

Technology Section

Pak. j. sci. ind. res., vol.39, nos. 9-12, September-December 1996

DYES FROM PLANT BIOMASS

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(Received September 9, 1995)

Series of dyes based on sulphur chromophores was manufactured by the baking process involving rice husk from the plant *Oryza sativa* and wood shavings of the plant *Entandrophragma angolense* at 230°C/125 mmHg in a pressure vessel for 3 hrs in presence of aqueous sodium sulphide. Following m-toluene extraction and crystallisation, two dyes were obtained, both of which showed remarkable ultra-violet/visible absorption maxima at λ_{\max} of 420nm indicating that they both are of one single colour shade. The dyes gave brilliant yellow colouration of average-good fastness ratings to light and alkaline wash on a bleached and mercerised cotton fabric.

Key words. Dyes, Sulphur chromophores, Plant biomass.

Introduction

Dyestuffs and pigments, for use generally on textiles, leather, food, cosmetics and related applications can be obtained in varied ways such as through:

(i) Crushing and/or extraction of seeds, backs, roots and leaves of many plants either using water, alcohol or any suitable organic solvents, (ii) Baking of vegetable matters with sulphides at elevated temperatures and pressure and (iii) Conversion of petrochemicals into dyestuff intermediates for dyes/pigments synthesis etc.

A much larger part of the dye and pigment industry has been taken over by the synthetic dye of the category (iii), introduced during the second half of the 19th century due to ease of manufacture and cheapness of cost of the products. Still a number of application outlets using dyes and pigments in a relatively low annual tonnage depends on supplies from natural sources i.e. (i) and (ii), partly because of their safety in use over their synthetic counter parts for speciality purposes where strict adherence category to safety regulations is required, such as in food, cosmetic and medicinal applications and partly because of low technology in the utilisation of the petrochemical route in dye and pigment synthesis in many under developed countries of the world.

A number of dye yielding plants has been screened for dye production basically from seeds and root tubers by the solvent-on-solid extraction method for use on fabric [1,2].

In the present work, dyes carrying sulphur chromophoric linkages are manufactured by the baking process involving two plants biomass of mainly rice husks and wood shavings. Following production, the dyes were purified and their potentials for imparting colours were assessed by determining their molar absorption coefficients and ultra-violet and visible absorption spectra. The objective of the work is to

produce commercially acceptable dyes for textile industry using the abundant plant biomass present in developing tropical countries.

Materials and Methods

Dyes were produced by collecting and baking separately without prior treatments of rice husks obtained as external testa from the seeds of the plant *Oryza sativa* and the wood shavings from the heart of the plant *Entandrophragma angolense* in a pressure vessel maintained at 230°C and 125mmHg for 3 hrs. Aqueous sodium sulphide was added. Following the heating, the dyes were extracted using m-toluene and subsequently recrystallised in m-cresol. The recrystallised dyes were then dried, both yields and melting points determined and the uv/visible spectra run on uv spectrosol U2030 of Eagle Scientific Model. The spectrographs are shown in Fig.1.

Dying of cotton using the dyes. The two dyes supplied by the Nigerian Chemical & Textiles Co. Limited, Lagos, were applied on bleached and mercerised cotton fabric by the conventional 'exhaust dyeing' method [3,4]. These dyes were insoluble in water and had to be applied by the vatting technique. The dyes were first solubilised by reduction to the unpigmented 'leuco' using aqueous sodium polysulphide to promote their absorption by the fabric. Following this process, the fabric was immersed in the dyebath and subsequently the soluble dye was converted to the colouring pigment by oxidising with $K_2Cr_2O_7$ (pot. dichromate) inside the fabric. After the desired deep shade had been obtained, the fabric was removed, rinsed in cold water and then boiled using 2% solution of non-ionic surfactant Sunaptol NN^(R). Final washing and rinsing was done in cold running tap water before drying of the fabric.

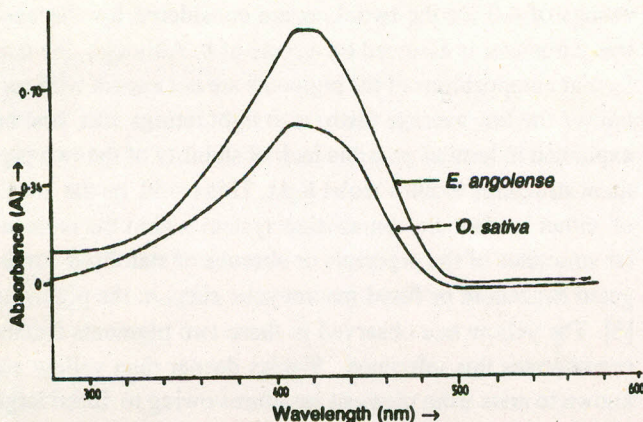


Fig. Electronic absorption spectrum of the purified dye extracts from *O. sativa* and *E. angolense*.

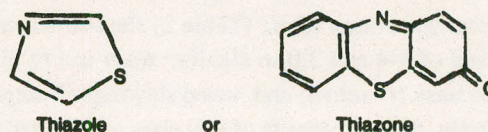
Determination of the fastness of the dyed fabric. Two fastness tests commonly carried out on dyed fabric, meant for interior decoration or wear, were made in accordance to the ISO procedure [5]. These tests measure fastness to light and alkaline wash. For testing its fastness to light, the dyed fabric was exposed to an artificial fading lamp source using the Shirley light fastness Tester Model SDL 237. The samples were mounted in cells. After preset test cycle, samples were assessed using the standard 8-point Gray scale. Ten samples were used for the test and the mean value was taken as the fastness rating for the test.

Evaluation of the dye stability to alkaline washing. The washing fastness was evaluated using the ISO-3 method designed for cellulosic fabric. Each fabric specimens measuring 10cm x 4cm were placed in turn between one piece each of undyed cotton and wool fabrics measuring 5cm x 4cm and stitched around leaving a portion of the specimens uncovered. A beaker containing 100ml solution of 0.5gm Sunaptol NN (R) was heated to boil (giving a liquor ratio of 50:1 on the 2 g weight of the fabric). The fabric in each case was allowed to remain in the solution at this temperature for 30 mins whilst stirring was carried out occasionally. The specimen was later rinsed in running cold water for about 10 mins, the stitch line along 2 sides was removed and the specimen was hanged out to dry. After drying, the change in colour of the dye fabric was assessed on the 5-point Gray scale both in terms of the change in colour of the uncovered portion of the fabric and the degree of staining of the undyed fabric. As in the case of fastness to light, ten specimens were used for the test and the mean value was used for rating. The results of these fastness tests are shown in Table 2.

Results and Discussion

The results of the yields, melting points and λ_{\max} (wavelength of maximum absorption) values for the two dyes are shown in Table 1.

The mean fastness ratings for stability to alkaline washing and exposure to artificial light fading test is shown in Table 2. Unlike pure organic compounds which are expected to have sharp melting points, it is noted that the dyes do not possess very sharp characteristic melting points. This was so inspite of repeated recrystallisations in m-cresol. The wide range observed in the melting points of organic compounds is often associated with low level of purity. In the present situation, however, this is far from being the case. It has been shown [6] that sulphur dyes do not often possess a definite molecular structure although they all contain -S-linkage as an integral part of the chromophoric unit such as:



It is the lack of a definite molecular composition rather than the presence of any impurity that is responsible for the wide ranging melting points for the two dyes. An evidence of high purity for the dyes can be obtained from the sharp peaks of the uv-visible spectra of the two dyes at λ_{\max} of 420nm as shown in Fig.1.

TABLE 1. PHYSICAL AND SPECTROSCOPIC DATA FOR DYES OBTAINED FROM *O. SATIVA* AND *E. ANGOLENSE*.

Parameter assessed	<i>O. sativa</i>	<i>E. angolense</i>
Yield, %	9.85	17.45
m.pt., °C	168-173	185-190
λ_{\max} · x104	420nm	420nm

TABLE 2. FASTNESS TO ALKALINE WASH AND LIGHT OF CITON FABRIC DYED USING DYESTUFFS OBTAINED FROM *O. SATIVA* AND *E. ANGOLENSE*.

Spec.	<i>O. sativa</i>			<i>E. angolense</i>		
	Alkaline wash	Light	Stain.	Alkaline wash	Light	Stain.
1	3	4	4	3	3	4
2	4	4	4	3	3	4
3	3	4	4+	3	3	4
4	3	4	4+	3	3	4+
5	3	3	4	3+	3	4
6	3	4	4	3	4	4
7	4	4	4	3	3+	4
8	3	4	4	4	3	4+
9	3	4	4	3	3	4
10	3	4	4	3	3	4
Mean	3.2	3.9	4	3.1	3.1	4

UV-visible spectrograph is often used to assess the quality and intensity of dyes. The sharper the spectrum obtained the more monochromatic the colour that is transferred. In other words, the sharper the spectrum, the more is the purity of the colour that generates it. Conversely, if the absorption spectrum is broad, it is an indication of mixture of colours (or the more polychromatic colour) in the dye source that generates the colour as the broadness of the spectrum is interpreted as transmission of colours of different wavelengths over the spectral spread. In the present case, brilliant yellow shade which also accords with the purity of the two dyes was obtained on the cotton dyed fabric [7].

The results of the fastness tests obtained on a bleached and mercerised cotton fabric (Table 2) showed a mean fastness rating of 3-4 and 3.0 to alkaline wash test by the dyes from rice husk (*O.sativa*) and wood shavings (*E-angolense*) respectively. Since dyestuffs of this class are applied by vating techniques, they are deposited as insoluble pigments only inside the fibre and are therefore, held in place by only non-polar Van der Waals forces. The fastness ratings of 3-4 and 3.0 obtained (on a scale of 5) are considered fairly good for textiles intended for wear. It is to be noted that the mean fastness result to washing is obtained on the assessment of both the alternation of shade of the dyed and washed fabric as well as on the degree of staining of the undyed fabric. The significance of this observation is that once applied by the technique employed, the dyestuff on solubilisation is adequately absorbed into the fibre and this is held in place after the subsequent washing and finishing operation to ensure non-weatherability of the pigment through transfer. The fastness to light

ratings of 4.0 for the two dyes are considered low because this parameter is assessed on a scale of 8. Although, the molecular compositions of the pigments are not known with certainty, the low average fastness to light ratings can best be explained in term of possible lack of stability of the two pigment structures to ultra violet light. This could be the result of either inadequate conjugation system within the molecular structures of the pigments or absence of stabilised conjugated benzenoid or fused macrocyclic rings in the pigments [8]. The yellow hue observed in these two pigments further corroborates this inference. Shades deeper than yellow are known to arise from pigment structures owing to fused large aromatic ring and/or longer length of conjugation.

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