmi et al. 2008,Kathir et al. 2013).Chemically, CNSL is composed of anacardic acid (**1**), cardanol (**2**), cardol (**3**) and traces of 2-methylcardol (**4**) (Figure 1) in various proportions depending on the method of extraction.

Figure 1: Chemical composition of *n*-CNSL

Extraction of CNSL can be thermal,solvent extraction, vacuum distillation as well as using supercritical carbon dioxide. The *thermally extracted*-CNSL is composed of mainly cardanol [60-95%], cardol [4-19%] and minute amounts of anacardic acid [1-2%] while the solvent extracted and supercritical carbon dioxide extracted CNSL (natural-CNSL; *n*-CNSL) is composed of anacardic acid [60-65%]; cardanol [10%]; cardol [10-15%], and traces of 2-methylcardol] (Philip et al. 2008, Gandhi et al. 2013).

Although a number of synthetic procedures towards azo dyes from CNSL have been reported; such as, Suwanprasopet al.(2004)who synthesized cardanol based azo dyes where cardanol was coupled with diazotized anilines;and Mkunguet al.(2013)who utilized anacardic acid from CNSL to couple with commercially available aminophenol, none of them have utilised CNSL as the only starting material (Mkungu et al. 2013,Suwanprasop et al. 2004). This article reports on the synthesis of azo dyes from CNSL in three main steps, namely; isolation of anacardic acid and synthesis of amino cardanol, followed by diazotization and lastly coupling. Other methods reported earlier utilized expensive and commercially available starting materials, thus, the focus was to shift to cheap, renewable and locally available starting materials. Therefore, this paper reports on the synthesis of azo dyes using CNSL as the sole starting material. Therefore, this paper reports on the synthesis of azo dyes using CNSL as the sole starting material.

MATERIALS AND METHODS

Materials

The cashew nuts were collected from Masasidistrict in Mtwara region and sent to Jumbo Industry at Vingunguti Dar es Salaam for unshelling to obtain the cashew nut shells. Analytical chemicals and reagents supplied by Sigma-Aldrich, England were used without any further purification. The fibers (100% cotton and 35% cotton: 65% polyester) were bought from K.H Khimji& Sons Ltd MnaziMmoja Dar es Salaam.

Instruments

Concentration of extracts throughout the experiment was done using Rotary evaporator Model R205. Hydrogen generator was used as the source of hydrogen used for hydrogenation of anacardic acids. UV measurements were done with SHIMAZDU 240 double beam UV-Visible spectrophotometer. Brucker FT-IR spectrometer was used for IR analysis.

2.3 Methods

Extraction of CNSL

Crashed cashew nut shells (3.6 Kg) were socked in 3.7 L of petroleum ether for 4 days. The petroleum ether solution was filtered and the extract was concentrated on a rotary evaporator at 45°C, yielding 326.54 g of CNSL asa dark reddish brown viscous liquid.

Isolation of Anacardic Acid

CNSL (100 g) was dissolved in 5% aqueous methanol (600 mL),50 g of calcium hydroxide were then added in small portions while stirring.When calcium hydroxide was completely added, the temperature of the reaction mixture was raised to 50 °C for 3 hrs with continued stirring. The mixture was cooled, filtered and washed thoroughly with methanol (400 mL) to yield 129.25 g of calcium anacardate. 100 g of calcium anacardateweremixed with 400 mL distilled water and concentratedHCl (120 mL) was added in small portions while stirringand left for 1 hour. The reaction mixture was extracted withethyl acetate (2 x 300 mL), the obtained organic layer was then washed with distilled water (2 x 200 mL) and dried over anhydrous sodium sulfate, to yield 58 g of unsaturated anacardic acid (Gandhi et al 2012; Kumar et al 2008; Paramashivappa et al 2001). The FT-IR spectroscopic analysis of the product had the following peaks: 3400 cm^{-1}, 3008.05 cm^{-1}, 2923.76 cm^{-1}, 2852 cm^{-1}, 1694.26, 1606 cm^{-1}, 1577.72 cm^{-1}, 1449.13 cm^{-1}, 1375.84 cm^{-1}, 1208.12 cm^{-1} and 822.63 cm^{-1}.

Hydrogenation of the Unsaturated Anacardic Acid

To 80 mL of ethanol were dissolved 40 g of unsaturated anacardic acid, followed by addition of 0.75 g of 10% Pd/C catalyst. The mixture was then placed into anautoclave connected to a hydrogen generator and the reaction proceeded for 24 hours. Then the content was filtered using celite and the anacardic acid solution rotary evaporated,to yield 25.5 g (63.75%) of grey solid saturated anacardic acid (TBS 1979; Mkungu et al 2013).The FT-IR analysis revealed absorption bands at, 3008.05 cm^{-1}, 2852 cm^{-1}, 3365.94 cm^{-1}, 2923.53 cm^{-1},1711 cm^{-1},1578 cm^{-1}, 1450.57 cm^{-1}, 1376.11 cm^{-1}.

Decarboxylation of Saturated Anacardic Acid

In a round bottomed flask were placed 20 g of saturated anacardic acid (SAA) and heated in a sand bath at 190 °Cfor 3 hours. At 80 °C SAA melted and bubbling occurred, indicating the melting point and the disappearance of residual water and solvents contained in the sample. At 180 °C active bubbling occurred, indicating elimination of CO_2. The sample was maintained at 190 °C for further 2 hrs to ensure complete decarboxylation (Rodrigues et al. 2011).The FT-IR spectrum of the product had absorption bands 3402.45 cm^{-1}, cm^{-1}, 2921.74 cm^{-1}, 2852.15 cm^{-1},2500-1700, 1588.55 cm^{-1}, 1267.73 cm^{-1}, 1486.31 cm^{-1} and 1455.63 cm^{-1}.

Nitration of Saturated Cardanol

In a 500 mL round bottomed flask were placed 16 g of $NaNO_3$and 40 mL distilled water wasadded to make a solution. To the $NaNO_3$ solution were cautiously added 11 mL of Conc. H_2SO_4. A suspension of 10 g of cardanol in 3.0 mL distilled water was added drop wise to sulfonitric mixture while stirring at low temperature. Once the addition was complete, the mixture was stirred for 30 minutes after which 200 mL of distilled water was added. The reaction mixture was extraction with ethylacetate to yield an oily dark-brown organic layer. The obtained organic layer was then washed with 100 mL distilled waterto yield nitrocardanol. The FT-IR spectrum showed absorption peaks at 3398.57 cm^{-1}, 2921.24 cm^{-1}, 2851.95 cm^{-1}, 1588 cm^{-1}, 1485.93 cm^{-1}, 1455.81 cm^{-1}, 1368.21 cm^{-1}, 1350.50 cm^{-1}, 1268.42 cm^{-1}.

Reduction of NitroCardanol

Nitrocardanol (6.15 g,0.02 moles) was placed in a 250 mL Erlenmeyer flask followed by addition of 3.9 g of Zinc dust (0.06 moles). The flaskwas then fitted with a reflux condenser and 35 mL of concentrated HCl were added dropwise through the condenser.The components were refluxed for 4 hours with stirring, followed by coolingto room temperature and filtering (Rughavendra and Kumar 2013, Dixit et al. 2010).To the filtrate, NaOH solution was added and extracted with diethylether to obtain nitro cardanol. FT-IR spectrum indicated 3567 cm^{-1}, 1525.22 cm^{-1}, 1626.39 cm^{-1}, 3379.72 cm^{-1}, 2922.07 cm^{-1}, 2851.59 cm^{-1}, 1570.10 cm^{-1}, 1456.28 cm^{-1}, 1404.33 cm^{-1}, 1308.02 cm^{-1}, and 1272.41 cm^{-1}.

Dye Synthesis

Two anacardic acid based azo dyes were synthesized, one being of saturated anacardic acid and the other of unsaturated anacardic acid. The synthesis of both dyesemployed two steps, namely diazotization and coupling reactions.

Diazotization

For both dyes, 3.19 g (0.01 moles) of amino cardanol were added to the mixture of 3 mL of Conc. HCl and 3 mL distilled water. The mixture was placed in ice bath and thoroughly stirred, when the temperature reached and maintained at 0 ^{o}C, 0.69 g (0.01 moles) of $NaNO_2$ dissolvedin 8 mL of distilled H_2O were added drop wise to the mixture. Brick red solution of diazonium salt was obtained.

Preparation of Coupling Components

0.4 g (0.01 moles) of NaOH in 4 mL of water was added in 3.6 g of unsaturated anacardic acid for ACUSA dyes while 3.0 g of saturated anacardic acid were used for ACSA dyes. The mixtures were then separately placed in a water bath, and were thoroughly stirred.

Coupling Reaction

The same procedure was followed for both ACSA and ACUSA dyes. A suspension of diazonium salt was added drop wise to a beaker containing aromatic coupling component while stirring vigorously at each addition. After complete addition the reaction mixture was stirred for 10 minutes. The mixture was then heated on a hot plate at 60 ^{o}C for 5 minutes and 2 g of NaCl was added andheating continued for 10 more minutes. The mixture was cooled to room temperature and extracted with methylene chloride, CH_2Cl_2. The methylene chloride layer was then washed 3 times, each with 20 mL of distilled water and later evaporated to dryness yielding 3.5 g of gelatinous dark redACUSA dye. Following the same procedure for ACSA dye yielded 3.11 g of a dark brown solid dye material. Whereas the FT-IR spectrum of the ACUSA dye showed peaks at 3008.86 cm^{-1}, 2922.81 cm^{-1}, 1687.34 cm^{-1}, 1570.19 cm^{-1}, 1606.14 cm^{-1}, 1644 cm^{-1}, 1302.45 cm^{-1}, 1208.78 cm^{-1}, 1449.46 and 1375.53 cm^{-1} that of ACSA dye had peaks at 3379.99 cm^{-1}, 2915.30cm^{-1}, 2956.17 cm^{-1}, 1702.29 cm^{-1}, 1651.63 cm^{-1}, 1570.19 cm^{-1}, 1308.00 cm^{-1}, 1218.74 cm^{-1}, 1247.97 cm^{-1}, 1465.08 and 1445.24 cm^{-1}.

Determination of the properties of synthesized dyes

The dyeing process

The prepared azo dye (0.35 g) was placed in a 1000 mL beaker and 350 mL distilled water were added and stirred. The 100% cotton fibric (23 g)was immersed in the dyeing bath and heated to 60 ^{o}C for 30 minutes. Then 2.5 g NaCl was added followed by 0.25 g Na_2CO_3 at constant temperature for another 30 minutes. Afterwards, 4 mL of 32% NaOH solution was added followed by 4 mL of 3.0 x 10^{-3} M $NaHCO_3$. The pH of the bath was maintained at 10.7 alkaline. Dyeing continued for further 45 minutes and the dye bath was cooled to room temperature. Dyed fabric was then rinsed with water at 30 ^{o}C followed by warm water(60 ^{o}C) until the final water was colorless (Chequer et al. 2013,Mkungu et al. 2013).

The same procedure was followed in dyeing 35:65 cotton/polyester fabrics.

The above process involved the ACSA and ACUSA dyes separately with two sets of fabrics composed of 100% cotton and 35% cotton: 65% polyester.

Determination of the extent of exhaustion (%E)

The extent of dye uptake by the fibres during the dyeing process was measured by monitoring the changes in the concentration of dye bath in the exhaustion stages.1 mL of liquid was sampled from dye bath at the start and at the end of the dyeing reaction. The sample was diluted using distilled water to obtain 10 mL.The absorbance of the original sample and that of exhausted dye bath weredetermined on the UV-Vis spectrophotometer.The extent of dye exhaustion (%E) for the two types of fibreswas determined using equation 1 (Sevim et al. 2011).

$$\%E = \frac{(Ai - Af)}{Ai}\ X\,100 \ldots\ldots(1)$$

Where:

A_i is the initial absorbance of the dye bath

A_f is the final absorbance of the dye in the bath during the dyeing process.

Determination of dye fixation (%F)

The dye was extracted from the dyed fabric using soxhlet extraction method, where, 5 g of piece of dry dyed fabric was extracted in 80 mL of 20% aqueous pyridine solution for 12 hours. The absorbance of the extract was analysed using UV-Vis spectrophotometer at the maximum wavelength of the respective dye. The extent of fixation (%F) was later evaluated using Equation 2 (Xie and Hou 2008,Wadia and Patel 2008).The values of the extent of fixation obtained were used to evaluate the extent of total fixation (%T) using Equation 3.

$$\%F = \frac{(Ai - Af - Ae)}{Ai - Af}\ x\,100\% \ldots(2)$$

Where:

A_i is the initial absorbance of the dye bath

A_f is the final absorbance of the dye in the bath during the dyeing process

A_e is the dye extracted from the fabric.

Total extent of fixation (%T)

The total extent of fixation is the overall fixation efficiency (%T), which depicts the amount of dye which has been exhausted (%E) from the total dye fixed (%F) in the fibre during the dyeing process. It is obtained by mathematical treatment of the values of extent of exhaustion and those of extent of fixation as in equation 3 (Anthoulias and Burkinshaw 2000).

$$\%T = \frac{\%F\ x\ \%E}{100} \ldots\ldots\ldots(3)$$

Washing fastness test

Color fastness to washing of the dyed fabric was assessed by TBS. The test method used was TZS 24 called ‘Test for color fastness-color fastness to washing” test 4. Under this method, the dyed fabrics were immersed in a bath of 0.5% detergent at 35 ^{o}Cand at liquor ratio of 50:1. After 30 minutes, the fabrics were removed, washed twice with deionized water and tap water four times, and finally air-dried at below 50 ^{o}C. Changes in shade of the fabrics were evaluated with the aid of gray-scales for color change (TBS 1979).

RESULTS AND DISCUSSION

Azo dyes were synthesized by coupling saturated and unsaturated anacardic acids separately with the diazonium salts derived from aminocardanol according to **Scheme 1**. The synthesized dyes were applied to 100% cotton and 35% cotton: 65% polyester fabrics.

Scheme1: General Scheme for the synthesis of Azo dye from anacardic acid

Several studies have revealed the structure of the dye produced after coupling reaction. Suwanprasop 2004 revealed that the disazo group occurred at the para position to the OH group of cardanol (Suwanprasop et al 2004).Maqboolet al.(2013) and Mkunguetal.(2013)also showed the azo group to be formed at the para position (Maqbool et al. 2013,Mkungu et al. 2013).Thus considering resonance and steric factors, the anticipated structures of the synthesized azo dyes are **5** and **6** as shown in Figure 2.

Figure 2: Generalized structures of the synthesized dyes

Spectral Properties

Anacardic Acid

The FT-IR spectrum of the isolated anacardicacidrevealed broad band from 2500- 3100 cm^{-1} indicating O-H stretching. Short and strong peak at 3008.05 cm^{-1} revealedsp^{2} C-H stretching, strong and sharp peak at 2923.76 cm^{-1}and 2852 cm^{-1} forsp^{3} C-H stretching. Short intensive peak at 1694.26 cm^{-1}for thearomatic C=O stretch of the carboxylic acid. Stretching frequencies at 1606 cm^{-1} and 1577.72 cm^{-1}are attributed to the C=C stretching. The FT-IR spectral data are consistent with those in literature for anacardic acid (Philip et al. 2008).

Hydrogenated Anacardic Acid

Hydrogenation of the mixture of unsaturated pentadecyl phenolic components of anacardic acid produced saturated anacardic acid as a brown solid. The FT-IR analysis revealed absorption band at 1711 cm^{-1}for the C=O stretch of the carboxylic acid. The disappearance of absorption band at 3008.05 cm^{-1} of *sp*^{2} C-H stretching indicated the conversion to saturated anacardic acid was successful. Broad band of O-H of the carboxylic acid occurred from 3100 – 3500 cm^{-1}. The C=C aromatic stretch at 1578 cm^{-1}coupled with the disappearance of alkenic band at 1606 confirmed the completion of hydrogenation.

Decarboxylation of Anacardic Acid to Cardanol

Saturated anacardic acid was heated at constant temperature of 190^{o}C to remove carbon dioxide from the sample and the process produced cardanol. The FT-IR spectrum revealed increased absorption band at 3402.45 cm^{-1} of O-H group stretching and disappearance of absorption band at 3365 cm^{-1} indicated the disappearance of –COOH group. The C=C of aromatic system appeared at 1588.55 cm^{-1}.

Nitration of Cardanol to Nitro Cardanol

Nitro phenol can be prepared by treating phenol with hot Conc. HNO_3*via* electrophilic aromatic substitution reaction. However, this reaction is very dangerous as it may cause explosion if not carried out at controlled temperature. Thus using a nitrating mixture of HNO_3 and H_2SO_4 is proved to be a convenient way of nitration. Sulphuric acid is used as a catalyst to ensure nitration takes place at lowest possible temperature. A powerful electrophile $^{+}NO_2$is produced when sulfuric acid reacts with nitric acid. Resonance contributors in phenol show presence of electron rich areas at *ortho* and *para* positions. However the use of $NaNO_3$ as source of nitric acid favours formation of *o* and *p* nitro phenol (mono nitration) (Bruce 2009).For this case, the mixture of $NaNO_3$ solution and Conc. H_2SO_4 was used as nitrating agent. The FT-IR spectrum showed absorption peaks at 3398.57 cm^{-1} for O-H stretching and 1588 cm^{-1} for the C=C aromatic vibrations at 1588. New peaks are identified at 1368.21 cm^{-1}attributed to the N=O stretching frequencies of the aromatic nitro group, 1350.50 cm^{-1}for the C-N stretching thus confirming the presence of the nitro group in the compound and a successful nitration of cardanol.

Reduction of Nitro Cardanol

Nitrocardanol was reduced using zinc powder with HCl to achieve a primary amine. The FT-IR spectrum revealed the presence of N-H stretch at 3567 cm^{-1} and N-H bending frequency at 1525.22 and 1626.39 cm^{-1} depicting amino cardanol was obtained. Other important peaks occurred at 3379.72 cm^{-1} (O-H stretching), 1570.10 cm^{-1} (C=C aromatic stretch), and 1308.02 cm^{-1} (C-N stretch).

Dye of the Unsaturated Anacardic Acid as a Coupling Component

Unsaturated Anacardic Acid (USAA) is a highly electron rich specie that was used to couple with diazonium salt as it has a strong activating group. USAA is insoluble in water and addition of base was done in constant stirring yielding dark red gelatinous dye. The failure to crystallize was probably due to the unsaturation nature of the anacardic acid. USAA has trigonal planar *sp*^{2} carbon- carbon bonds which lower the melting points hence attain liquid state at room temperature (Darley and Darley 2005).The FT-IR spectrum revealed important peaks at 3008.86 cm^{-1}for the sp^{2}

C-H stretch, 1687.34 $cm^{-1}$for C=O stretch of the carboxylic acid, 1570.19 cm^{-1} aromatic C=C stretch, 1606.14 cm^{-1} alkene C=C stretch, 1644 cm^{-1} N=N azo group and 1302.45 $cm^{-1}$for C-N stretch.

Saturated anacardic acid as a coupling component

The mixture of the unsaturated anacardic acids exist as a single compound due to the fact that all double bonds were hydrogenated to one saturated anacardic acid. It doesn't dissolve in distilled water thus addition of base with constant stirring was necessary. The use of SAA as a coupling component resulted into a dark brown solid dye. Changes of molecular structure of the unsaturated sp^2 carbon-carbon bonds to saturated sp^3 carbon-carbon bonds of anacardic acid increased the melting point to the level of changing physical state from gelatinous to solid (sp^2 carbons are trigonal planar while sp^3 are tetrahedral). Therefore this structural change caused SAA to stack well resulting in a solid stateat room temperature (Table 1), as increasing the number of double bonds lowers the melting points (Darley and Darley 2005). The FT-IR spectrum showed the presence of O-H stretch at 3379.99 cm^{-1} C=O stretch of the carboxylic acid at 1702.29 cm^{-1}, N=N azo group at 1651.63 cm^{-1}, C=C stretch of an aromatic at 1570.19 cm^{-1} andC-N stretch at 1308.00 cm^{-1}

Table 1: Summary of thePhysical Characteristics of the synthesized dye

Dye	Chemical Class	Colour	State
ACUSA	Mono azo	Red	Gelatinous
ACSA	Mono azo	Brown	Solid

Dying Properties of the Synthesized Dyes

Dying properties for the synthesized unsaturated and saturated anacardic acid dyes were determined using 100% cotton and 35% cotton: 65% polyester fibers as indicated in table 2.

The Extent exhaustion (%E)

The extent of exhaustion was measured by monitoring the changes in the absorbance of the dye at the start and at the end of the dyeing process (Figure 3). The changes in absorbance of the dye bath during the dyeing process and the extent of exhaustion that was obtained using Equation 1 are shown in Table 2. The values of the extent of exhaustion so obtained for both the ACUSA and ACSA dyes on the two sets of fabrics were compared. The highest value of extent of exhaustion obtained was 60% for ACUSA dye applied to 35% cotton: 65% polyester as indicated in figure 4. The significance of measuring the extent of exhaustion in the dyeing process was to determine the changes in concentration of the dye bath due to the adsorption of the dye molecules onto the fibres and their diffusion extent into the fibres. The high percentage extent of exhaustion is desired for better dyeing effect.

Extent of Fixation (%F)

The extent of fixation of the dye on fabrics with varied cotton content was evaluated using Equation 2. The bar chart in figure 4 depicts the percentage fixation of dyes on fabrics used.

Extent of Total Fixation (%T)

The values of the extent of fixation and the values of the extent of exhaustion in Table 2 were further used to calculate the extent of total fixation of the dyes to the fabrics using equation 3. Figure 4 gives the comparison in the extent of total fixation for the dyes

ACUSA and ACSA on the two sets of fabrics. The highest value for the total extent of fixation is 33% for ACUSA on the fibre with 100% cotton while the lowest value is 11.9% which was obtained using ACSA on the fibre with 35% cotton and 65% polyester. These values suggest that the dyeing effect was moderate, as it had been observed in the literature information that mono azo dyes do not work well with cotton as compared to the diazo (Pavia et al. 1976).

Figure 3: Dyeing process

Table 2: Dyeing properties of the synthesized dyes on fabrics

Parameter	ACUSA		ACSA	
	CP*	C*	CP*	C*
A_i	3.35A	3.3A	3.25A	3.25A
A_f	1.29A	1.485A	2.11A	1.92A
Extracted Dye	1.078A	0.726A	0.72A	0.78A
% Exhaustion	60%	55%	35%	41%
% Fixation	45%	60%	34%	32%
% Total Fixation	27%	33%	11.9%	13.12%

A_i= initial absorbance of the dye bath., A_f= final absorbance of a dye bath., CP*= 65% cotton and 35% polyester fibres., C*= 100% cotton fibres.

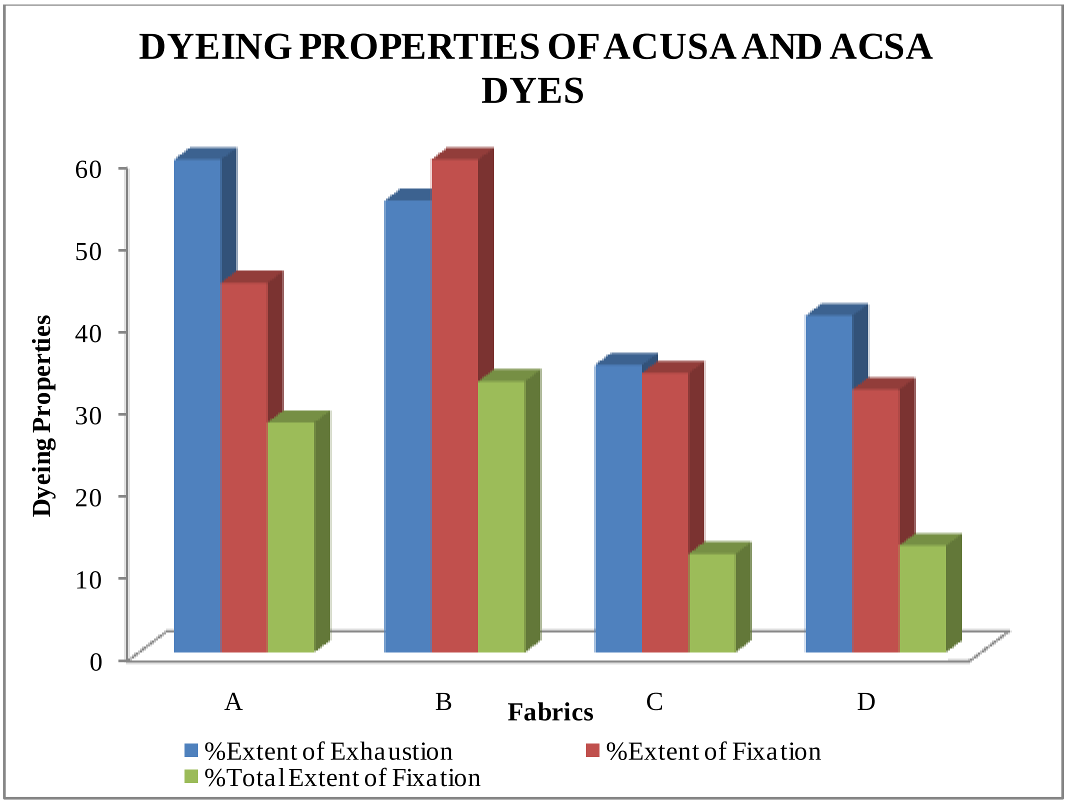

Figure 4: Total Extent of Fixation, extent of exhaustion, extent of fixation of the dyes on the fabrics

A=35% cotton, B=100% cotton using ACUSA; C=35% cotton, D=100% cotton using ACSA.

Fastness to Washing

The dyed fabric was assessed for color fastness to washing by TBS, member of ISO. The test method used was TZS 24 “Test for color fastness-color fastness to washing” test 4. Changes in color fading of the fabrics were analyzed using gray-scales for color change. Table 3 shows the color fastness to washing for the dyes. The level of fastness to washing achieved for both dyes can be classified as poor except for100 % cotton in ACUSA dyes the fastness to washing was fair.

General assessment of the dyeing effects shows that the dyes have low dyeing effect and poor fastness to washing. Thus there is a need to improve staining ability and fastness property by adding auxiliary substances such as mordant and surfactants, however, the objective of synthesizing azo dyes was attained as indicated in figure 5.

Table 3: Color fastness to washing

Dye	Color quality before washing		Color fastness to washing	
	C*	CP*	C*	CP*
ACUSA	2	2	2	1
ACSA	1	1	1	1

(Scale rating: 5 = Excellent, 4 = Very Good, 3 = Good, 2 = Fair, 1 = Poor)
C*= 100% cotton fibre, CP*= 65% cotton and 35% polyester fibre.

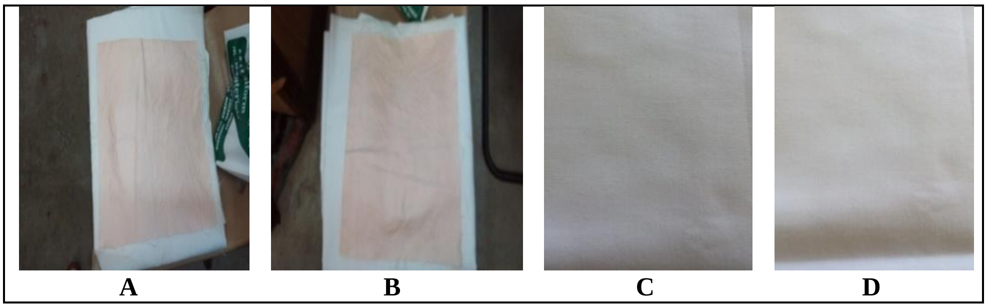

Figure 5: Photos of dyed fabrics (A= 35:65% cotton polyester dyed with ACUSA; B= 100 % Cotton with ACUSA and undyed at the bottom of both A and B fabrics; C= 100% Cotton dyed with ACSA; D= 35:65% cotton polyester dyed with ACSA

CONCLUSION

Dyes of ACUSA and ACSA origin were successful prepared through a series of steps from anacardic acids. The prepared dyes were observed to have moderate performance on textile fabrics with varying cotton content. The dyeing efficiency of the dyes of ACUSA origin to fabrics composed of varying cotton content was better than the dyes of ACSA origin. The total extent of fixation was 33% for ACUSA on the fabric with 100% cotton and was 27% for fabric with 35% cotton and 65% polyester content. Likewise, the total extent of fixation was 11.9% for ACSA on the fabrics with 100% cotton and was 13% on fabric with 35% cotton and 65% polyester content. The fastness test to washing showed that 100% cotton dyed with ACUSA had fair fastness while the rest had poor fastness to washing. To the best of our knowledge, this is the first time the synthesis of azo dyes is accomplished from CNSL as the sole source of both coupling component and aminocardanol.

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