



Dyeing Performance of Some Mono Azo Reactive Dyes on Cotton Fabric Base on Quinazolinone Moiety

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ABSTRACT

Various monoazo reactive dyes with quinazolinone moiety were synthesized starting with the preparation of 6,7-dimethoxy-2-phenyl-4H-benzo[d][1,3]oxazin-4-one from 2-amino-4,5-dimethoxybenzoic acid and fusing with different di-amino compounds to give dye intermediates A, 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one (A), which was diazotized, followed by azo coupling with various cyanurated coupling components such as H-acid, gamma acid and J-acid. All the reactive dyes were characterized by their percentage yield, UV-Vis spectroscopy, IR spectroscopy and dyeing performance on cotton fabric have been assessed. The UV-visible spectrophotometric investigation of the synthesized dyes was carried out in different solvents to obtain the absorption maxima, molar coefficients and solvatochromic effects of the dyes. The synthesized reactive dyes were applied on cotton and the percentage exhaustion and fixation of the dyes were evaluated and usage properties of the dyes also examined. The percentage of dye bath exhaustion on the fibre is reasonably good and acceptable. The dyeing performance of all dyes on cotton fabric gave moderate to good light fastness, good to very good wash fastness and fair to very good fastness to perspiration – acid and alkaline. The dyes gave colour ranges from purple to red to pink shades.

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INTRODUCTION

Reactive dyes are coloured compounds which contain one or two groups capable of further establishing covalent bond between carbon phosphorus atom of the dyes and oxygen, nitrogen or sulphur atom of the substrate [1]. Such covalent bonds are formed with the hydroxyl group of the cellulosic fibre and with the amino groups of polyamides [2]. Reactive dyes are anionic compounds soluble in water due to the presence of the sulfonic group in the molecule. After dyeing, the dye molecule and the textile macromolecules formed uniquely coloured molecules with very good resistances to wet treatment [3]. Bi-functional reactive dyes are coloured compounds that possess more than one reactive moiety per molecule or groups, capable

of forming covalent bonds between dye ions or molecules and the substrate [4]. The covalent bonds that attach reactive dye to natural fibres make them among the most prominent of dyes. They can be applied at room temperature, they are the best choice for dyeing cotton and other cellulose fibres [2]. They have good fastness properties and exhibit higher fixation yield than those with only one reactive group [5]. With hetero bi-functional dyes such as monochlorotriazine/vinyl sulphone dyes, the difference in reactivity levels between the two functional groups compensates for the variation in dyeing conditions such as temperature/pH and results in the dye being more robust [6]. Chromophores function by altering the energy in the delocalized electron cloud of the dye and thus

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absorbing radiation from within the visible range [7]. If this change in the wavelength to be absorbed is sufficient to cause any absorption within the visible range, then the compounds will be coloured [1]. These dyes produced have substantial improved dye ability with high percentage exhaustion and fixation properties unlike monofunctional reactive dyes. The aim of this research is to synthesize reactive dyes derived from quinazolinone moiety and their dyeing performance on cotton fabric.

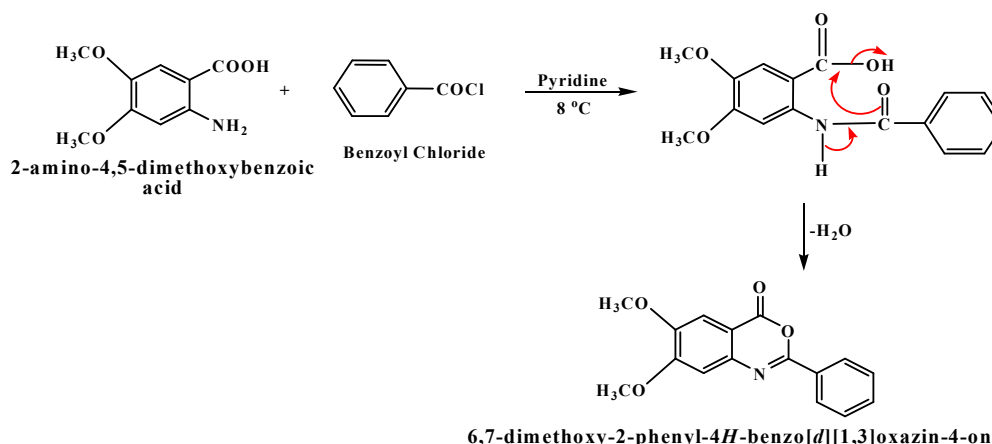
MATERIALS AND METHOD

All commercial products were purchased from Sigma-Aldrich. Melting points were determined by the open capillary method using the Gallenkamp melting apparatus. The visible absorption spectra were measured using Agilent CARY 300 UV/Vis spectrophotometer; IR was measured and recorded in KBr pellets using

the Agilent CARY 630 Fourier Transform Infra-red Spectrometer.

Synthesis of 6,7-dimethoxy-2-phenyl-4H-benzo[d][1,3]oxazin-4-one [8]

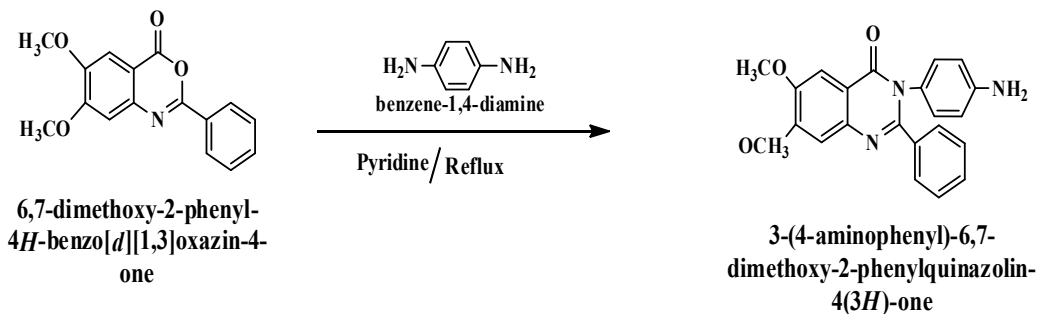
2-amino-4,5-dimethoxybenzoic acid (39.41g, 0.2mol) was dissolved in pyridine (100 ml) and stirred. Thereafter, benzoyl chloride (23.22 ml, 0.2mol) was added dropwise with constant stirring to the solution, maintaining the temperature near 0-5°C for one hour. The reaction mixture was stirred for another one hour at room temperature until a solid product was obtained. At the end of the reaction, the solid mass obtained was filtered, washed successively with saturated sodium bicarbonate solution, to remove unreacted acid, and finally washed with water, dried and recrystallized from pure ethanol. The percentage yield was calculated and the melting point determined.



Synthesis of the dye intermediate (A); 3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one [8]

Benzene-1,4-diamine (2.16g, 0.02mol) and 6,7-dimethoxy-2-phenyl-4H-benzo[d][1,3]oxazin-4-one (5.66g, 0.02mol) were dissolved in pyridine (40 ml) and heated under reflux for 9h under anhydrous reaction conditions and thereafter was allowed to cool at room

temperature. The reaction mixture was then treated with ice-cooled dilute hydrochloric acid (10%) and stirred. A solid product precipitated out and was filtered off and washed with water to remove any adhered pyridine. It was dried under a vacuum and recrystallized from ethanol. The percentage yield was calculated and the melting point determined.



Diazotization of the Intermediates A [8]

3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one (Intermediate A) (0.75g, 0.002mol) was dissolved in water (60 ml), and hydrochloric acid (10 ml, 0.008 mol) was added dropwise to the suspension formed and stirred, thereafter it was gradually heated up to form a clear solution and then the solution was

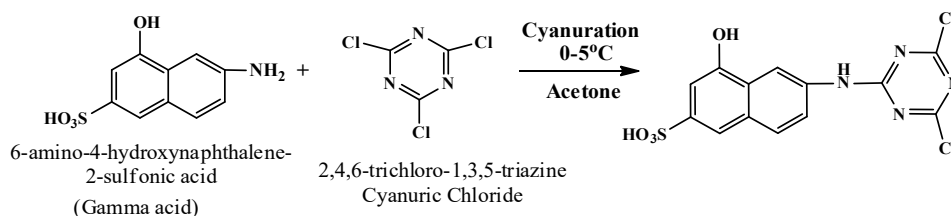
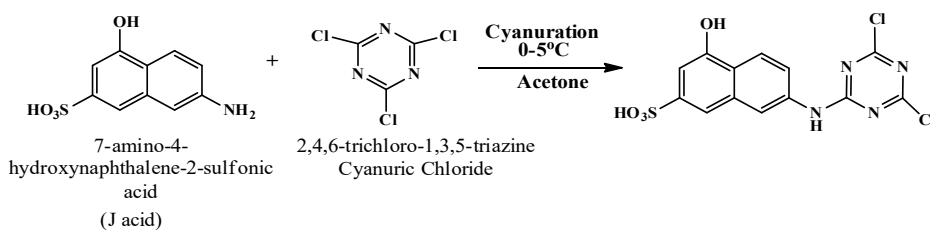
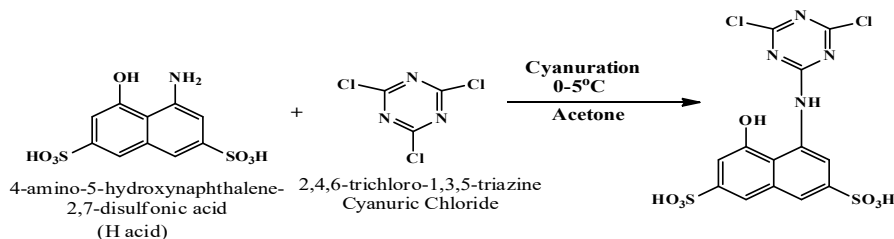
cooled to 0–5°C in an ice bath. A solution of NaNO₂ (0.6 g) in water (4 ml) previously cooled to 0°C, was added for 5 min with stirring. The stirring also was continued for an hour, maintaining the same temperature, for diazotization to occur. A clear diazo solution of 'A' at 0– 5°C was obtained and used for the subsequent coupling reaction.

Preparation of coupling components [9]

H-acid (3.19 g, 0.01mol) was dissolved in water (15 ml) at pH 7.5, using 20% (w/v) Na₂CO₃. A solution of cyanuric chloride (1.85 g, 0.01mol) was stirred in acetone (25 ml) at a temperature of 0-5°C and was added dropwise to the stirred H-acid solution at 0-5°C. After 10 min, the solution was adjusted to a neutral pH by

adding 20% (w/v) Na₂CO₃, and the reaction was continued for about 4 hours at 0-5°C to obtain a clear solution. The cyanurated H-acid solution thus obtained was used for coupling

The same procedure and condition were used for other coupling components; J-acid and Gamma acid.



Purification of the Dyes

The dyes were purified through the same process of recrystallization as highlighted above for the intermediates. Some of the dyes required the mixed solvent of ethanol, methanol /DMF (9/1 solvent mixture) according to a procedure suggested by [12]. The purity of each synthesized dyes were confirmed by melting point.

The percentage yield of the synthesized dyes and intermediates were determined using the formula shown below [13].

$$\% \text{Yield} = \frac{MP}{MMP} \div \frac{MR}{MMR} \times 100$$

where;

MP is the mass of the product
MMP is the molar mass of the product
MR is the mass of the reactant
MMR is the molar mass of the reactant

Percentage Yield of Dyes and Intermediates [16]

Melting point of the dyes

The melting point of each dye was determined using Gallenkamp melting apparatus.

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Small amount of each dye was filled into a capillary tube each placed in to the apparatus, the melting point of each dye was obtained by consistently focusing on the apparatus as the apparatus gradually heat the dye in the tube where the melting point is obtained.

Dyeing of cotton Fabric

The fabric was introduced into the dyebath at 30°C and the temperature was raised to 70°C, over 30 min. at 2°C/min, as soda ash (Na₂CO₃) solution (10% v/v) was be added to bring about fixation and the dyeing will be continued for 50 min more at the same temperature. The material was then removed, rinsed with cold water and dried.[10]

Application of dyes solution

A solution was prepared by dissolving about 1g of dried dye powder in 100 mls of distilled water. To determine the qualities required for the experiment the following prameter was utilized.

$$\text{Number of ml of stock solution required} = \frac{W \times P}{C}$$

Where W = weight (in grams) of sample to be dyed

P = percentage of dye to be used

C = concentration (%) of stock solution [12].

General procedure of dyeing chrome tanned leather

1 % of dye (on weight of the materials)

50 + 2°C dyeing temperature

0.1 % of formic acid on weight of the dye

Time of dyeing: one hour

Liquor ratio 20:1

Determiration of dye bath exhaustion

Dye uptake was determined by measuring the absorbance of diluted dye bath samples at the wavelength of the maximum absorption. The bath was sampled before and after dyeing. A 1ml aliquot was taken from the bath and diluted in 20ml of distilled water. This is to ensure that the absorbance falls within the

readable range of 1.5. The percentage dye bath exhaustion (%E) for each substrate was calculated using the equation below [13].

$$\% E = \frac{A_0 - A_1}{A_0} \times 100$$

Where A₀ and A₁ are the absorbance at λ_{max} of the dye bath prior to dyeing and after dyeing respectively.

Determiration of dyed fixation and fixation efficiency

The term fixation ratio refers to the radio of the amount of dye absorbed (which is covalently bonded to the fibre) to the hydrolyzed dye on the surface of the surface.

$$\text{Percentage fixation} = \frac{OD_1 - OD_2 - OD_3}{OD_1 - OD_2} \times 100$$

Where OD₁ = optical density of the dye before dyeing

OD₂ = optical density of the dye after dyeing

OD₃ = optical density after stripped

Each dyed fabric was stripped in a 25% (w/w) pyridine in water solution (100 ° C IR 10:1) for 30 minutes and the part of the solution was taken to the spectrophotometer to give OD₃; the optical density after stripping.

Optical overall fixation efficiency value (T) is related to the original amount of dye applied. A simple relationship exist between % T % F, and % E (dye bath exhaustion) given by:[14]

$$\% T = \frac{\% F \times \% E}{100}$$

Light fastness of dyed substrates (Fastness to Sunlight) SLT 401 (IUF 401)

This test was carried out in accordance with the Society of Leather Technology and Chemists. The test is carried out on the dyed samples under daylight facing south sloping at an angle 45° from the horizontal. The procedures involved aligning both the eight dyed wool standards together with a. 2 cm x 2cm cut pieces of the dyed samples on a card and covering one third of the setup with opaque cover.

Exposure is carried with regular inspection noting when the non-exposed part and exposed part of each dyed sample had contrast equivalent to grade 4 of ISO grey scale after which and opaque cover was placed covering part of the

exposed sample part, exposure was continued till the blue standard 7 faded. The rating of the dyed samples is taken to be those equivalents to- that of standard dyed blue wool samples, which faded to the same extent as the specimen at the same time

Wash fastness of the dyed substrates

This is to assess the leather resistance to prolong action of water. 2 x 2cm of the dyed leather was dipped into solution made by 5 g (0.5 %) of detergent powder into 200 cm³ of distilled water. This was placed in water bath and the temperature allowed to rise to 40 °C. This was vigorously stirred for about 30 min and the leather was transferred to 100 cm³ distilled water for washing and rinsing was done five times and dried. The change in colour was assessed by the blue wool scale.

Fastness to Perspiration

This test measures the resistance of the colour of textile fabrics of all kinds to perspiration in all forms. Perspiration was carried out under acidic and alkaline solutions.

Acidic solution: Sodium chloride (NaCl 5g/l), disodium hydrogen orthophosphate dehydrate (Na₂HPO₄.2H₂O 2.5 g/L), histidine monohydrochloride monohydrate

(C₆H₉O₂N₃HCl.H₂O 0.5g/L), brought to pH 5.5 with 0.1N sodium hydroxide (NaOH) in a liquor ratio of 20:1.

Alkaline solution: Sodium chloride (NaCl 5g/l), disodium hydrogen orthophosphate dehydrate (Na₂HPO₄.2H₂O 2.5 g/L), histidine monohydrochloride monohydrate (C₆H₉O₂N₃HCl.H₂O 0.5g/L), brought to pH 8 with 0.1N sodium hydroxide (NaOH) in a liquor ratio of 20:1

Procedure

A composite sample was made by sand witching the dyed sample measuring (5x5) cm between two pieces of un-dyed bleached cotton fabric measuring (5x5) cm. The composite specimen was thoroughly wetted in this solution (acidic and alkaline) at room temperature for 30mins. At the end of 30mins, the composite specimen was removed from the solution and the composite sample placed between two glasses plates measuring about 7.5x6.5cm under a force of about 4.5kg. The apparatus containing the treated composites was then placed in a perpirometer at 37 + 2°C for 4 hours. After 4 hours, the specimens were removed from the perspirometer and dried at room temperature. The change in colour of the specimen and the staining of the white cloth were assessed using greyscale.

Results and Discussion

Table 1.1 shows the Physical properties of intermediates

Intermediate	Structures	Molecular Formulae	Molecular Weight (g/mol)	Melting Point °C	Yield %
3[H]		C ₁₆ H ₁₃ NO ₄	283	225-227	78

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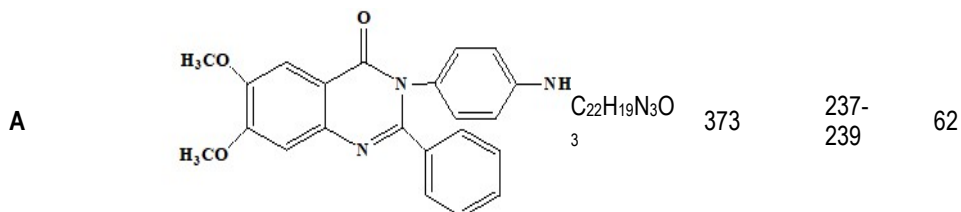
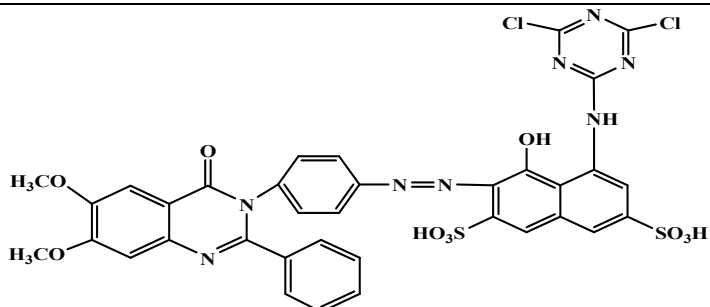
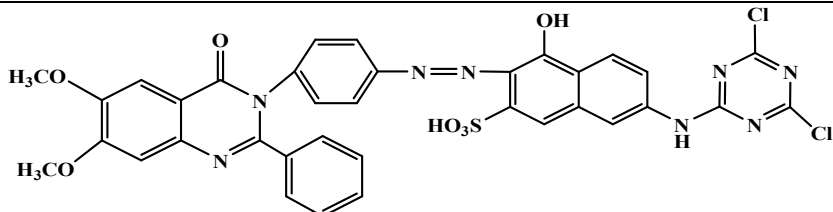


Table 1.2 shows the FT-IR spectra of the intermediates

Intermediate	FT-IR (KBr) : ν (cm^{-1})
3[H]	1751 (C=O), 1612 (C=N), (C-O-C), 3071 (C-H), 1273 (C-O)
A	1728 (C=O), 1620 (C=N), 3394 (N-H), 3063 (C-H), 1280 (C-O)

The various dyes 1A, 2A, and 3A, were successfully synthesized using diazotization and coupling reaction and the structures and properties are shown below in Table 1.3

Table 1.3 Shows the synthesised dyes structures

Dye No	Structure
1A	
2A	

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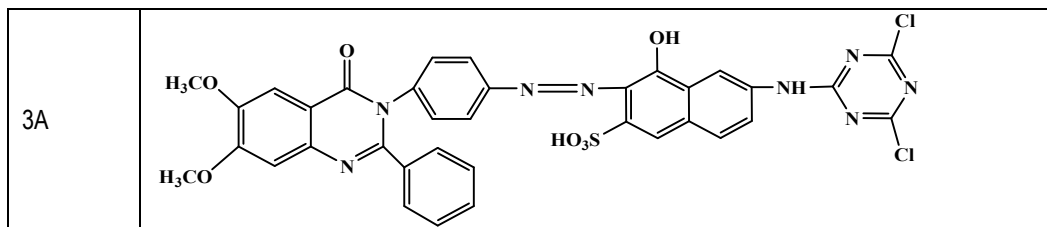


Table 1.4 shows the Physical properties of synthesized dyes

Dyes	Molecular Formulae	Molecular Weight (g/mol)	Melting Point °C	Yield %	Physical Appearance (Colour)
1A	C ₃₅ H ₂₄ N ₈ Cl ₂ O ₁₀	787	310-312	76	Light purple
2A	C ₃₅ H ₂₄ N ₈ Cl ₂ O ₇	739	290-293	85	Purple
3A	C ₃₅ H ₂₄ N ₈ Cl ₂ O ₇	739	347-350	90	Light pink

Table 1.5 shows the FT-IR spectra of the dyes

Dye No.	FT-IR (KBr): ν (cm ⁻¹)
1A	1651 (C=O), 1443 (-N=N-), 3402 (O-H), 1203 (C-N), 3279 (N-H), 3047,2931 (C-H aromatic, aliphatic), 864 (C-Cl)
2A	1736 (C=O), 1443 (-N=N-), 3463 (O-H), 1204 (C-N), 3279 (N-H), 1350 (S=O), 3187 2924 (C-H aromatic, aliphatic), 787 (C-Cl)
3A	1728 (C=O), 1574 (-N=N-), 3449 (O-H), 1195 (C-N), 3279 (N-H), 1365 (S=O), 3047,2931 (C-H aromatic, aliphatic), 748 (C-Cl) 1728 (C=O), 1451 (-N=N-), 3449 (O-H), 1211 (C-N), 3279 (N-H)

Table 1.6 The wavelength of maximum absorption and Molar extinction coefficient of the dyes

Dye No.	ϵ_{max} in DMF $\times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$	H ₂ O λ_{max} (nm)	DMF λ_{max} (nm)	Methanol λ_{max} (nm) a	Methanol + HCl λ_{max} (nm) b	Change in λ_{max} (nm) (b-a)
1A	2.92	529	527	524	528	+4
2A	2.79	533	535	533	529	-4
3A	2.92	521	516	514	510	-4

Fastness Tests

The wash, light and perspiration fastness of the dyed cotton fabric were presented in table 4.7

Table 1.7 Shows result of Exhaustion and Fixation of reactive dyes on cotton

Dyes	Colour	Exhaustion (%)	Fixation (%)
1A	Light purple	86	71
2A	Purple	89	69
3A	Light pink	84	67

Table 1.8 shows the Fastness Properties of the synthesized dyes

Dyes	Washing Fastness		Light Fastness	Fastness to Perspiration	
	Colour change	Staining		[Acid]	[Alkaline]
1A	3-4	4	4	4	4

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2A	4	4	4	4	4
3A	4	3-4	3	2	4

Synthesis of 6,7-dimethoxy-2-phenyl-4H-benzo[d][1,3]oxazin-4-one

6,7-dimethoxy-2-phenyl-4H-benzo[d][1,3]oxazin-4-one was synthesized to give a white crystal solid after recrystallization from ethanol as showed in the reaction scheme 4.1. the percentage yield and melting point was found to be 78% and 225-227°C respectively as shown in Table 1.1.

Synthesis of Intermediates A,

6,7-dimethoxy-2-phenyl-4H-benzo[d][1,3]oxazin-4-one was refluxed with Benzene-1,4-diamine to obtain intermediate A in the presence of pyridine, as shown in the reaction scheme 4.2 below. The melting point and other physical properties are shown in Table 1.1

Synthesis of dye 1A

3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one was diazotized and coupled with cyanurated H-acid to give lilac purple dye 1A. The yield and melting point was 76% and 310-312°C as shown in Table 1.3

The infra-red (IR $\nu_{max} \text{ cm}^{-1}$ Appendix A5) spectrum shows absorption at 3047 and 2931 which is due to C-H stretch for aromatic and aliphatic. The signal at 1651 is due to the C=O stretch. The signal at 1443 is responsible for -N=N- stretch. The signal at 3402 indicates O-H stretch. The signal at 1203 is due to the C-N stretch. The signals 3279 and 864 are attributed to N-H and C-Cl stretch as shown in Table 1.5

Synthesis of dye 2A

3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one was diazotized and coupled with cyanurated J-acid to give purple dye 2A. The yield and melting point was 85% and 290-293°C as shown in Table 1.3

The infra-red (IR $\nu_{max} \text{ cm}^{-1}$ Appendix A6) spectrum shows absorption at 1736 which is due to C=O stretch. The signal at 1443 is attributed to -N=N- stretch. The signal at 3463 indicates the O-H stretch. The signals 1204 and

3279 is attributed to C-N and N-H stretch. The signal at 1350 is due to the S=O stretch. The signal at 3187 and 2924 is due to the C-H stretch for aromatic and aliphatic. The signal 787 is due to C-Cl stretch. as shown in Table 1.5

Synthesis of dye 3A

3-(4-aminophenyl)-6,7-dimethoxy-2-phenylquinazolin-4(3H)-one was diazotized and coupled with cyanurated Gamma-acid to give light pink dye 3A. The yield and melting point was 90% and 347-350°C as shown in Table 1.3

The infra-red (IR $\nu_{max} \text{ cm}^{-1}$ Appendix A7) spectrum shows absorption at 3047 and 2931 which is due to C-H stretch for aromatic and aliphatic. The signal at 1728 shows a C=O stretch. The signal at 1574 indicates a -N=N- stretch. The signal 3449 is responsible for the O-H stretch. The signals 1195 and 3279 is attributed to C-N and N-H stretch. The signal 1365 is due to the S=O stretch. The signal 748 is due to the C-Cl stretch, as shown in Table 1.5

Visible Absorption Spectra and Molar Extinction Coefficient of the Dyes

Absorbance is the measure of the amount of light absorbed. The visible absorption properties were measured in water, dimethylformamide (DMF) methanol and methanol+HCl. The result is summarized in Table 1.6. The colour of the reactive monoazo dyes depends on the nature of both the diazo and coupling component. The wavelength of the maximum absorption of the quinazolinone based dyes ranges from 470 – 540 in water, 460 – 550 in DMF, 470 – 540 in Methanol and 490 – 540 in Methanol+HCl.

The molar extinction coefficient (ϵ) of the dyes was calculated based on the concentration in dimethylformamide (DMF) as a solvent and are also listed in Table 1.6

The λ_{max} shifts in solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvent. The measurement of λ_{max} in methanol, water and

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DMF showed that the λ_{max} of the intramolecular charge transfer bonds exhibits a marked redshift on transfer from non-polar to polar solvent. This behaviour indicates that the polar excited states of the synthesised dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased.

Solvent effect on the UV-Vis spectra (Solvatochromism)

Solvatochromism is due to various solute-solvent interactions in both the ground state and the excited states. Effect of solvent polarity on the maximum absorption wavelength of dyes i.e. the ability of a chemical substance to change colour due to change in solvent polarity was studied. With the increasing polarity of the solvent, the absorption maximum is shifted to a longer wavelength [11]

The bathochromic shift observed on changing to a more polar solvent suggests that the dye molecule has a more polar excited state than the ground state and this will lower the energy of the transition. The energy difference between the ground and the excited states is reduced leading to a bathochromic shift of the visible band. On the other hand, those dyes with hypsochromic shift (negative solvatochromism) mean that the dyes molecules have a more polar ground state than the excited state.

And when 0.1 M HCl was added to the dye solution in methanol, dye 1A showed a bathochromic shift (positive halochromism). This showed that these dyes exist in the cationic form in an acidic methanolic solution. Dyes 2A and 3A show negative halochromism on the effects of acids in the dye solution in methanol, this may be due to an electron-withdrawing strength of the substituent, if the electron-withdrawing strength of the substituent is sufficiently high, negative halochromism can be observed.

Wash fastness properties

Coloured fabric must withstand condition which it may encounter during processing following colouration and their subsequent daily use. If the dye is not covalently bonded to the fabric, it may be lost during washing. Wash fastness properties of the synthesized dyes

were generally moderate to very good for all dyes, as all the dyes fall between 3-5 as shown in Table 1.8. This is because the dyes containing reactive groups are compatible with the fibre and were covalently bonded with the reactive sites in the fibre. The fastness rating of 4, 4-5 shows that the binding forces between the dye and the fibre are secure. This means the formation of a covalent bond between the reactive sites in the dye and the fibre is relatively strong as there is little or no staining on the adjacent fabric. However, some exhibited good to moderate values of 3, 3-4 an adjacent fabric due to poor uptake of the dye into the fibre.[14]

Fastness to light

Light fastness is the resistance of dyes to the effect of sun, heat and light energy. The light fastness was fair, moderate to fairly good, as value ranges from 3-5 for all the dyes applied on cotton as seen in Table 1.8. The poor light fastness of 3 may be due to the poor planarity of the dyes. Many factors can affect light fastness, some of them are depth of shade, the presence of foreign substances and inherent photo-stability of the dye chromophore and how this stability is affected by the chemical nature of the fabric. Generally, reactive dyes have moderate resistance to light. Also, darker depths of shades show good resistance to light whereas brighter/lighter shades of dyes show poor resistance to light. The electron mobility of brighter shades dyes is high and so the electrons can easily move to the excited state causing breakage in the chromophore system of the dye which results in fading. Generally, factors that affect the colour fastness of textiles are internal and external. Internal factors may include the dye and the fibre type while external factors are products imposed by external forces or conditions [12].

Fastness to perspiration

The perspiration produced by the human body is a chemical fluid that can have adverse effects on a coloured fabric in regular contact with it. All perspiration contains common salt which can affect some dyes but can vary in acidity or alkalinity according to a particular

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individual (S.D.C, 1991). Two chemical solutions which approximate human perspiration was used, one being slightly acidic and the other being slightly alkaline [15]. The fastness to perspiration carried out in both acidic and alkaline solutions of histidine is summarized in Table 1.8.

All the dyes had a very good fastness to perspiration of values ranges from 3-5. This result shows that the dyed cotton samples had good fastness to perspiration in alkaline than in acid medium.

CONCLUSION

The diazotization of the synthesized quinazolinone intermediates followed by coupling with various cyanurated acid coupling components gave corresponding monoazo reactive dyes. These dyes gave a wide range of fast shades like purple, orange and pink shade on cotton fabric. This type of dye synthesis is generally convenient and economical for use. The dyeing performance of all dyes on cotton fabric gave moderate to good light fastness, good to excellent wash fastness and moderate to good fastness to perspiration – acid and alkaline.

The presence of the triazine group of the dye molecule improves the exhaustion, fixation and fastness properties. Thus, the exhaustion and fixation of these dyes are very good; this indicates that the dyes have good affinity and solubility with the fabric. The remarkable degree of levelness and brightness after washing indicates the good penetration and affinity of these dyes to the fabric

The colour difference may be attributed to both the nature and position of the substituent. The dyes gave a satisfactory performance for percentage exhaustion and fixation on cotton fabric. The fastness properties to washing, fastness properties to light and fastness properties to perspiration – acid and alkaline of the dyes on cotton showed good to excellent performance. The remarkable degree of levelness after washing indicates the good penetration and affinity of these dyes to the various fabrics.

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