SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF AZO DYES FROM ANACARDIC ACID, AN INEXPENSIVE RENEWABLE RESOURCE

John Mkungu, Quintino A. Mgani* and Stephen J.M. Mdachi
Chemistry Department, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania
* Corresponding author: qamgani@yahoo.co.uk

ABSTRACT

Six new azo dyes have been synthesized by coupling the diazonium salts from 3-aminophenol (3AP) and 4-aminophenol (4AP) with both unsaturated (UA) and saturated (SA) anacardic acids and the calcium salt (CA) of the unsaturated acid. The six prepared dyes are, thus, given the acronyms 3APSA, 3APUA, 3APCA, 4APSA, 4APUA, and 4APCA depending on the source of the diazonium salt and the form of anacardic acid used. The dyes were characterized using UV-Vis and FT-IR spectroscopic techniques. The UV-Vis absorption spectra of the dyes were found to have maximum peaks at 520 nm for the dyes of 3AP origin and at 295 nm for the dyes of 4AP origin. The FT-IR spectra for the dyes indicated presence of the azo group around 1450 to 1520 cm^{-1}*. The dyes showed moderate performance on textile fabrics used. The total extent of fixation was 39% for 3APSA on the fabric with 100% cotton and 31% for fabric with 35:65% cotton/polyester content. On the other hand, the total extent of fixation was 33% for 4APSA on the fabrics with 100% cotton and 29% on fabric with 35:65% cotton/polyester content. The fastness test showed that the change in shade for one of the dye was 2/5 implying fair fastness to washing.*

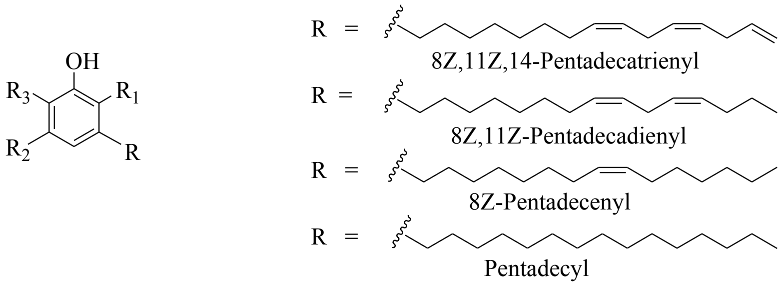
Key words: Anacardic acid, azo dyes, 3-aminophenol, 4-aminophenol, cashew nut shell liquid

INTRODUCTION

Cashew Nut Shell Liquid (CNSL) is a dark-brown viscous oil obtained as a by-product in the cashew nut processing industries. Depending on the method of its extraction from the shells, it is branded as either natural or technical CNSL. Natural CNSL and technical CNSL is obtained by solvent extraction and roasting of the cashew nut shells, respectively. Natural CNSL can also be obtained by physical pressing of the shells (extrusion method). Usually, natural CNSL contains anacardic acid (60-65%) (**1-4**), cardol (15-20%) (**5-8**), cardanol (10%) (**9-12**), and traces of methylcardol (**13-16**) depicted in Figure 1. On the other hand, technical CNSL contains mostly cardanol (60-65%), cardol (15-20%), polymeric material (10%), and traces of methylcardol. Due to the high temperatures attained (*ca.* 200 °C) during the roasting process, anacardic acid, which is the major component of natural CNSL, decarboxylates to form cardanol (Dholakiya *et al.* 2012 and Kumar *et al.* 2002).

The *meta* substituent in each of the four phenolic constituents of CNSL (*i.e.*, **a-d** in Fig. 1) occurs as a mixture of a pentadecyl, 8*Z*-pentadecenyl, 8*Z*,11*Z*-pentadecadienyl and 8*Z*,11*Z*,14-pentadecatrienyl carbon chain. It is worth noting that the monoenyl (8*Z*-pentadecenyl) side chain constitutes the predominant structure of the *meta* substituent in all the CNSL phenols.

The utility of CNSL and its individual phenolic constituents cannot be overstated. CNSL resourcefulness is apparent not only from its reported diverse uses as a mixture (Mukhopadhyay *et al.* 2010, Olotuah and Ofuya 2010, De Jesus *et al.* 2011, Parasa *et* *al.* 2011, Mann and Kaufman 2012) but also from the various known applications of its isolated constituent phenols, especially cardanol and anacardic acid (Lubi and Thachil 2000, Mkayula *et al.* 2004, Makame *et al.* 2005, Gopalakrishnan and Sujatha 2010, Philip *et al.* 2012, Mwangi and Mbugua 2013). As a contribution to the global efforts and interest in utilization of bio-raw materials in the syntheses of useful chemical products, we embarked on the syntheses of anacardic acid based azo dyes with potential textile applications. Precedence was available from the earlier similar studies by Suwanprasop *et al.* (2004) and Gopalakrishnan *et al.* (2011) in which cardanol was coupled with diazotized aniline and its derivatives to produce cardanol based azo dyes. The present paper, therefore, reports on synthetic conversion of anacardic acid from CNSL, an abundant and inexpensive locally accessible renewable resource, to azo dyes for possible textile applications.



(**a**) Anacardic acids **1- 4**; $R_1 = CO_2H$, $R_2 = R_3 = H$ (**b**) Cardols **5 - 8**; $R_1 = R_3 = H$, $R_2 = OH$

(**c**) Cardanols **9 - 12**; $R_1 = R_2 = R_3 = H$ (**d**) Methylcardols **13 -16**; $R_1 = H$, $R_2 = OH$, $R_3 = CH_3$

Figure 1: Phenolic constituents of Cashew Nut Shell Liquid (CNSL)

MATERIALS AND METHODS

Materials and Reagents

The steam processed cashew nut shells were collected from cashew processing plants in Mtwara region and Tunduru district, Ruvuma region. Unless otherwise indicated all analytical grade reagents were used without further purification. Other grades were purified according to known procedures before use. All reagents were supplied by BDH laboratory supplies, England. The fabrics (100% cotton and 35:65% cotton/polyester) were obtained from local markets.

General Procedures

Infrared (IR) spectra were recorded on a Perkin-Elmer FT-IR System Spectrum BX. Ultraviolet (UV) spectra were recorded on a Shimazdu 240 double beam UV-VIS Spectrophotometer.

Extraction of CNSL and Isolation of Anacardic Acid

CNSL was obtained by solvent extraction. Cashew nut shells (2 kg) were crushed using a pestle and motor to increase the surface area. The crushed material was socked in 1 L of petroleum ether for 48 h. The extract was concentrated on BUCHI rotavapor R-205 at 40 °C and reduced pressure to give 150 g of CNSL. 50 g of CNSL was dissolved in 5% aqueous MeOH (300 mL), and $Ca(OH)_2$ (25 g) was added portion-wise with stirring. After complete addition of $Ca(OH)_2$, the temperature of the reaction mixture was raised to 50 °C and stirring was continued for 3 h. The precipitate formed was then filtered and washed thoroughly with MeOH (200 mL) to give 60 g of the calcium anacardate (CA) cake. A portion of 5 g of the cake was set apart for the coupling reaction. The rest of calcium anacardate (55 g) was suspended in distilled water (160 mL) and 11 M HCl (20 mL) was added and stirred for 1 h. The resultant solution was extracted with EtOAc (2 × 150 mL). The combined organic phase was washed with distilled water (2 × 100 mL), dried (Na_2SO_4), and concentrated under reduced pressure to yield 30 g of unsaturated anacardic acid (UA), *i.e.*, a mixture of mainly compounds **1-3** (Fig. 1). About 10 g of this mixture were set aside for the coupling reaction while the rest (20 g) was hydrogenated. The procedure for the isolation of anacardic acid described above is essentially that developed by Paramashivappa *et al*. (2001).

Hydrogenation of Unsaturated Anacardic Acid

Unsaturated anacardic acid (20 g) was dissolved in 40 mL of EtOH. To this solution, 0.3 g of 5% Pd/C catalyst was added. The mixture was put into the Autoclave connected to a hydrogen generator for the hydrogenation reaction. The reaction proceeded for 24 h. Then the content was filtered using celite to separate the catalyst from the anacardic acid solution. The solution was then concentrated under reduced pressure leaving a solid substance which was further dried to obtain 14 g of saturated anacardic acid (SA) as grey solid. This represents *ca.*70% conversion of UA.

Synthesis of Anacardic Acid Based Dyes

The six dyes that were synthesized can be grouped into two sets based on the aromatic amines used. One set being dyes of 3-aminophenol (3AP) origin and the other set is those of 4-aminophenol (4AP) origin. Each set comprises three dyes based on the form of anacardic acid used. These are the dyes from calcium anacardate (CA), unsaturated anacardic acid (UA) and saturated anacardic acid (SA). Thus, the acronyms for the six dyes are as follows: 3APCA, 3APUA, 3APSA, 4APCA, 4APUA and 4APSA. The synthesis of any of these dyes involved a general three-step procedure consisting of: preparation of the anacardic acid based aromatic coupling compound, preparation of an aminophenol based diazonium salt and the coupling reaction of the two. The following descriptions for the preparation of the dye 3APSA typify this three-step procedure.

General Procedure for the Preparation of an Aminophenol Derived Diazonium Salt

The 3AP derived diazonium salt, for example, was prepared as follows: A suspension obtained from 1.17 g (10.7 mmol) of 3AP and 10 mL of 2.6 % aqueous Na_2CO_3 was combined with an aqueous $NaNO_2$ solution made by dissolving 0.4 g (5.8 mmol) $NaNO_2$ in 1 mL of water at room temperature. The resulting solution was placed into a dropping funnel and subsequently introduced drop-wise with stirring into a 100 mL beaker containing 1 mL of 11 M HC1 maintained at 0 °C in ice bath (Hartwell and Fieser, 1936). The diazonium salt, formed as a brick red precipitate, was stirred further at 0 °C for 5 min. to ensure its complete formation. To avoid decomposition of diazonium salt, the resulting suspension was kept in an ice bath ready for the azo coupling reaction.

General Procedure for the Preparation of Coupling Reagent Form of Anacardic Acid

To prepare the coupling aromatic compound, 1.8 g (5.2 mmol) of saturated anacardic (SA) acid, for example, was placed in a 250 mL beaker. Then 4 mL of a freshly prepared 2.5 M NaOH aqueous solution was added. The mixture was stirred thoroughly until a white paste was formed. The content was then cooled in an ice bath for 10 min. to lower the temperature of the paste to about 0 °C ready for coupling reaction.

General Procedure for the Azo Coupling Reaction

The suspension of 3AP derived diazonium salt was added portion-wise to a beaker containing the aromatic coupling reagent (SA) prepared beforehand. The reaction mixture was stirred with a glass rod after each addition. When the addition was complete, the reaction was left to proceed for 10 min. with occasional stirring. The reaction mixture was then heated on a hot plate at 60 °C for 5 min. NaCl (2 g) was added and heating was continued for further 10 min. The content in the beaker was cooled to room temperature first and in an ice-water bath afterwards. The dye product was extracted from the reaction mixture using CH_2Cl_2 (20 mL) according to Suwanprasop *et al*. (2004). The organic phase was washed with distilled water (3 × 20 mL) in a separating funnel. The organic phase was concentrated using a rotavapor at reduced temperature and pressure to give 1.5 g (47% yield) of the dye 3APSA as an orange powder.

The syntheses of the remaining five dyes (*i.e.,* 3APUA, 3APCA, 4APSA, 4APUA and 4APCA) were similarly carried out using the generalized three-step procedure detailed above while making use of the appropriate form of anacardic acid and aminophenol in each case.

Physico-chemical Studies of the Synthesized Azo Dyes

The Dyeing Process

The process involved the dyes, 3APSA and 4APSA, and two sets of fabrics; one set made of 100% cotton and the other made of 35:65% cotton/polyester. In 500 mL beaker was placed 0.36 g of a dye in 378 mL of water and stirred at room temperature. 18 g of the fabric was subsequently immersed in the dye bath and heated up to 60 °C within 30 min. 2.5 g of NaCl were added followed by 0.25 g of Na_2CO_3. The temperature was then held constant at 60 °C. After 30 min., 4 mL of 32% NaOH solution was added followed by 4 mL of 3.0×10^{-3} M of $NaHCO_3$. The pH of the dye bath was found to be 11.5. The dyeing process was continued for 45 min. and then the bath was cooled to room temperature. The dyed fabric was rinsed with warm water at 30 °C followed with water at 60 °C so that the final rinse water was colorless. In order to determine the effect of temperature on the extent of exhaustion, the dyeing process was also carried out at 90 °C and at room temperature in similar manner as described above.

Determination of the Extent of Exhaustion (%E)

The extent of dye uptake by the fabrics was measured by monitoring the changes in concentration of the dye bath in the exhaustion stages of the dyeing process. A liquid sample (1 mL) from dye bath was taken at the beginning and at the end of the dyeing process. The sample was diluted using distilled water to obtain 10 mL. The absorbance of the sample for original and exhausted dye bath was determined on the UV-Vis spectrophotometer at 290 nm for 4APSA and 520 nm for 3APSA, the maximum wavelengths of the respective dyes. The extent of dye exhaustion (*%E*) achieved for each of the two types of fibers was determined by using Equation 1 (Burkinshaw & Paraskevas 2011, Sevim *et al.* 2011).

$$\%E = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

where A_i is the initial absorbance and A_f is the final absorbance of the dye bath.

Determination of Dye Fixation

The dye was extracted in 80 mL of 20% aqueous pyridine solution from 5 g dry piece of the dyed fabric using soxhlet extraction apparatus for 12 h. The absorbance of the extract was measured on UV-Vis spectrophotometer at the maximum wavelength of the respective dye. The extent of fixation (*%F*) was afterward evaluated using Equation 2.

$$\%F = \frac{(A_i - A_f) - A_e}{A_i} \times 100 \quad (2)$$

where A_i is the initial absorbance, A_f is the final absorbance of the dye bath and A_e is the absorbance of the dye extracted from a dyed fabric.

The values of the extent of fixation obtained were used to evaluate the extent of total fixation (*%T*) using Equation 3.

$$\%T = \frac{\%F \times \%E}{100} \quad (3)$$

Washing Fastness Test

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

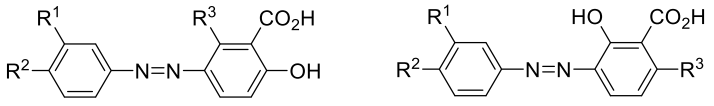
RESULTS AND DISCUSSION

Six potential textile dyes of azo type were synthesized by coupling anacardic acid in three forms with the diazonium salts derived from two isomers of aminophenol. The three forms of anacardic acid were unsaturated calcium anacardate (CA), unsaturated anacardic acid (UA) and saturated anacardic acid (SA) and the two isomers of aminophenol used were 3-aminophenol (3AP) and 4-aminophenol (4AP). The dyes synthesized were identified using acronyms related to those of the material used in the coupling reactions. The dyes are listed in Table 1 below.

Table 1: The Dyes Synthesized and Their Acronyms Derived from the Aminophenol Isomer and the Form of Anacardic Acid Used

Aminophenol	Form Anacardic Acid Used and Dye Acronym		
	CA	**UA**	**SA**
3AP	3APCA	3APUA	3APSA
4AP	4APCA	4APUA	4APSA

Since the study by Suwanprasop *et al.* (2004) showed that the diazo group took up *para* position to the hydroxyl group in cardanol, we thus anticipated that the azo dyes synthesized in the present study to have the general structure **17** shown in Fig. 2. Considering steric factors, structure **18** would appear to be the more likely product. However, Paebumrung *et al.* (2012) and Maqbool *et al.* (2013) report that the *para* azo product is formed as the major product. Thus, mesomeric rather than steric factors appear to be more important in the azo coupling reaction reported above.



17 **18**

Figure 2: Generalized Structures of Dyes Synthesized in this Work
R^1 = OH, R^2 = H, R^3 = $C_{15}H_{31}$ (3APSA); R^1 = H, R^2 = OH, R^3 = $C_{15}H_{31}$ (4APSA)

As pointed out in the materials and methods section, the synthesized dyes were applied on two types of fabrics (100% cotton and 35:65% cotton/polyester).

Spectral Properties of Anacardic Acid

The UV-Vis spectrum of anacardic acid had strong and broad absorption between 265 nm and 350 nm. When the broad peak was resolved at low concentration, three peaks were observed at 282 nm, 290 nm and 315 nm. The observed maximum absorption wavelength at 320 nm was comparable to that found in the study by Philip *et al.* (2008). The other minor peaks appearing at 374 nm and 474 nm were explained by the same authors to be due to impurities in the sample.

The FT-IR spectrum showed all the characteristic bands for anacardic acid and the results were comparable to those reported by Philip *et al.* (2008). The presence of OH groups is indicated by the broad band of O–H stretching vibration in the range 3600–3050 cm^{-1}. The presence of alkyl chain is indicated by the strong peak of C–H vibrations in the range 3000–2800 cm^{-1} and the C–H and deformation vibrations in the range 1475–1350 cm^{-1}. The strong absorption bands observed at 1610–1600 cm^{-1} indicate stretching vibration of the C=O. The presence of both O–H and C=O stretching vibrations also indicate the presence of the carboxyl group.

Physico-chemical Properties of the Dyes

Most of the commercial azo dyes are yellows, oranges and reds. The physico-chemical properties of the dyes being reported are summarized in Table 2 and Fig. 3. The dyes that were derived from 3AP were orange while those derived from 4AP were violet (Table 2). This may be attributed to the different positions of the hydroxyl group in the two compounds. In the 3AP derived dye the OH of the amino phenol component is not involved in the resonance with the azo group thus affecting its wavelength relative to the 4AP derived dye where the OH resonates with the azo group. It was also observed that, the dyes based on the unsaturated anacardic acid did not solidify. On the contrary, dyes obtained from saturated anacardic acid were solids. The failure of the dye to solidify may possibly be associated with the unsaturation in the alkyl group of the anacardic acid which is a mixture of monoene, diene and triene acids (Figure 1).

Table 2: Physico-chemical Properties of the Dyes Synthesized

Dye	Chemical Class	Hue	State	Solubility
3APCA	Mono azo	Orange	Gelatinous	Water/ethanol
4APCA	Mono azo	Violet	Gelatinous	Water/ethanol
3APUA	Mono azo	Orange	Gelatinous	Water/ethanol
4APUA	Mono azo	Violet	Gelatinous	Water/ethanol
3APSA	Mono azo	Orange	Crystalline	Water/ethanol
4APSA	Mono azo	Violet	Crystalline	Water/ethanol

The UV-Vis spectra for dyes of 3AP origin were observed to have three peaks whereby the maximum absorption was at 520 nm and the minor peaks were observed at 365 and 375 nm. On the other hand, the spectra for dyes originating from 4AP were found to have the maximum absorption 295 nm. It was observed that the dyes of 3AP origin have major absorption peaks in both UV and Visible region while those of 4AP have major absorption peaks within the UV region only. The appearance of absorption peaks in both UV region and in the visible range may be due to the conjugations occurring through the azo group between the π and *n* electrons from the aromatic systems disposed on both sides of the azo bond (Labudzinska *et al*. 1993). The broad absorption of the 3AP based dye in the visible region may be due to the interaction between the auxochromes OH available in both aromatic rings. In the literature, the characteristic peak of the azo group is observed as the interaction between the π→π* absorption band in the far UV region and *n*→π* transition at 320–350 nm for the azo compounds (Yildiz *et al*. 2010).

Characteristic bands in the FT-IR spectra of the synthesized dyes included the broad absorbance between 3600–3050 cm^{-1}, which is assigned to O–H stretching vibration. The strong absorbance band between 3000–2800 cm^{-1} is assigned to C–H stretching vibrations while the band in the range 1475–1350 cm^{-1} is assigned to C–H deformation vibrations in the alkyl side chain. The strong absorption bands observed at 1610–1600 cm^{-1} indicate stretching vibration of the C=O. The absorption around 1500 cm^{-1} is linked to the presence of the azo group. The presence of both O–H and C=O stretching vibrations also indicate the presence of carboxyl group.

Dyeing Properties of the Synthesized Dyes

In order to study the dyeing properties, the dyes 4APSA and 3APSA were applied to two sets of the fabrics. One set contained 100% cotton and the other was made of 35:65% cotton/polyester. The dyeing properties were studied using methods existing in the literature. The dyeing properties that were investigated are: the extent of exhaustion, extent of fixation, total extent of fixation and the fastness to washing.

Extent of Exhaustion, Extent of Fixation and Extent of Total Fixation

The extent of exhaustion (*%E*) was

measured by monitoring the changes in the absorbance of the dye bath during the dyeing process. Table 3 shows the changes in absorbance of the dye bath during the dyeing process and the *%E* for 4APSA and 3APSA that was obtained using equation 1 (*vide supra*). The highest value of *%E* obtained was 67% for 4APSA applied to 100% cotton. Percentage *%E* indicates the extent of adsorption of the dye molecules onto the surface of the fabric and the diffusion of the same into the fabric. Therefore, a high *%E* is desirable for better dyeing effect. Table 3 also presents data for extent of fixation (*%F*) and total extent of fixation (*%T*). The *%F* for a dye was calculated using equation 2 (*vide supra*). The values of the *%F* and the values of the *%E* were further used to calculate the *%T* of the dyes to the fabrics using equation 3 (*vide supra*).

The highest value for the total extent of fixation is 39% for 3APSA on the fabric with 100% cotton while the lowest value is 29%, which was obtained for 4APSA on the fabric with 35:65% cotton/polyester. These values suggest that the dyes had moderate dyeing effects on the fabrics (see pictures of dyed fabrics, Fig. 3). These results are in agreement with the literature, which reports that mono azo dyes do not work well with cotton as compared to the disazo dyes (Pavia *et al.* 1976).

Table 3: Dyeing Properties of Dyes 3APSA and 4APSA on Different Fabrics

Parameter	3APSA		4APSA	
	35:65% cotton /polyester	**100% cotton**	**35:65% cotton /polyester**	**100% cotton**
A_i	3.454A	3.454A	3.616A	3.695A
A_f	1.195A	1.311A	1.633A	1.213A
A_e	0.976A	0.794A	0.941A	1.257A
%E	65%	62%	55%	67%
%F	47%	63%	53%	49%
%T	31%	39%	29%	33%

Key: A_i = Initial Absorbance; A_f = Final Absorbance; A_e = Extracted Dye Absorbance; *%E* = Extent of Exhaustion; *%F* = Extent of Fixation and *%T* = Extent of Total Fixation

Fastness to Washing

Colour fastness to washing was tested according to Tanzania Bureau of Standards' test method TZS 24 (TBS 1979). Table 4 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 in one case whereby the fastness to washing observed was fair. The poor fastness to washing may be attributed to weak interaction between dye molecule's functional groups and the fabrics. As was also noted by reviewers, the color of the dyed fabrics does not match with those of pure compounds. This is expected since the dyeing process involves chemical interactions between the dye functional groups and the groups on the fabric as well as the interaction of mixing the fabric color and that of the dye. The result of these interactions is likely to yield a different color which was observed.

Table 4: Color Fastness to Washing

Dye	Color quality before washing		Color fastness to washing	
	100% cotton	**35:65% cotton/ polyester**	**100% cotton**	**35:65% cotton/ polyester**
3APCA	2	2	1	1
4APCA	2	2	1	1
3APUA	2	2	1	1
4APUA	2	2	1	1
3APSA	3	2	2	1
4APSA	2	2	1	1

Scale Rating Key: 5 = Excellent, 4 = Very Good, 3 = Good, 2 = Fair, 1 = Poor

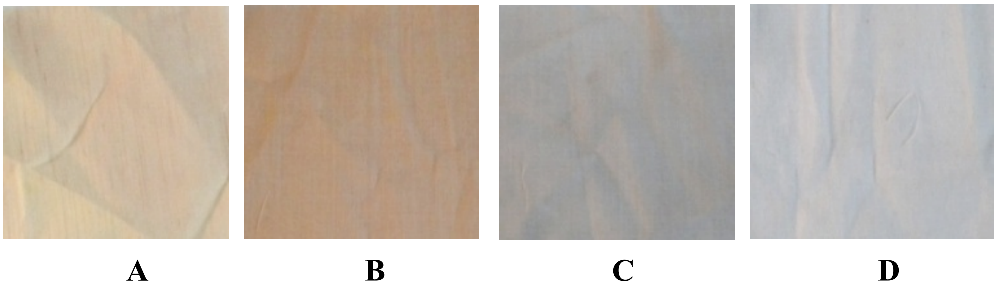


Figure 3: Pictures of Dyed Fabrics: **A** = 35:65% cotton/polyester (dyed with 3APSA); **B** = 100% cotton (dyed with 3APSA); **C** = 100% cotton (dyed with 4APSA); D = 35:65% cotton/polyester (dyed with 4APSA)

Effect of Dyeing Temperature on the Extent of Exhaustion

Temperature is one of the important factors in the dyeing process. It affects both the extent of dye uptake (exhaustion) and fixation which in turn affects the levelness of the dyed article. Levelness in the dyeing process refers to consistency in colour shade that is, having colour shade which is uniform and without any variation in tone or depth. To determine the effect of temperature on the *%E* for the dye 3APSA, three pieces of the fabric with 100% cotton content were investigated. In dyeing the first and second pieces of the fabric, the dye baths were kept constant at 90 and 60 °C, respectively. The third piece of the fabric, the exhaust stage was conducted at room temperature for 30 min. Afterwards the temperature was raised up to 90 °C in 5 min. and held constant at this temperature until the end of the dyeing process. The extent of exhaustion was again calculated using equation 1 (*vide supra*).

Figures 4-6 show the variations in the rate of dye uptake at different temperatures. All three cases show that the dye uptake was very rapid during the first few minutes of the dyeing process. However, dyeing at the temperature of 60 °C was found to have a moderate rate of dye uptake compared to the rest. Moreover, the rate of dye uptake was observed to be more rapid when dyeing at the constant temperature of 90 °C compared to other temperatures. It is known that rapid dye uptake adversely affects the levelness of the dye leading to an uneven coloring of the dyed fabric. In such situations, apart from adjusting the dyeing temperature, it is suggested that the rate of dyeing could be decreased using retarding agents in the dye bath so as to improve the leveling (Peters 1975). On the other hand, the dyeing starting from room temperature to 90 °C showed that the dye uptake was slow compared to that attained at 90 °C. The slow rate of dyeing has some economic implication to the process, so the rate of dyeing can be increased by adding accelerating agents to the dye bath (Yen & Chen 1998).

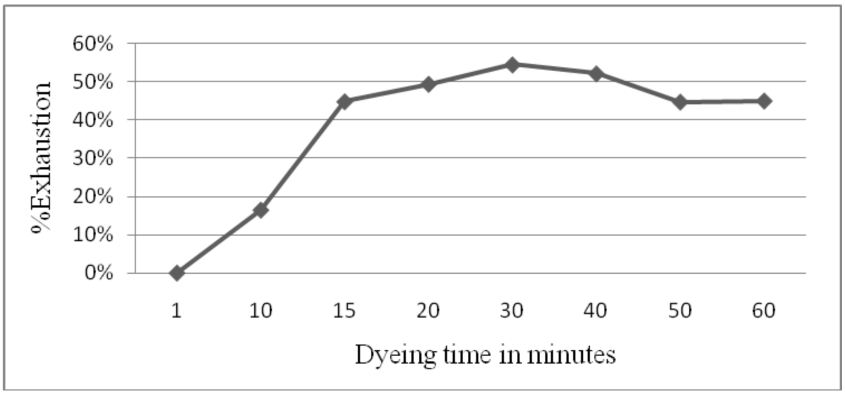


Figure 4: Plot of 3APSA %Exhaustion on 100 % Cotton *versus* Dyeing Time at 60 °C

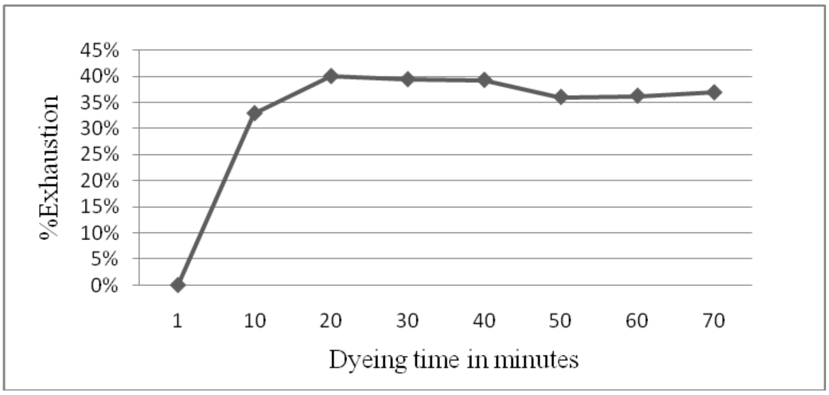


Figure 5: Plot of 3APSA %Exhaustion on 100% Cotton *versus* Dyeing Time from Room Temperature to 90 °C

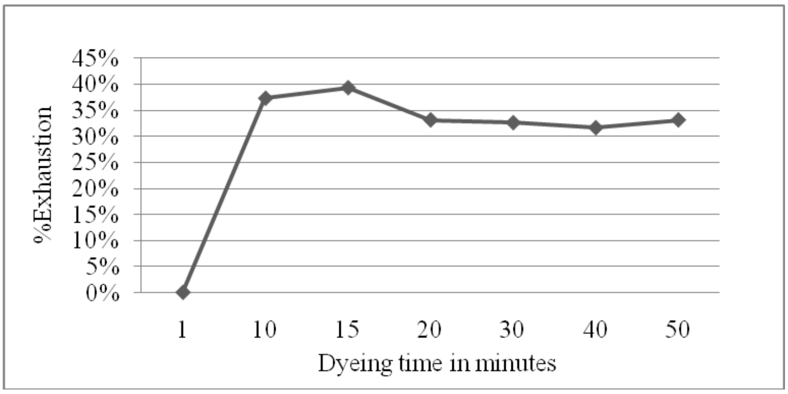


Figure 6: Plot of 3APSA %Exhaustion on 100 % Cotton *versus* Dyeing Time at 90 °C

Generally, the dyeing effects and the fastness to washing of the synthesized dyes were low, which call for the search of some improvement strategies. In the textile industry, dyeing processes in most cases include the addition of surfactants. These are molecules consisting of both hydrophobic and hydrophilic moieties. When added to the dye bath during dyeing process, surfactants improve the dyeing properties especially the leveling effect of the dye on the fabric (Chen *et al*. 2010). In this study, surfactants were not added so as to determine the effect of the hydrophobic (*i.e.,* the alk(en)yl side chain) and hydrophilic (*i.e.,* the hydroxyl and carboxyl) moieties already embedded in the structure of the dye itself. However, the present results suggest that the non-application of surfactants may have contributed to the observed low dyeing effects and fastness.

CONCLUSION

CNSL is an abundant industrial by-product which is generally still considered a waste in Tanzania although elsewhere it is a valuable raw material for many products. In this study, anacardic acid, a component of natural CNSL, has been used for the synthesis of azo dyes. To the best of our knowledge, this is the first time anacardic acid is being reported to be used in the synthesis of azo dyes. The dyes prepared were observed to have moderate performance on textile fabrics with different cotton content. The dyeing efficiency of the dyes of 3-aminophenol origin to fabrics composed of varying cotton content was better than the dyes of 4-aminophenol origin. The total extent of fixation was 39% for 3APSA on the fabric with 100% cotton and was 31% for fabric with 35% cotton plus 65% polyester content. Likewise, the total extent of fixation was 33% for 4APSA on the fabrics with 100% cotton and was 29% on fabric with 35% cotton plus 65% polyester content. The fastness test to washing showed that the change in shade for one dye (3APSA on 100% cotton) was 2/5 indicating that it had fair fastness to washing. Currently we are exploring the synthesis of disazo dyes by attaching an azo group to both the *para* and *ortho* positions to the hydroxyl group on anacardic acid to improve their performance.

ACKNOWLEDGEMENTS

We would like to thank Mkwawa University College of Education, MUCE, (a constituent college of the University of Dar es Salaam) for financial support.

REFERENCES

Burkinshaw SM and Paraskevas M 2011The Dyeing of Silk: Part 4 Heterobifunctional Dyes. *Dyes*

Pigm. **88**: 396-402.

Chen KM, Lin LH, Wang CF and Hwang MC 2010 Interactions Between New Multi-anionic Surfactants and Direct Dyes and Their Effects on the Dyeing of Cotton Fabrics. *Colloids and Surf., A.* **356**: 46–50.

De Jesus T, dos Santos Andrade A, Araújo BQ, das Graças Lopes Citó A M, da Silva J, Saffi J, Richter MF and de Barros Falcão Ferraz A 2011Antioxidant Properties and Chemical Composition of technical Cashew Nut Shell Liquid (tCNSL). *Food Chem.***126**: 1044-1048.

Gandhi T, Patel M and Dholakiya BK 2012 Studies on Effect of Various Solvents on Extraction of Cashew Nut Shell Liquid (CNSL) and Isolation of Major Phenolic Constituents from Extracted CNSL. *J. Nat. Prod. Plant Resour.* **2**:1 35-142.

Gopalakrishnan S and Sujatha R 2010 Synthesis and Thermal Properties of Polyurethanes from Cardanol-Furfural Resin. *J. Chem. Pharm. Res.***2**: 193-205.

Gopalakrishnan S, Nevaditha NT and Mythili CV 2011 Synthesis, Characterization and Thermal Studies of Some Diazotised *p*-Anisidine Cardanol Formaldehyde Resins. *Der Chemica Sinica* **2**: 138-146.

Hartwell JL and Fieser LF 1936 Coupling of *o*-Tolidine and Chicago Acid, *Org. Synth.* **16**:12.

Kumar PP, Paramashivappa R, Vithayathil PJ, Rao PVS and Rao AS 2002 Process for Isolation of Cardanol from Technical Cashew (*Anacardium occidentale* L.) Nut Shell Liquid *J. Agric. Food. Chem.* **50**: 4705-4708.

Labudzinska A, Galka S and Gorczynska K 1993 Studies of the Carbazole Azo Dyes by Means of UV/VIS Spectroscopy *J. Mol. Struct.* **294**: 241-250.

Lubi MC and Thachil ET 2000 Cashew nut shell liquid (CNSL) - a Versatile Monomer for Polymer Synthesis. *Des. Mon. Poly.* **3**: 123–153.

Makame YMM, Johnson W and Mkayula LL 2005 Micron-Sized Polymeric Particles from Cashew Nut Shell Liquid: Influence of Reaction Parameters on Particle Size. *Tanz. J. Sci.* **31**: 35-43.

Mann RS and Kaufman PE 2012 Natural Product Pesticides: Their Development, Delivery and Use against Insect Vectors. *Mini-Rev. Org. Chem.* **9**: 185-202.

Maqbool H, Ganesh SD, Chandra U, Kumaraswamy BE and Pai VK 2013 Cyclic Voltametric Studies of Synthesized Cardanol Based Azo Dyes. *Res. J. Chem. Sci.* **3**:44-50

Mkayula LL, Makame YMM and Matechi TH 2004 Preparation of Spherical Polymer Particles from Tanzanian Cashew Nut Shell Liquid by Suspension Polymerization. *Tanz. J. Sci.* **30**: 1-10.

Mukhopadhyay AK, Hati AK, Tamizharasu W and Babu PS 2010 Larvicidal properties of Cashew Nut Shell Liquid (*Anacardium occidentale* L) on Immature Stages of Two Mosquito Species *J. Vector Borne Dis.* **47**: 257–260.

Mwangi PM and Mbugua BK 2013 Novel Unsaturated Polyester (UPE) Resin Based on Cashew Nut Shell Liquid (CNSL). *Int. J. Cur. Res.* **2**: 285-292.

Olotuah OF and Ofuya TI 2010 Comparative Protection of Cowpea, *Vigna unguiculata* (L.) Walpers against Field Insect Pests Using Cashew Nut Shell Liquid and Cypermethrin (Cymbush). *Pak. J. Nutr.* **9**: 158-161.

Paebumrung P, Petsom A and Thamyongkit P 2012 Cardanol Based Bis(azo) Dyes as Gasoline 91 Colorant. *J. Am. Oil Chem. Soc.* **89**:321-328.

Paramashivappa R, Kumar PP, Vithayathil PJ and Vittal ASR 2001 Novel Method for Isolation of Major Phenolic Constituents from Cashew (*Anacardium occidentale* L.) Nut Shell Liquid *J. Agric. Food Chem.* **49**: 2548-2551.

Parasa LS, Sunita T, Rao KB, Rao AH, Rao JS and Kumar LCA 2011Acetone Extract of Cashew (*Anacardium occidentale, L.*) Nuts Shell Liquid against Methicillin Resistant *Staphylococcus aureus* (MRSA) by Minimum Inhibitory Concentration (MIC). *J. Chem. Pharm. Res.* **3**: 736-742.

Pavia DL, Lampman GM and Kriz GS Jr. 1976 Introduction to Organic Chemistry Laboratory Techniques: a Contemporary Approach. 1st edn, WB Saunders Co., Philadelphia.

Peters RH 1975 *Textile Chemistry: The Physical Chemistry of Dyeing*. Vol. III, Elsevier Scientific*,* New York, p. 379.

Philip JYN, Francisco JEC, Dey ES, Buchweishaija J, Mkayula LL and Ye L 2008 Isolation of Anacardic Acid from Natural Cashew Nut Shell Liquid (CNSL) Using Supercritical Carbon Dioxide *J. Agric. Food Chem.* **56**: 9350-9354.

Philip JYN, Buchweishaija J, Mkayula LL and Ye L 2012 The Influence of Aliphatic Side Chain of Anacardic Acid on Molecular Recognition Properties of Imprinted Polymers. *Tanz. J. Sci.* **38**: 104-117.

Suwanprasop S, Nhujak T, Roengsumran S and Petsom A 2004 Petroleum Marker Dyes Synthesized from Cardanol and Aniline Derivatives. *Ind. Eng. Chem. Res.* **43**: 4973-4978.

Sevim AM, Ilgün C and Gül A 2011 Preparation of Heterogeneous Phthalocyanine Catalysts by Cotton Fabric Dyeing. *Dyes Pigm.* **89**: 162-168.

TBS 1979 Textiles: Test for colour fastness: Colourfastness to washing, Test 4 TZS 24.

Yen PH and Chen KM 1998 Preparation and Properties of Novel Low-foaming Dyeing Auxiliaries. Part 1. Preparation and Properties of Ethoxylated Hydroxysulpho-betaines in Nylon Dyeing. *J. Soc. Dyers Colour*. **114**: 160-164.

Yildiz E, Cetinkol T and Serindag O 2010 Synthesis and Characterization of Mono- and Dinuclear Metal Complexes with Novel Azo Compounds and their Dyeing Properties *Synth. React. Inorg. Met.-Org. Nan. Met. Chem*. **40**: 19–26.