Synthesis and Application of Monoazo-Anthraquinone Disperse Dyes on Polylactide Fibres

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Abstract: 1-Substituted-2-hydroxy-4-methyl-5-cyano-6-pyridone-azo-antharaquinone disperse dyes having high light fastness on polylactide fibres were synthesized from 1-anthraquinone via a diazotization-coupling reaction with substituted pyridones. The structures of these dyes were confirmed using IR spectroscopy. Their dyeing behavior on polylactide fibres was also determined whereupon it was found that the title dyes could be applied at temperatures of 90 to 100 oC and that the corresponding dyed fabrics had good fastness properties.

Keywords: Polylactide; Pyridone; lightfastness; Dyeing; Extiction coefficient; Disperse dyes; Azoanthraquinone.

1. Introduction

Recently, substrates based on polylactide (PLA) fibres have received attention worldwide because of their attractive advantages [1], including their availability from a naturally renewable carbohydrate resource. In principle, PLA decomposes to carbon dioxide and water over time, without causing pollution to the environment. PLA can be conveniently produced from corn, sugar or sweet vegetables, and is not a petroleum-based material. At present, the proportion of corn crops used for PLA synthesis is < 0.029 % [2]. Therefore, the production of PLA need not lead to a potential food crisis. PLA is aliphatic polyester that is subject to high ultraviolet (UV) penetration into fabric composed of its fibres. Also, dye performance is normally different on PLA compared with polyethylene terephthalate (PET). For instance, many commercial disperse dyes have exhaustion levels of < 50 % on PLA but have exhaustion levels over 90 % on PET [3, 4]. Light fastness levels are also quite different on PLA compared with PET. Therefore, in addition to developing alternative dyeing methods for PLA [5], the synthesis of dyes that take the structural nature of PLA into consideration is essential to improving dye exhaustion and light fastness.

It has been shown by the previous researchers that alkylamino-anthraquinone disperse dyes (Figure 1) gave good exhaustion levela on PLA, but the light fastness of the dyed fabrics was not good [6]. It has also been found that the phenylazopyrazolone dye CI Disperse Yellow 16 (Figure 2) displayed good light fastness but low exahaustion on PLA fibres. With these points in mind, new azo-anthraquinone disperse dyes have been synthesized (Scheme 2), where 1-aminoanthraquinone was used as a diazo component to increase the dye-PLA substantivity and the pyridone system was used as a coupling component to provide good light fastness. The resulting azo-anthraquinone dyes (6a-e) were then applied to study the effects of dyeing conditions on the coloration of PLA.
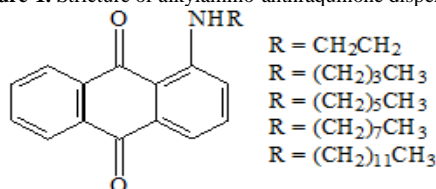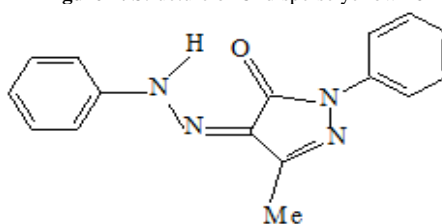
Figure-1. Stricture of alkylamino-anthraquinone disperse

R = CH₂CH₂
R = (CH₂)₃CH₃
R = (CH₂)₅CH₃
R = (CH₂)₇CH₃
R = (CH₂)₁₁CH₃

Figure-2. Structure of CI disperse yellow 16

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2. Experimental

2.1. General Information

All the chemicals used in the synthesis of the dyes and intermediates were of analytical grade and were used without purification. Melting points were determined by the open capillary method. The visible absorption spectra were measured using HEX10SY UV-visible pectrophotometer. IR spectra were recorded on a Nicolet FTIR-100 Thermoelectron spectrophotometer and the Mass spectra were determined on an Agilent 6890 Mass spectrometer.

2.2. Synthesis of 1-Amino-2-Hydroxy-4-Methyl-5-Cyano-6-Pyridone (4a)

A mixture of ethylacetoacetate (11.3 g, 0.1 mol), ethyl cyanoacetate (13.0 g, 0.1 mol), ethanol (50 ml) and ammonia water (72 ml, 0.3 mol) was stirred and refluxed until the reaction was completed (about 7-8 h). The reaction mixture was poured into 400 ml distilled water and acidified with hydrochloric acid to obtain white precipitate which was washed, dried and recrystallised from ethanol. 4b), (4c), (4d) and (4e) were similarly obtained by replacing ammonia water with methylamine, ethylamine, butylamine and dodecylamine respectively [7].

2.3. Diazotisation of 1-Aminoanthraquinone and Coupling to Pyridones (4) To Get Dyes (6)

Sodium nitrite ($NaNO_2$) (1.04 g, 0.015 mol) in water (5 ml) was added dropwise to a solution of 1-aminoanthraquinone (2.32 g, 0.01 mol) dissolved in concentrated sulphuric acid (98 5) w/w, 20 ml) with stirring at 5 ^{o}C. After 1 hour, tetrafluoroboric acid (HBF_4) (4 g, 40 % w/w) was added as a precipitating agent at 5 ^{o}C and the mixture was stirred for another 30 minutes. The diazonium salt (5) was isolated by filtration of the tetrafluoroborate salt which was then washed with 300 ml of water. A solution of the diazonium compound in dimethylformamide (DMF) (30 ml) was cooled to 5 ^{o}C and 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone (1.5 g, 0.01 mol) dissolved in 10 ml of 1 M sodium hydroxide solution was added in four equal proportions at 3 minutes interval. After stirring the mixture for 30 minutes at 5 ^{o}C, 250 ml of water was added, filtered and washed with 300 ml of water to obtain dye 6a. Using this same procedure dyes (6b-e) were obtained using the corresponding pyridone derivatives. The crude dye was purified by recrystallisation from toluene. The yields and physical data of the resulting azo-anthraquinine dyes are given in Table 1.

2.4. Dyeing of the PLA

Dye bath was prepared using a liquor ratio of 50:1 and 2 % shade on the weight of the fabric. For each respective dyeing 1 g of fabric was wetted in water for 5 minutes and excess water squeezed out. The wetted fabric was then introduced into the dye solution on a regulatory steam bath with the dyeing temperature at 40 ^{o}C initially and raised gradually to the boil over 30 minutes while agitating the sample. Dyeing was carried out at the boil for 1 hour. After dyeing was completed, the fabric was removed, thoroughly rinsed with cold running water and dried at room temperature. The percentage exhaustion of the dyes was calculated using the stripping method with DMF as the solvent. Series of the concentrations of the synthesized dyes were prepared in 20 % DMF. The absorbance values of each concentration were taken using UV-visible spectrophotometer. The absorbance values were plotted against concentrations to obtain a calibration curve which gave a straight line in agreement with Beer-Lambert's law. Each dyed fabric 1.0 g was placed in a beaker and 20 % DMF in a liquor ratio 50:1; this was boil and stirred until all the dyes have been stripped into the solution. Again the absorbance values of the stripped dye solutions were measured. The corresponding concentrations of these absorbance values were traced out from the calibration curve and each was expressed as a percentage of the dye-bath concentration. This gives the percentage exhaustion of the dyes on the PLA. The results obtained are shown in Figure 3.

2.5 Effect of Temperature on Dyeing

The dyeing temperatures were varied from 20 ^{o}C to 100 ^{o}C and the time was made constant. The results obtained are shown graphically in Figure 3.

2.6. Effect of Time on Dyeing

This was carried out by varying the time of dyeing while the temperature was made constant at 100 ^{o}C. The results obtained are shown in Figure 4.

2.7. Effect of pH on Dyeing

This was done by varying the pH of dyeing and maintaining the time and temperature constant. The results obtained are shown in Figure 5.
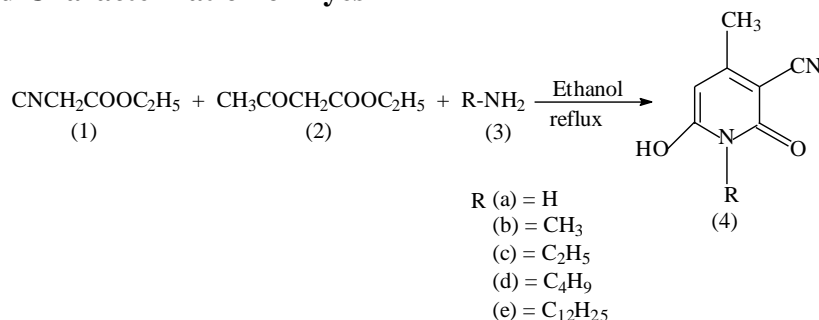
2.8. Fastness Testing

The colour fastness of the dyed PLA to washing and light was assessed using ISO standard methods 105-CO3:1989 and 105-BO2:1994, respectively. Wash fastness was assessed using a 5 g/l standard soap solution containing 2 g/l sodium carbonate at 60 ^{o}C for 30 min in an S-1002 two-bath dyeing and testing apparatus (Roaches International Ltd. UK). Light fastness was assessed using a Heraeus 15OS weather-ometer and continuous exposure
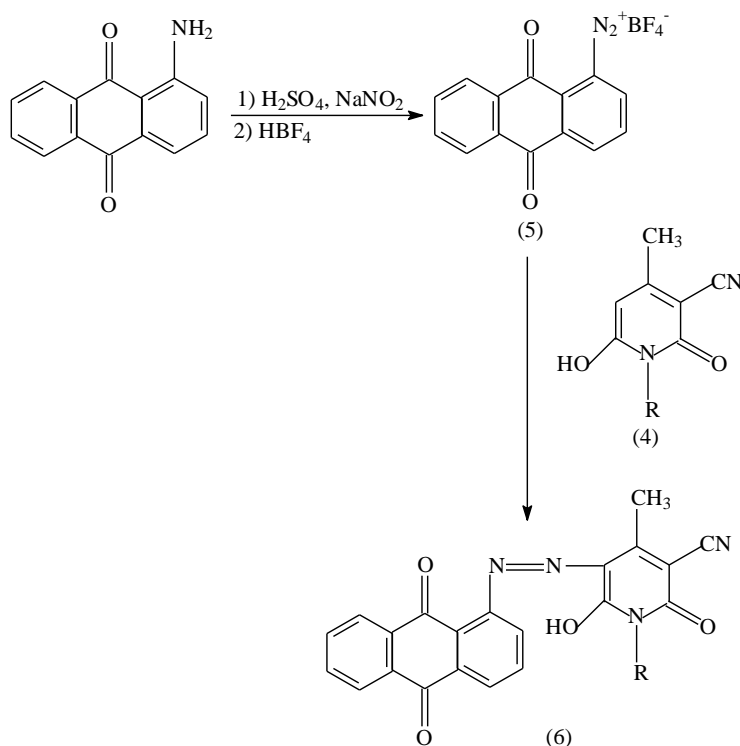
to sunlight. The black panel temperature did not exceed 50 ^{o}C and all fabric samples were evaluated using the ISO Standard grey scales.

3. Results and Discussion
3.1. Synthesis and Characterization of Dyes

$$CNCH_2COOC_2H_5 + CH_3COCH_2COOC_2H_5 + R-NH_2 \xrightarrow[\text{reflux}]{\text{Ethanol}}$$
(1)   (2)   (3)

R (a) = H
  (b) = CH$_3$
  (c) = C$_2$H$_5$
  (d) = C$_4$H$_9$
  (e) = C$_{12}$H$_{25}$

Scheme 1: Synthesis of Pyridones

Scheme 2: Synthesis of Azo-anthraquinone Dyes (6a - 6e)

1-Substituted-2-hydroxy-4-methyl-5-cyano-6-pyridones (4a – 4e) were prepared from a mixture of ethylcyanoacetate (1), ethylacetoacetate (2) and corresponding amines (3a – 3e) in ethanol under reflux as shown in Scheme 1. The method used for the dyes synthesis is illustrated in Scheme 2. In this Scheme, diazotization of 1-aminoanthraquinone was conducted in concentrated H$_2$SO$_4$ because (i) the amine was readily dissolved in this medium and (ii) nitrosylsulphuric acid efficiently diazotized the amine. In the coupling reaction, solid pyridone powders were used because this minimizes the amount of DMF required, making dye isolation easier and more efficient. Results in Table 1 show that dyes (6a – 6e) were obtained in moderate to good yields ranging from 64 % to 84 %. The colour of the dyes in crystal form after purification was mainly yellow as shown in Table 1.

Table-1. Physical characteristics of the dyes

Dye No.	Molar mass (g/mol)	Melting point (^{o}C)	Yield (%)	Colour of crystal	Colour of dyed samples
(6a)	386	320	77	Yellow	Yellow
(6b)	400	310	72	Brown	Yellow
(6c)	414	277	84	Yellow	Yellow
(6d)	442	270-271	81	Yellow	Yellow
(6e)	554	198-200	64	Yellow	Yellow

3.2. FT-IR Analysis of the Dyes

The absorption of infra-red radiation resulting from atom containing in the molecules showed the functional group present in the molecule of the dyes synthesized Silverstein and Webster [8]. There are two regions of the infra-red spectrum of interest to the organic chemist; these are the functional group and the finger print regions. The function group region extends from 4000-450cm^{-1} and the finger-print region extends from 1450-600cm^{-1}. In this functional group region are found absorption bands due to the stretching frequencies of various functional groups such as CH, OH, NH and so forth. This is the most vital region of the spectroscopic analyst, because from the position of the peaks inferences can be made of the functional group that are present and that which are absent, while the finger-print region which contains certain functional group absorptions may be spotted in this region. It is most useful for comparison purpose. In fact, all organic compounds have a unique infra- red spectrum.

Each of the dyes synthesized gave characteristic absorption peaks in the finger print region and also in the functional groups regions. As can be seen from the infra-red spectrum results in Table 2, all the dyes gave absorption peaks due to azo group, -N=N- stretching vibration at 1450-1510cm^{-1}; aromatic C-H stretching vibration bands appeared in the region of 3030-2900cm^{-1}; C≡N stretching vibration bands appeared in the region of 2260-2220cm^{-1}; C-C stretching vibration bands appeared in the region of 1450-1600cm^{-1}; C=O stretching vibration bands appeared in the region of 1680-1780cm^{-1}; O-H stretching vibration bands appeared in the region of 3890-3650cm^{-1}; respectively. However, m-disubstituted of the pyridones exhibited a vibration stretching band of 680-705.97 cm^{-1}, while the p-disubstituted of the dyes is responsible for the vibration band of 814.4-853.53cm^{-1}

Table-2. IR spectra data of the dyes

Funtional group	Azo N=N	Carbonyl C=O	Nitrile C≡N	Aromatic C-H	Aromatic C-C	M-Disubstituted	p-Disubstituted	OH
Type of vibration	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching
Dye No	-	-	-	-	-	-	-	-
6a	1515.99	1610.25 1705.64	2371.66 2337.59	3005	1469.23	680.12	816.49	3752.7 36230
6b	15154	1625.56 1704	2369.08	2980.82	1460.78	690.92	819.48	3951.04 3645.63
6c	1477.53	1659.16	2218.21 2486.33	2935.76	1477.52	705.97	853.53	3600.25 3775.75
6d	1520.21	1657.78	2372.63 2360.33	2925.73	1480.42 146.84	680.1	814.4	3680.37 3651.61
6e	1520.68	1704.47	2370.97	2915.28	1478.93	-	817.36	3650.55

3.3. Visible Absorption Spectra of the Dyes

The visible absorption spectra of the dyes were measured in ethanol, toluene, dimethylformamide (DMF). The wavelength of maximum absorptions were highest in DMF, because DMF is the most polar of these solvents. The results of UV- spectral are summarized in Table 3.

Table-3. Visible Absorption Spectra of the Dyes

Dye No	ε_{max} in DMF x 10^4 (Lmol^{-1}cm^{-1})	λ_{max}/nm in DMF	λ_{max}/nm in Toluene	λ_{max}/nm in Ethanol	λ_{max}/nm in Ethanol + HCl	Change in λmax (b-a)/nm
6a	5.22	484	420	452	441	-13
6b	5.15	446	400	400	400	0
6c	3.95	483	401	420	404	-16
6d	2.97	486	459	463	463	0
6e	1.2	488	461	441	465	+ 24

Ultraviolet – visible absorption are indicative of electron transition between the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). All the compounds showed absorption in the visible region greater or equal to 400nm which were characteristic of all compounds of the dyes studied. From the results in Table 3, the mono azo dyes 7a, 7b, 7c,7d and 7e absorbed maximally at 484nm, 446nm, 483nm, 486nm and 488nm respectively in DMF. Dye 7e is bathochromic compared with dyes 7a, 7b, 7c and 7d as it absorbed in longer wavelength. Dye 7e was made from the coupling component of 1-dodecyl-2- hydroxyl -4-methyl-5-cyano-6-pyridone which contains longer alkyl group in its molecule. This is followed by dye 7d containing 1-butyl-2-hydroxyl-4-methyl-5-cyano-6-pyridone as coupling component which absorbed at 483 nm and is bathochromic when compared with dyes 7a, 7b and 7c which absorbed at 484 nm, 446 nm, 483 nm respectively. Dye 7b absorbed at 446 nm is more hypsochromic than dye 7a which absorbed at 484nm as it absorbed at lower wavelength. However, the monoazo dyes (7a- 7e) absorbed highest at λ_{max} in DMF (484 nm, 446 nm, 483 nm, 486 nm 488 nm, respectively) than that of toluene (420nm, 400nm 401nm, 459 nm, 461 nm respectively) and in ethanol (452 nm, 400 nm, 420 nm, 463 nm, 441 nm, respectively.

3.4. Solvatochromic Effects

Solvatochromism is the ability of a chemical substance to change colour due to change in solvent polarity. With increasing polarity of the solvent, the absorption maximum is shifted to longer wavelengths [9]. Usually, in many dye molecules the ground state is less polar than the excited state so that the polar solvent will tend to stabilize the excited state more than the ground state leading to bathochromic shift in the visible absorption maximum, which is termed positive solvatochromism. The interaction of the solvent with the dye molecule is greater in polar solvent [10].

The phenomenon of solvatochromism arises from a change in the electronic structure and distribution of charge of the excited state as compared with the ground state. If the excited state is more polar than the ground state, it will be better stabilized by polar solvation and its energy lowered, so that the transition will occur at longer wavelengths, i.e. there will be a bathochromic shift (red shift) with increasing solvent polarity [9].

Most of the shifts in maximum absorption wavelength observed were bathochromic for majority of the dyes where measurements were done in solvent of higher polarity. The maximum absorption wavelengths values shifted to longer wavelengths when the solvent was changed from ethanol to dimethylformamide (DMF), for example, dye 7a absorbs at 420 nm in toluene, 452 nm in ethanol and 484 nm in DMF. For example, dye 7c absorbs at 401 nm, 420 nm, 483 nm in toluene, ethanol and DMF respectively.

Solvent polarity effects on visible absorption band of dyes have been thoroughly studied and well documented in literature [11]. The literature reported that $\pi\text{-----}\rightarrow\pi^*$ transition exhibits bathochromic effect when the polarity of the solvent is increased while $n\text{----}\rightarrow\pi^*$ transition shows hypsochromic effect with increase in solvent polarity. This is a clear indication that in this study, the visible band is due to $\pi\text{----}\rightarrow\pi^*$ transition since a positive solvatochromism occurred in some of the dyes and $n\text{----}\rightarrow\pi^*$ transition since a negative solvatochromism also occurred in some of the dyes. Solvatochromism is due to various solute-solvent interactions in both the ground and excited states. The red shift observed on changing to a polar solvent suggests that the dye molecules has a more polar excited state than the ground state and this will lower the energy of the $\pi\text{----}\rightarrow\pi^*$ transition. Thus the energy difference between the ground and the excited state is reduced leading to a bathochromic shift of the visible band.

3.5. Effect of Acid on Visible Absorption Band (Halochromism)

The effect of few drops of acid (HCl) on the visible absorption band, which could decrease or increase the maximum absorption wavelengths, is referred to as halochromism. The increase of λ_{max} in acidic medium is referred to as positive halochromism while the decrease in λmax in same acidic medium is referred to as negative halochromism. The effect of few drops of acid on ethanol solution of the dyes was inspected and the results are summarized in Table 3. Only dye 6e exhibit positive halochromism all the other dyes showed a negative halochromism. For example,, dyes 7a, 7c absorbed in neutral ethanol solution at 452 nm, and 420 nm but absorbed maximally at 441 nm, and 404 nm in acidic solution of ethanol, indicating a hypsochromic shift of -13 nm, and -16 nm respectively. Dyes 7b and 7d showed no halochromism effect as they both absorbed at 400nm and 463nm respectively in both neutral and acidic solution of ethanol.

3.6. The molar Extinction Coefficient (ε_{max})

The molar extinction coefficient (ε_{max}) is a constant for each molecule of any given wavelength representing the absorbance in 1 cm thickness of a medium containing 1 mole of the absorbing substance per litre [12].The molar extinction coefficient is actually a measure of the probability that photon of the correct wavelength striking the molecule will be absorbed [13].

The molar extinction coefficient was calculated based on the concentrations of the dyes in DMF as a solvent. The molar extinction coefficient, also a measure of the amount of light absorbed by a compound in solution, was calculated for each dye. From the results in Table 3, it could be seen that all the dyes possess high molar extinction coefficient and appear on the fabric brighter. This may be attributed to the fact that they transmit more light in comparison to others and therefore have narrow absorption bands with sharp peaks

3.7. Effect of Temperature on Dye Exhaustion

Temperature affects the rate of dye exhaustion since diffusion is directly proportional to the thermodynamic temperature. The higher the temperature of the dye bath the greater the kinetic energy of the dye molecules and the faster the diffusion of the dye molecules in and out of the substrate. Increase in temperature also tends to increase fabric porosity by increasing the molecular entropy and amorphous region of fabric polymer matrix. Figure 3 shows the effect of temperature of the rate of exhaustion of all the dyes on PLA. Tt was observed that increase in temperature increases the dye exhaustion. A rise in temperature increases exhaustion rather than diminishes [12], therefore, the exhaustion was greater at higher temperature. It has been shown in the recent study [14] that in the cause of investigating PLA crystallization that mobile amorphous phase increased as the dyeing temperature increased. The monoazo dyes have a smaller molecular size hence can diffuse faster and much of its molecules may have been retained in the fabric. By comparison dye 7a exhausted better with percentage exhaustion values of 95.25 %.

Figure-3. Effect of Temperature on dyeing
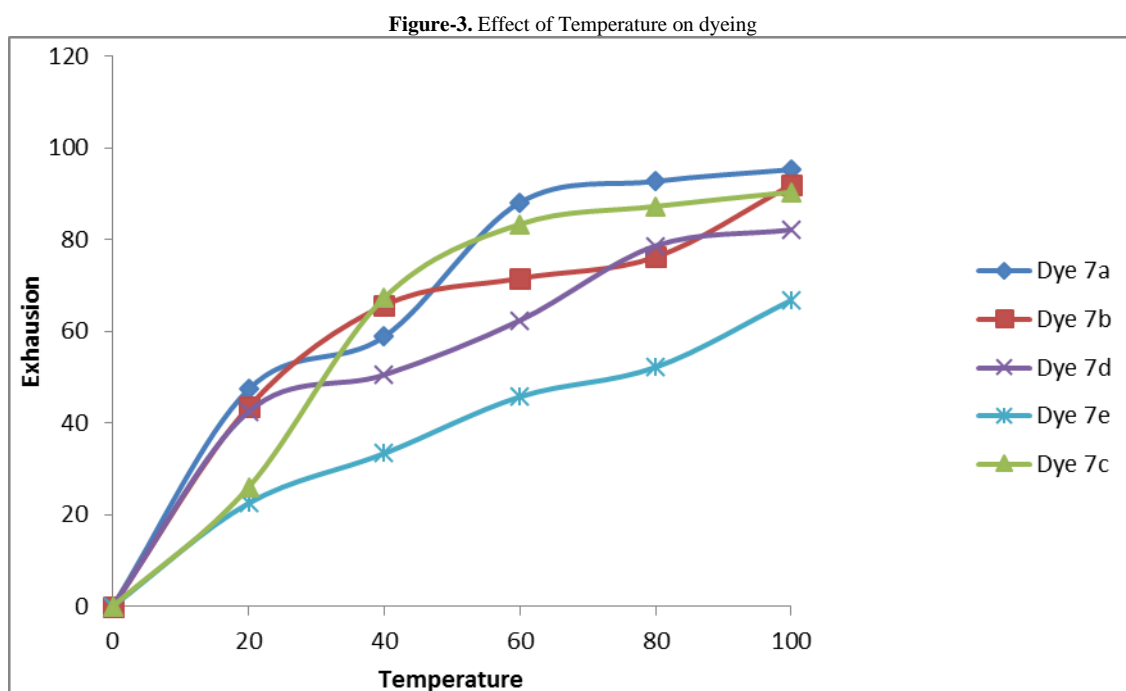
3.8. Effect of Time on Dye Exhaustion

From Figure 4, time of dyeing was varied, the temperature was kept constant at 100 ^{o}C and the liquor ratio was 50:1. It was observed that increase in time of dyeing increases the exhaustion. The reason may be at shorter time of dyeing the dye exhaustion was fairly achieved but at higher time of dyeing the exhaustion was fully achieved. At the initial stage of the dyeing only few of the dyes' molecules may have dissolved inside the water, as disperse dyes are known to have low solubility in water and dyeing takes place from a monomolecular dilute solution of the dye in water [15], the concentration of which was maintained by the progressive dissolution of solid dye from the finely dispersed dye particles in suspension. With time, the molecules of dye are transferred from solution to the surface of the fabric and adsorbed dye diffused monomolecularly into the fabric to form a solid solution [15]. From Figures 4, it can be seen for all the dyes, as the dyeing time increases, the percentage exhaustion as well as the depth of shade on the fabric increases. The dyes attained equilibrium at faster time of 60 minutes, this may be attributed to smaller sizes of the dye molecules. Among the dyes, dye7a diffused faster and exhausted better. This was followed by dye 7b and dye 7c respectively. Dye 7e which contains the longest alkyl chain in pyridone diffused slowest and exhausted less than other dyes.

Figure-4. Effect of time on dye exhaustion

3.9. Effect of pH on Dye Exhaustion
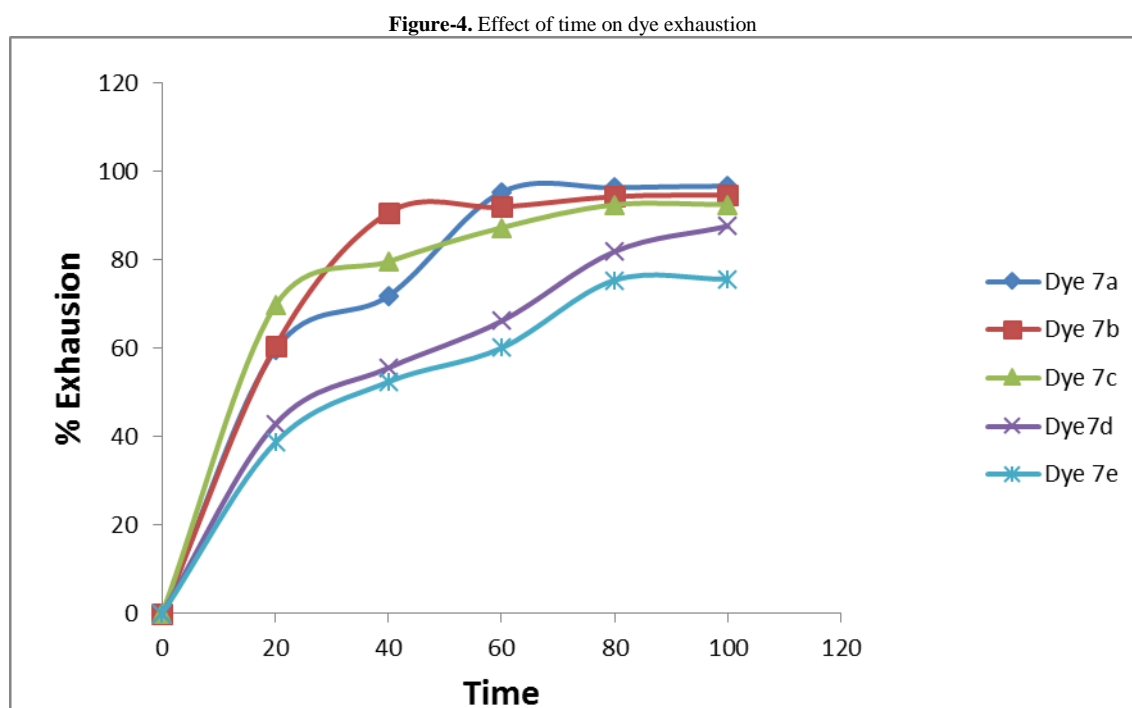
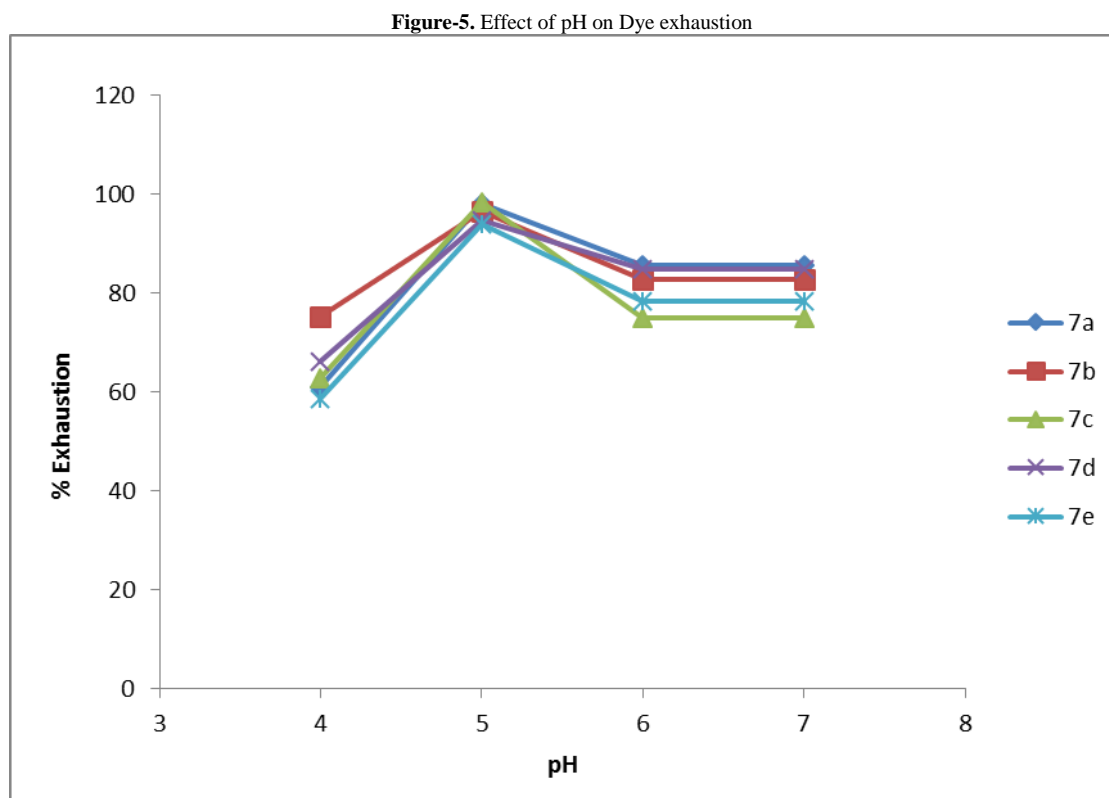**Figure-5.** Effect of pH on Dye exhaustion

Figure 5 shows the effect of pH on dyeing exhaustion of the dyes at 100 ^{O}C for 60 minutes. It was observed that there was an increase in dyeing exhaustion in the range pH 4-5 and then subsequent decrease exhaustion above the pH of 5. This may be attributed to achieving the dye solubility at pH of 5 which is a commonly used level for the application of disperse dyes in batch dyeing procedures [16]. Also the decrease in dyeing exhaustion observed at pH greater than 5 may be as a result of loss of fibre strength and elongation.

3.10. Assessment of Washing and Light Fastness

The resistance of dyeing materials to laundry treatment such as washing is referred to as washing fastness. This is very important and there are several washing tests that are applied according to the purpose for which the material is intended. Using ISO wash test NO.3, it can be observed in Table 4 that the washing fastness is generally good with little or no stain on adjacent fabric. The ratings vary from good to very good for the dyes. Generally the good washing fastness observed on the synthesized dyes may be attributed to the difficulty generally encountered by disperse dyes in their diffusion into polylactide fibre, meaning that once in, migration of the dye out of the fibre, will equally be difficult, thereby giving dyeings of high fastness to washing.

Table-4. Washing and Light fastness rating

Dye No	Change in shade	Staining of cotton white	Light fastness rating
6a	4	4	6
6b	4	4	6
6c	4	4	6
6d	4	4	6
6e	4	4	6

Light fastness is the resistance of colour of dyed materials to the influence of light. The fastness test can be done using day light for a long period or by a xenon arc, which is the accelerated version of the test [17]. In the present studies day light was employed, the dyed samples were exposed to daylight alongside with eight blue wool standards and the results are shown in Table 4. The fastness to light of dyed fibre depends on many factors, the most important of which are the inherent photo stability of the dye chromophore and the way in which this stability is affected by the chemical nature of the substrate. The results of light fastness shown in Table 4 indicate very good fastness to light of all the dyes with rating of 6. However, other higher ratings include7 which is excellence, 8 is the maximum light fastness rating. Rating of 1 is very poor, while ratings 2, 3 and 4 are poor, moderate and fairly good respectively. Generally, all the synthesized dyes show very good fastness properties to light fastness. The result may be attributed to the molecular structure of the dye planarity and dye substituents that provided shield from radiant energy on azo chromophore. Therefore, this effect conferred good light fastness properties on the dyes.
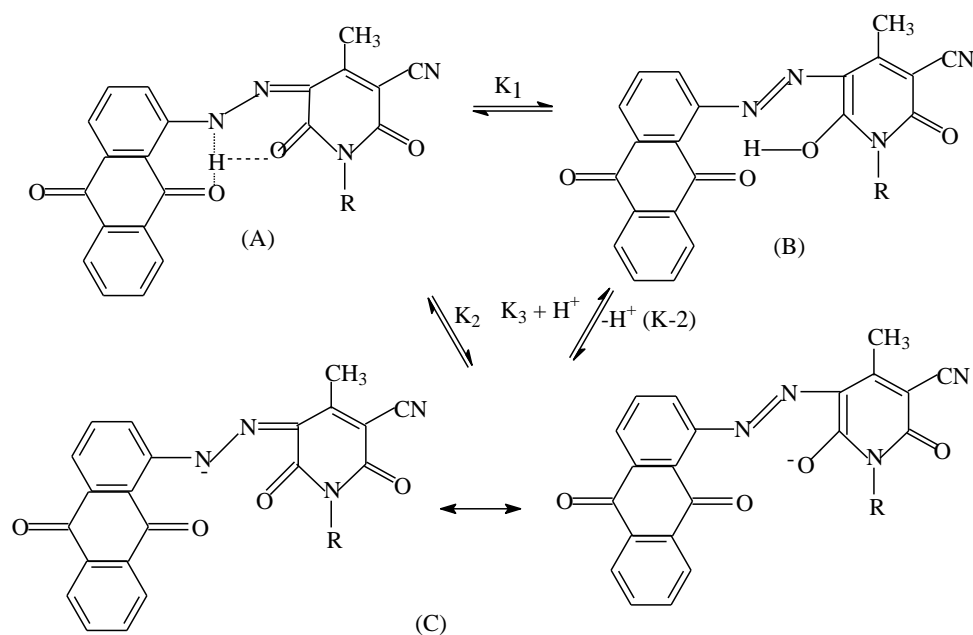
Scheme 3: hydrazone-common anion equilibrium

However, It has been reported that low light fastness among anthraquinone dyes arises from the ease of electrophilic attack at the N-atom of amino-substituted anthraquinone dyes in the excited state [18]. In the present case, on the one hand, diazotization of the amino group in the anthraquinone ring led to an azo group, which reduced the electron density on the corresponding-atom. On the other hand, the introduced pyridone system is known to improve photostability [19]. In this case, it is possible that the formed hydrazone structure gives rise to a bifurcated proton as shown in Scheme 3, enhancing dye stability.

4. Conclusions

New monoazo-anthraquinone disperse dyes with high affinity for polylactide fabric have been synthesized from pyridone as coupling component. FT-IR analysis indicated that these dyes exist mainly in the hydrozone form, as would be anticipated. Optimum dyeing conditions for the title dyes were found to be 90 – 100 $^{\circ}$C, pH 5 and 60 min of dyeing and the resultant dyeings had good wash fastness and very good light fastness.

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