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Synthesis and Analytical Characterization of Monoazo Bifunctional Reactive Dyes on Cotton

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ABSTRACT

In this study, two mono dichlorotriazinyl reactive dyes were synthesized. The synthesis involved diazotization, coupling with 1-naphthol-8-amino3-6-disulphomic acid (H-acid), and condensation with cyanuric chloride. The reactive dyes were applied on grey cotton fabric to assess dyeing performance. Spectrophotometric studies were carried out to investigate the wavelength of maximum absorption (λmax)—the percentage dye exhaustion, effects of temp. pH and duration of dyeing of the dyed samples were evaluated. The resultant dyes were characterized using standard spectroscopic methods. The results of the spectrophotometric analysis revealed that the λmax of the two dyes were 590mm and 600nm for dye (a) and (b), respectively. The wavelength of maximum absorption of the dyes in ethanol, water, and acetone was 600nm and 590nm for dye (a) and 600, 570, and 480nm for (b). The %dye exhaustion was 70 – 80%, and the fastness rating was very good and excellent.

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INTRODUCTION

Dyes are organic molecules containing Chromophores and Auxochromes. The chromophore gives the color of a particular dye, while the auxochromes intensify the hue of the dye, Usman *et al*. (2018). Thus making the dye more water soluble and improving the fastness properties of dyed samples. Reactive dyes are colored compounds with one or two groups capable of forming a covalent bond between carbon atoms or phosphorous of the dye and the substrate's oxygen, nitrogen, or sulfur atoms (Lawal et al., 2018). Reactive dyes, although emerging into the field of synthetic dyes late, have immediately achieved a commercial wet fastness, high applicability, and convenient or easy handling. (Gumel *et al*., 2023). The high wash fastness of the dyed fabrics results from covalent links between the dye and the substrates (Lawal et al., 2018).

Reactive dyes are either monofunctional, having only one reactive moiety, or bifunctional, having two reactive moieties. Many reactive dyes are bifunctional with mono or hetero-reactive grouping systems. These types have good fastness properties and exhibit higher fixation yields than those with only one reactive moiety (Ezetimibe *et al*., 2018). While hetero bifunctional reactive dyes, such as monochlorotirazinyl sulphones dyes, differ in reactivity because of the two functional groups that compensate or lead to the variation in dyeing conditions, such as temp, pH and this results in the dye being more robust. The presence of triazine groups in the reactive dye, e.g., in suffix supra dye, tends to increase the substantivity of the dye to the substrates, increasing the degree of exhaustion and possibly the fixation (ezetimibe et al., 2018).

Dyes that bond through triazine tend to be more resistant to alkaline hydrolysis. Reactive dyes are the best choice for dyeing cotton and cellulosic fibers. However, the efficiency with which the dyer removes the unfixed dyes from the fabric, the stability of the dye fiber bonds to attack during washing, and related wet treatments lead to credence (Ezetimibe *et al.*, 2018). Fixation in reactive dyeing is by nucleophilic substation or elimination mechanisms, indicating the most favored leaving the group to be chlorine. Although methoxy groups have been used, more electronegative atoms or groups can achieve much higher reactivity. Hence, the main objective of this study is to synthesize dyes based on p-aminobenzoic acid and p-bromo aniline coupling with H-acid and analyze their dyeing performance on cellulosic fabrics.

EXPERIMENTAL

Dye synthesis

Synthesis of the dyes involves diazotization of primary aromatic amine, namely, P-bromo aniline and P-aminobenzoic acid, and then each coupled with H-acid condensed with cyanuric chloride.

Synthesis of intermediates (Diazotization of P-aminobenzoic acid)

An amount of 0.025mol (3.4g) of p-amino benzoic acid was dispersed in 20 ml of distilled water in a beaker equipped with a mechanical stirrer on an ice bath. 7ml of cold concentrated HCl was added to the mixture with constant stirring for homogeneity. A mixture of an ice salt and 1.73g (0.025mols) of sodium nitrite dissolved in 10ml of distilled water was added to the mixture in drops for 30 minutes. The mixture was stirred for 45 minutes at -1 to 2^0C to achieve good diazotization. (Usman et al., 2018). The resultant diazonium ion is coupled with the coupling component (H-acid condensed with cyanuric chloride). The reaction is shown in Figure 1.

Diazotization of 4-bromoanline

An amount of 2.95g (0.025mols) of 4-bromoaniline was dispersed in 20 ml of distilled water in a breaker equipped with a magnetic stirrer on an ice bath. Using an ice salt mixture, 14ml of cold concentrated HCl (36%) was added with constant stirring for homogeneity at a temperature range of -1^0C to 2^0C. 1.725g (0.025mol) of sodium nitrite in 10 ml of distilled water was added to the mixture in drops over 30 minutes. The solution was stirred further for 45 minutes to achieve good diazotization. The resultant diazonium ion formed was then coupled with a coupling component (1-naphthol-8-amino-3, 6-disulphomic acid). The content was stirred for 45 minutes and condensed with cyanuric chloride. The reaction scheme is shown in Figure 2.

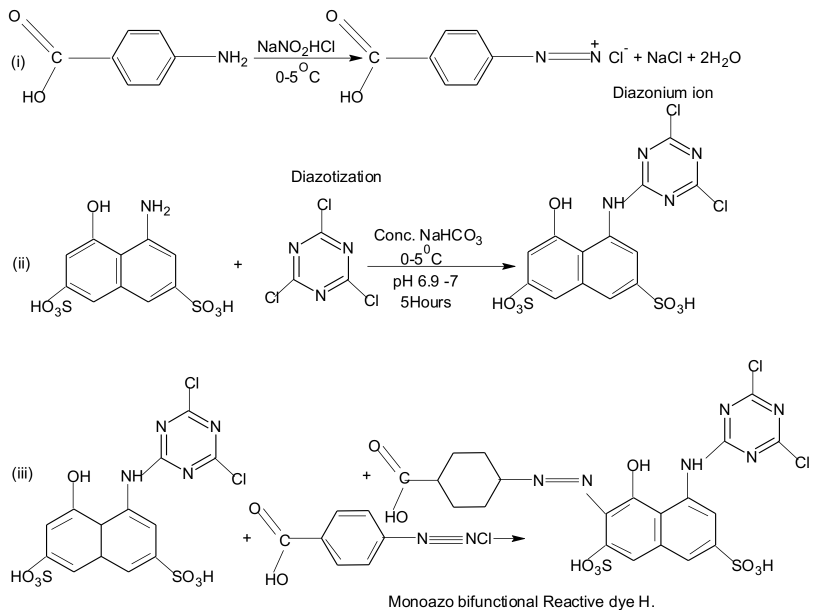

Fig. 1: Synthesis of Monoazo Bifunctional Reactive Dye H

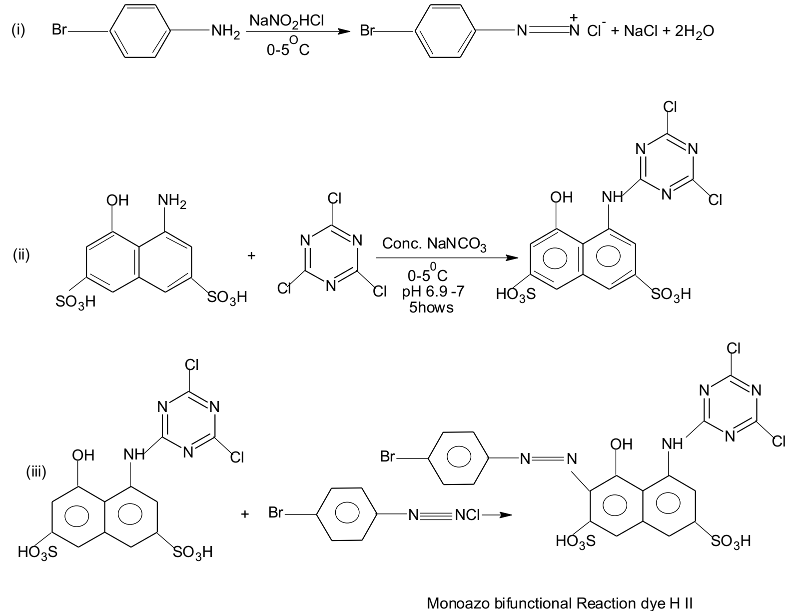

Fig. 2: Synthesis of Bifunctional Monoazo Reactive Dye H II

Dyeing of grey cotton fabrics

The two dyes synthesized were applied to grey cotton fabrics using the exhaust method. The dye bath was prepared by dissolving 1g of each dye sample in 100 ml of distilled water to obtain 1% solution of the dye. 1g of the fabric was immersed into the dye solution with the dye liquid to solid ratio of 1:50 at a temperature of 60^0C for 30 minutes with mechanical agitation; the temperature of the bath was raised to 100^0C gradually at the rate of 2^0C per minute for another 30minutes the percentage dye exhaustion was determined from UV-visible spectrophotometric analysis of optical density of dye bath before and after dyeing. The percentage of dye exhaustion was determined using Equation 1.

$$\% E = \frac{D_0 - D_1}{D_0} \; where \qquad E = \% \text{ Dye Exhaustion} \qquad (1)$$

D_0 = Optical density before dyeing

D_1 = Optical density after dyeing

Fastness testing

The dyed fabrics were tested according to the American Association of Textile Chemists and Colourists (AATCC) standard methods (AATCC-1999).

Washing fastness of the dyed fabrics

A composite of the dyed grey cotton fabric and bleached cotton fabric was stitched together and immersed in an aqueous solution containing 5g soap of non-ionic detergent at 60^0C with an ML ratio of 1:50. The composite squeezed in the rinse bath for 20min and then removed and rinsed in a hot and cold distilled water. The washing fastness was determined using a grey scale for color change and the degree of staining (BS 1006, 1978)

Fastness to light

The dyed fabrics and standard blue wool samples are exposed to a Tungsten filament lamp for 72 hours to assess the degree of fading. The color change was determined using a standard grey scale (BS 1006, 1978). The fastness rating was recorded.

RESULTS AND DISCUSSION

Physical characteristics of the synthesized dyes

The percentage yield and theoretical molecular weight of the two dyes are depicted in Table 1. The percentage yield for Dye 1 (48%) is higher compared to Dye 2 (36%). This difference could be attributed to variations in reaction efficiency, reagent purity, or the stability of intermediates during synthesis. The slightly lower molecular weight of Dye 1 (640.5 g/mol) compared to Dye 2 (670.5 g/mol) may also influence the yield, as the formation of larger molecules often involves higher steric hindrance or incomplete reactions.

Table 1: Physical characteristics of the dyes

Dyes	Yield(g)	Yield(5)	Mwt (g/mol) theoretical
1	4.8	48%	640.5
2	4.2	36%	670.5

The maximum absorption wavelengths of Dyes 1 and 2 vary depending on the solvent. Table 2 shows that the dyes (1&2) gave maximum absorption of 590nm and 570nm in water, 600nm in ethanol, and 490nm and 480nm in acetone, respectively.

Table 2: Maximum wavelength of absorption (λ-max) in different solvents

Dyes	Water (λ-max)	Acetone (λ-max)	Ethanol (λ-max)
1	590	490	600
2	570	480	600

Effect of temperature on percentage dye uptake

The UV-visible spectrophotometric analyses of the dye liquor before and after dyeing yield an absorption maximum of the dyebath. The % dye exhaustion of the two mono azo bifunctional reactive dyes is affected by temperature, as depicted in Table 3. From Table 3, it was established that dye II has the highest dye uptake on grey cotton fabric near boil (92.80) at 100^0C. This may be due to the bromine atom's high negativity on the aniline's para position. This result agrees with the results obtained by Gumel *et al.* (2018). The authors have investigated the effects of varying temp. During the dyeing of grey cotton fabrics modified with chitosan and Cellulase enzyme, with reactive red 22, Direct yellow G and C.I. Vat yellow 28: the results obtained have shown that C.I. Reactive red 22 has the highest dye exhaustion (89.8%) at 100^0C at the concentration-dependent manner of the modifier at a very high temper or near boil.

Table 3: Dye exhaustion of the two monoazo bifunctional reactive dyes on cotton

Dyes	% dye exhaustion (a) different temp				
	20^0C	40^0C	60^0C	80^0C	100^0C
Dye I	38.32	41.82	48.35	62.7	68
Dye II	43.67	50.97	59.8	73.5	92.8

Effects of time of dyeing on % dye exhaustion

Dyeing of grey cotton fabrics with monozo bifunctional reactive dyes I & II at different dyeing times from 10 minutes to 120 minutes at 30-minute intervals. From Table 4, it was observed that dyeing of grey cotton fabrics at different time intervals yields variable results depending on the reactive group of the dyes. Thus, dye II yields better exhaustion in the four dyeing intervals (i.e., 38.56, 45.62, 78.21, 95.69). Compared to dye I, that yield (31.62,60.20, 78.34 & 89.76).

The results conform with that obtained by Gumel et al. (2021). The authors were able to investigate the effects of varying times, one dyeing of grey cotton fabrics with the synthesized dyes. The results have shown that increased dyeing duration increases the dyebath's exhaustion. The result may be attributed to the reactivity of the dye and the cationic modifier.

Table 4: Effects of dyeing time on % dye exhaustion of monoazo bifunctional reactive dyes I & II on grey cotton fabrics

Dyes used	% dye exhaustion at a different interval			
	Time (min)			
	30	60	90	120
Dye I	31.62	60.20	78.34	89.76
Dye II	38.56	45.62	78.21	95.69

Effect of dye shade on exhaustion of the dyebath

The result of the effects of the percentage dye shade on the dyebath exhaustion of the two dyes is depicted in Table. The dyes showed higher exhaustion at high dye shades. The results agree with Usman *et al.* (2018), who reported that a high % dye shade leads to high dyebath exhaustion in the concentration-dependent manner of the dyes.

Table 5: Effects of % dye shade on dye uptake of grey cotton fabrics

Dyes used	% dye exhaustion			
	Dyes shade (5)			
	2	4	6	8
Dye I	98.32	51.82	62.7	68.9
Dye II	43.67	59.79	68.23	72.61

Fastness properties of the two dyes to light washing

Reactive dyes generally have good fastness properties. Thus, their dyeing fastness rating to both light and washing is depicted in Table 6. From Table 6, it was observed that the fastness of the two dyes to both washing and light at variable pH had shown appreciable ratings in a pH-dependent manner. However, the two dyes have shown excellent fastness in washing at an acidic pH (between 2 and 5). The light fastness was very good to excellent at an alkaline pH (between 6 – 13). The results agree with those of Usman *et al.* (2018). The authors reported a similar work by applying acid dyes on nylon fabrics. The fastness ratings were reported to be very good to excellent at acidic pH values. The excellent wash fastnesses of the two dyes were probably due to their hydrophobicity and polar substituents on the dye molecules that enhanced the strong dye-fabric covalent bond.

Table 6: Fastness properties of the two dyes at various pH

pH range	Dye 1		Dye 2		Dye 1	Dye 2
	Colour change	Colour stain	Colour change	Colour stain	Lightfastness	Lightfastness
2	4	3	5	2	4	4
3	4	2	5	2	4	4
4	4	2	5	2	4	4
5	3	3	5	2	3	5
6	3	3	4	3	6	6
8	4	4	4	3	5	7
9	3	4	4	3	6	7
10	2	4	3	4-5	5	7
11	2	4	2	4-5	6	6
12	2	4	1	5	6	7
13	1	5	1	5	7	8

CONCLUSION

Two monoazo bifunctional reactive dyes were synthesized and successfully applied on grey cotton fabrics. The dyeing performance was found to be very good to excellent. This is evident from the results of UV-visible spectrophotometric analysis, which shows maximum absorption of the two dyes at comparatively varying λmax. The variation in the maximum absorption wavelength was due to the difference in the electronegativity of the substituents on the dyes. Varying the dyeing conditions also yields an important output. Varying the dyeing time and temp dye shade have shown that dye II yields the best dyeing characteristics. This might be due to the polarity of substituents attached to the dyes.

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AUTHOR'S CONTRIBUTION

All authors contributed equally in writing, revising, and approving the publication submission.

CONFLICT OF INTEREST STATEMENT

The authors affirm that there are no competing interests regarding the publication of this paper.

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