Kinetics and Thermodynamic Studies of Disperse Dyes Derived from 4-Amino-3-Nitrobenzaldehyde on Polyester fabrics.

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***Abstract*-Adsorption kinetics and thermodynamic studies of disperse dyes derived from 4-Amino-3-Nitrobenzaldehyde on polyester fabrics was carried out at various temperatures, pH, liquor ratios, time and carrier concentrations. The results showed the equilibrium adsorption isotherms of disperse dyes on polyester fabrics. The values of the thermodynamic parameters recorded and the adsorption isotherms deduced from the experiment suggests that the adsorption kinetics of the disperse dyes on polyester fabric is in agreement with a pseudo second-order kinetic model [11]. Van der Wa'als forces are thought to have played significant role in dye – fibre attraction and the adsorption of disperse dyes on polyester was an exothermic process. It was found that on application, the dyes had very good fastness to both wash and light and moderate fastness to perspiration.**

***Key words*: Kinetics, Thermodynamic , 4-Amino-3-Nitrobenzaldehyde, Disperse dyes, fastness, Polyester .**

I. INTRODUCTION

Disperse dyes are unarguably the most important class of dyes used in dyeing cellulose acetates and polyester and are also of importance in the coloration of other hydrophobic fibres such as nylons, acrylics and polypropylene.

Disperse dyes are often substituted azo, anthraquinone or diphenylamine compounds which are non-ionic and contain no water solubilising groups. When pure, they are crystalline compounds of comparatively low molecular weight (240 – 350) which melt on heating (150 – 250^{0}C) and sublime without decomposition [12]. It is essential for disperse dyes to be able to withstand various dyeing conditions e.g., pH and temperature, resulting in negligible changes in shade and fastness [1], [2].

Studies have shown that although disperse dyes have low solubility in water, dyeing takes place from a monomolecular dilute solution of the dye in water. The process of dye transfer onto fibre involves three stages viz:

(1) Dissolution of the dye – some of the dye dissolve in water of the dyebath
(2) Transfer of dye from the solution to the surface of the fibre
(3) Diffusion of the dye monomolecularly from the surface to the interior of the fibre.

In the laboratory, conditions such as temperature, pH, time e.t.c., are adjusted so that stage 3 becomes the rate determining step [4].

Fick was the first to propose that the rate of diffusion ds/dt is proportional to the concentration gradient dc/dx, mathematically expressed as ds/dt = -Ddc/dx (Fick's law).

Where ds is the amount of dye diffusing across a unit area in a very small interval of time dt.

c is the concentration at a point x, the distance diffused and D (a constant) is the diffusion coefficient.

Several factors affect the dyeing of polyester fibre with disperse dye such as crystal form of the dye, dispersing agents, particle size of the dye, pH of the dyebath, temperature of dyeing and heat setting, and fibre fineness [9].

Variables under investigation in this work however, are limited to time, temperature, liquor ratio, carrier concentration and pH.

After a thorough and exhaustive search there seem to be no records in literature on the kinetics and thermodynamics of disperse dyes derived from 4 – Amino – 3 – Nitrobenzaldehyde. This paper therefore, reports the kinetics and thermodynamic studies of disperse dyes of the above derivatives with a view to enhancing and enriching the dyeing parametric inclusion of the data obtained to the database of colour chemistry and textile coloration in particular.

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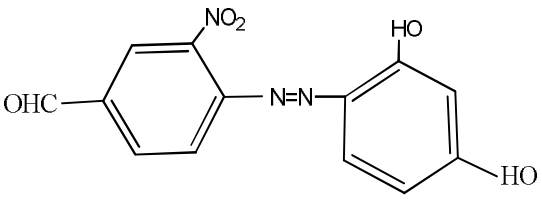
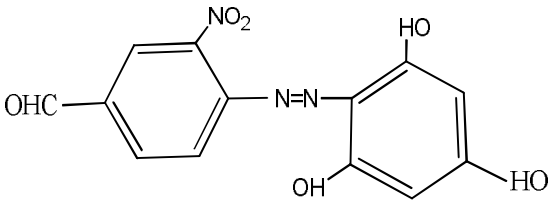


D1



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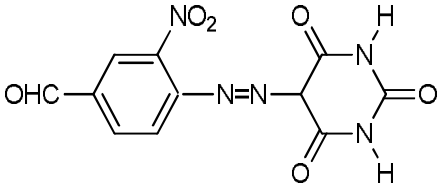

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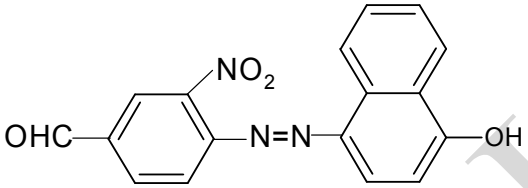
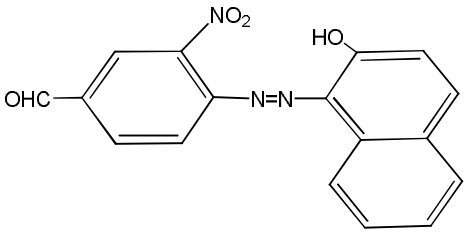
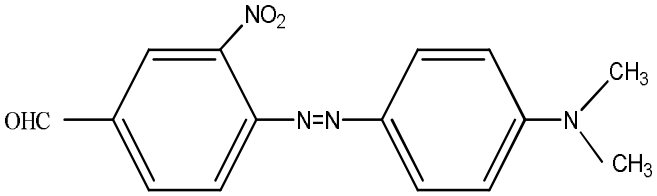


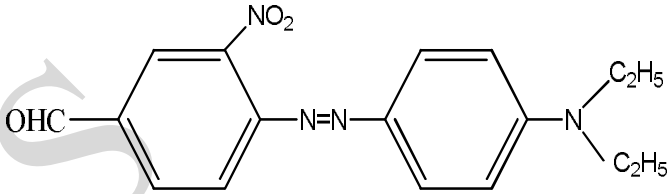
D4



D5



D6



D7

Fig 1: Structures of Dyes 1 - 7

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II. MATERIALS AND METHODS

Materials

100% polyester fabric, digital thermometer, electronic weighting balance, pH meter, beakers (500 ml) constant temperature magnetic stirrer, spatula, Xenon arch lamp, unitest fastness tester. Perkin- Elmer 100 FTIR spectrophotometer, phenol (carrier)

Methods

Synthesis of Dyes

Dyes 1 – 7 were synthesized by methods described by Bello [3] and Lams [10]. The diazo component in this work is 4 – Amino - 3–Nitrobenzaldehyde and the coupling components are resorcinol, phloroglucinol, Barbituric acid, α-naphthol, β-naphthol, N,N-dimethyl aniline and N,N-diethyl aniline.

Application of Dyes.

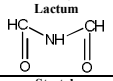
1g of the polyester fabric was wetted for few seconds and excess water squeezed out. The wetted fabric was introduced into the dye bath containing 2% o.w.f. of 1% stock solution of the dye, carrier (phenol) (1.5ml) and dispersing agent (Albatex PON) (1ml). at an initial temperature of 20^0C on the hot plate and the temperature raised to the boil. Dyeing continued for 1hr 15mins at the boil at constant pH, liquor ratio and carrier concentration at the initial stage. At the end of dyeing, the fabric was removed and rinsed thoroughly in cold running water and dried at room temperature. Subsequent dyeings were carried out by varying all the variables (temperature pH, time, liquor ratio and carrier concentration) under investigation. The results are shown in tables 1 -5 and figures 1 -5.

Reduction Clearing

Commonly, the dyed polyester is cleared of surface-deposited dye as well as auxiliaries (e.g. carriers, surfactants) by means of treatment with detergent or reductive or oxidative treatments, in order to secure optimum fastness of the dyeing and also to improve the brightness of shade [6].

The reduction clearing treatment was carried out in an aqueous bath containing the following agents; 1.5g/l of dispersing agent, 2g/1 of caustic soda (NaOH) and 2g/1 of sodium dithionite (hydros) $Na_2S_2O_4$ in 20-30 minutes at 50-80^{0}C followed by rinsing. The aim of the reduction clearing process was to remove surplus, unreacted and unfixed dye molecules with a view to obtaining dye uniformity and brighter hues [12].

TABLE 1: Infra-red spectral results (functional group wave number cm^{-1}) for the dyes.

DYE	Aromatic C-H	Aliphatic C-H	Carbonyl C=O, Lactum 	Azo N=N	Ether C-O-C	Aldel-hyde CHO	Hydroxyl OH	Aromatic C-H	Aromatic Nitro NO_2	Me 	Et	α-sub Naphthol	β-sub Naphthol
	Stretch	Bending	Stretch	Stretch	Stretch	Stretch	Stretch	Bending	Bending				
D1	2950.00	2810,00.	---	1423.08	---	1692.99	3433.97	820.22	1560.01	---	---	---	---
D2	2925.35	2852.00		1406.78	---	1600.07	3410.53	833.81	1509.10	---	---	---	---
D3	2927.06	2849.95	1635.30	1423.51	---	1678.34	3434.91	839.05	1583.35	---	---	---	---
D4	2924.40	2852.49	---	1404.27	---	1697.93	3434.49	816.90	1573.76	---	---	835.85 872.72	---
D5	2960.00	2815.00	---	1407.95	---	1693.76	3390.47	814.22	1557.56	---	---	---	844.00 878.14
D6	2950.00	2804.92	---	1425.24	---	1701.31	3412.32	821.53	1541.07	2724.74	---	---	---
D7	2948.13	2817.00	---	1419.80	---	1705.00	3411.22	815.07	1550.90		2718.06	---	---

III. RESULTS

The spectral results of **Dyes 1 -7** presented in Table 1 showed characteristic bands around 2924 – 2960 cm^{-1} indicating the presence of aromatic C- H stretching vibration. The aliphatic C-H bending vibration occurred at 2810 – 2852 cm^{-1}. Absorption peaks due to lactum group in **Dye 3** appeared at 1635 cm^{-1}. The strong bands which appeared around 1600 – 1697 cm^{-1} are due to aromatic(CHO)stretching vibration. The bands 1404 – 1423 cm^{-1} arise from the presence of azo group (N=N) while the broad peaks around 3390 -3434 cm^{-1} are due to aromatic (ArOH) stretching vibration. Other important absorption bands that appeared in the dyes include 1509-1583 cm^{-1} nitro group (NO_2) bending vibration, 814-839 cm^{-1} aromatic $(C-H)$ bending vibration, 2724 cm^{-1} [$N(CH_3)_2$] group for **Dye 6**, 2718 cm^{-1} [$N(C_2H_5)_2$] for **Dye 7** 835 - 872 cm^{-1} (α-substituted naphthol) for **Dye 4** and 844 – 878 cm^{-1} (β-substituted naphthol) for **Dye 5** respectively.

Table 2: Percentage exhaustion of dyes on polyester fabrics at various Times.

Time (mins.)	% Exhaustion						
	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6	Dye 7
30	43	28	35	39	41	45	37
45	59	39	55	57	55	51	53
60	63	60	69	71	70	75	73
75	76	70	74	81	82	85	80
100	82	87	94	95	92	95	96

Table 3: Percentage exhaustion of dyes on polyester fabrics at various temperatures.

Temp. (^{0}C)	% Exhaustion						
	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6	Dye 7
20	30	15	20	35	30	25	27
40	59	45	50	66	60	65	62
60	69	67	75	70	72	73	74
80	88	75	84	82	86	81	83
100	92	87	93	95	92	98	95

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Table 4 : Percentage exhaustion of dyes on Polyester fabrics at various liquor ratio.

L:R	% Exhaustion						
	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6	Dye 7
25	92	82	90	89	93	95	92
50	88	75	85	78	80	87	83
75	73	52	68	53	55	78	75
100	23	26	20	28	30	48	39

Table 5: Percentage exhaustion of dyes on polyester fabrics at various carrier concentrations.

Carrier (g/l)	% Exhaustion						
	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6	Dye 7
0.5	20	22	18	26	22	15	17
1.0	47	31	35	43	42	50	48
1.5	75	64	70	67	65	73	77
2.0	92	91	90	89	93	95	96

Table 6: Percentage exhaustion of dyes on polyester fabrics at various pH.

pH	% Exhaustion						
	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5	Dye 6	Dye 7
2.5	92	85	90	83	80	95	92
3.5	87	71	82	79	77	83	80
4.5	75	67	74	68	68	74	70
5.5	69	63	66	55	50	67	65
6.5	59	59	52	45	47	63	61
7.5	43	55	43	39	45	59	57
8.5	30	49	36	33	40	52	53
9.5	27	41	25	27	34	49	50
10.5	22	37	20	25	30	47	42
11.5	18	31	16	20	25	39	37
12.5	15	27	14	17	16	30	29
13.5	12	23	10	10	12	25	20

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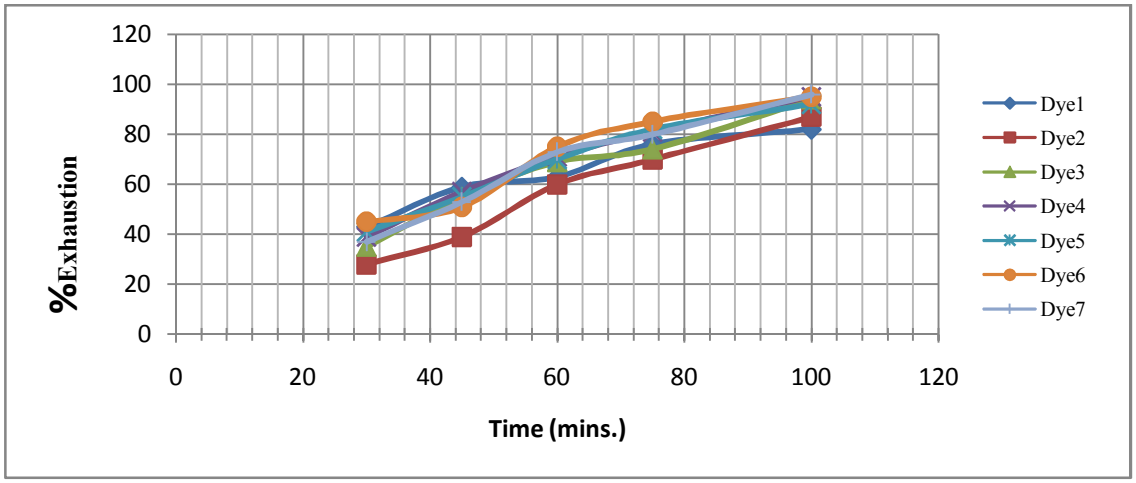

Fig 2: Percentage exhaustion of dyes 1 – 7 on polyester fabric at various times.

The results in fig.2 show the percentage exhaustion of **dyes 1 - 7** at various times while keeping other variables constant. It was observed that increase in time of dyeing increase the percentage exhaustion. Percentage exhaustion was low at lower times. The reason might be that at the initial stage of dyeing only few of the dye molecules might have dissolved inside the dye bath 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, 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 the dye are transferred from solution to the surface of the fabric and adsorbed dye diffused monomolecularly into the fabric to form a solid solution [12]. All these observations may be attributed to the molecular size of the dyes as well as rate of diffusion of the dye.

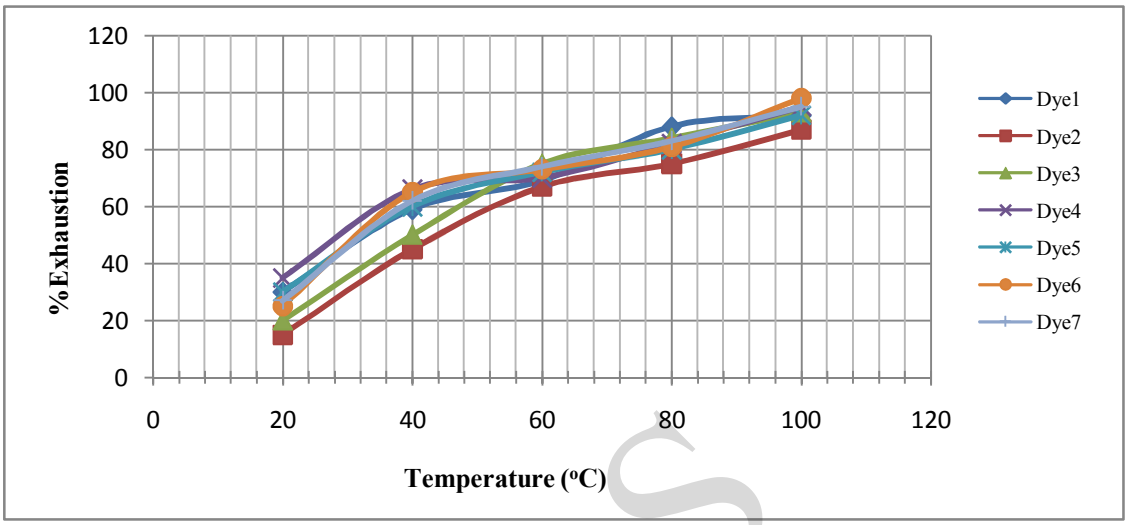

Fig 3: Percentage exhaustion of dyes 1 – 7 on polyester fabrics at various temperatures.

From fig.3 it is clearly seen that a rise in temperature increased the percentage exhaustion. This is in quite agreement with literature. The adsorption and diffusion of disperse dyes on polyester are generally influenced by temperature as increase in temperature increases the mobility of the polymer chains in the amorphous regions of the fibre [9].

It is thought that the higher the temperature of the dye bath the greater the kinetic energy of the dye molecules and faster the diffusion of the dye molecules in and out of the substrate since diffusion is directly proportional to the thermodynamic temperature. Increase in temperature also tends to increase fabric porosity by increasing the molecular entropy and amorphous region of the fabric polymer matrix. Temperature was varied at constant time of dyeing and liquor ratio. This experiment was limited to a maximum temperature of 100^0C as it was an exhaustion dyeing Therefore the exhaustion was greater at higher temperatures, for the dye-hydrophobic fibre system, the affinity of the disperse dyes decreases with increase in dyeing temperature while the saturation value of the dye in the fibre increases with increasing temperature [4].

An important difference between the dyeing behaviour of polyester fibres and that of other fibres such as nylon and secondary acetate, which also accept disperse dyes, is in their rates of dyeing. Polyester fibres dye very slowly at temperatures much below 100^0C [8], [15].

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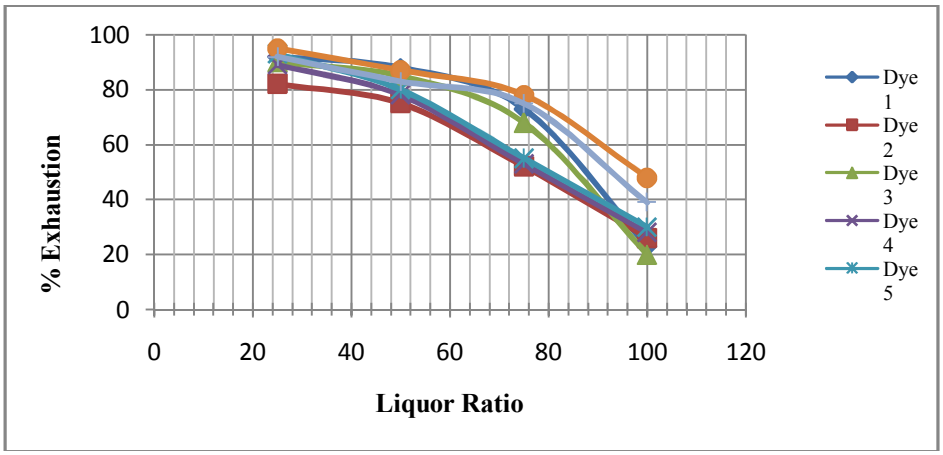

Fig4: The percentage exhaustion of dyes 1 - 7 on polyester fabric at various liquor ratios.

Fig 4: shows the effect of change in liquor ratio on the percentage exhaustion of **dyes 1 -7** on polyester fabrics. It was observed that the percentage exhaustion of the dyes decreased with increase in dyeing liquor ratio. It is thought that at smaller liquor ratios the concentration of the disperse dyes in the dye bath is higher. It is equally thought that a dye bath of lower liquor ratio exert higher kinetic energy on the dye molecules enabling them to move faster into the fibre matrix. The experiment revealed that at lower liquor ratios the percentage exhaustion is high resulting to darker shades of the dyes on the substrate. On the other hand, percentage exhaustion decreased with increase in liquor ratio.

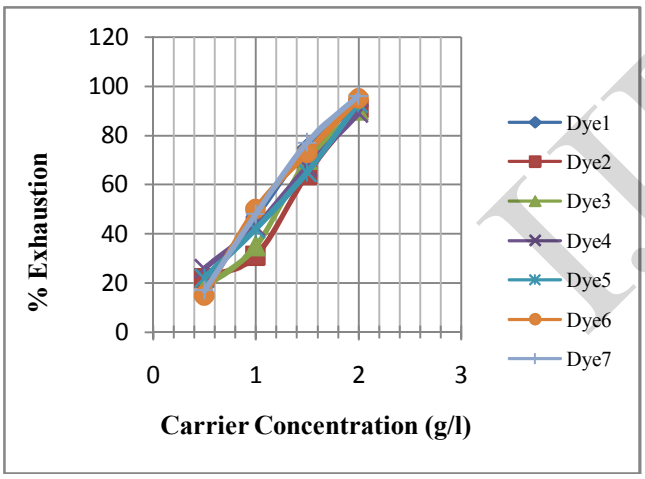

Fig 5: The percentage exhaustion of dyes 1 – 7 on polyester fabric at variou carrier concentrations.

From Fig 5, it is observed that at carrier concentration of 0.5g/l, the percentage exhaustion is minimal when compared with the concentration of 1.0g/l, 1.5g/l and 2.0g/l respectable. It was also observed that at carrier concentration of 1.0g/l, a deep shade was obtained and at 1.5g/l carrier concentration a deeper shade was obtained, and similar results were obtained at a concentration of 2.0g/l for all the seven **(7) dyes**. Generally there was a progressive increase in depth of shade with increase in phenol concentration. It was also observed that the accelerated rate of diffusion of disperse dyes into synthetic fibre is caused by carrier concentration which has been correlated with their plasticizing action. The variation of the diffusion co-efficient of dyes with temperature and carrier concentration confirmed that the dyeing process is controlled by the segmental mobility of the polymer [7]. The benefits of carriers were overwhelming in the early days of polyester dyeing because polyester fabrics could be dyed in unpressurized becks with no more dyeing problems than with direct dyes. However, carrier dyeing has steadily declined since the development of suitable machines for yeing polyester under pressure at temperature around 130^0C [5].

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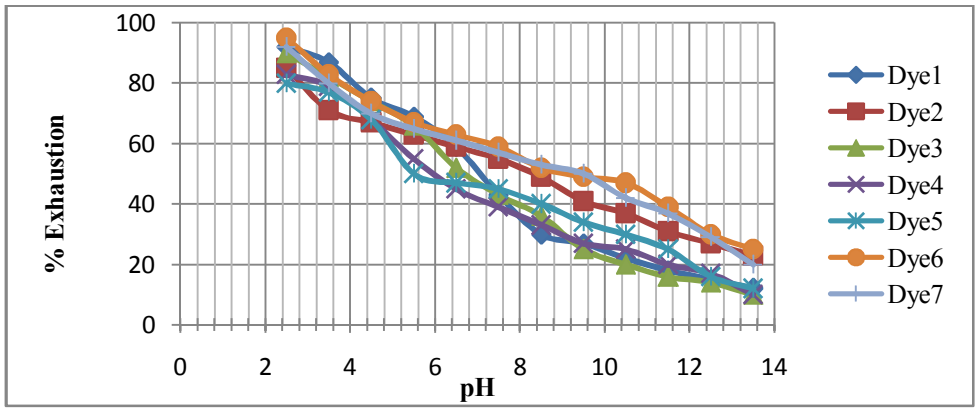

Fig 6: Percentage exhaustion of dyes 1 - 5 on polyester fabric at various pH.

The effect of pH on the percentage exhaustion of the disperse dye on polyester was studied using 2% o.w.f dye concentration with a pH range from 2.5 to 14 as shown in **Fig 6.** It was observed that the absorbance of the fabrics decreased with increase in dyeing pH. It was also observed that at pH 2.5 deep shades were obtained and subsequent decrease in exhaustion above the pH 5.5. At a pH of 10.5, the fabrics were observed to be slightly coloured. The decrease in dyeing exhaustion at pH greater than 6.5 may be as a result of loss of fibre strength and elongation. Generally, in the commercial dyeing of polyester with disperse dye, dyeing is carried out with the pH range 5.5 to 6.5. Strongly alkaline or acidic conditions, such as higher than pH 9 and lower than pH 4, induced hydrolysis of the fibre as well as decomposition of azo disperse dyes [13]. In the case of high temperature dyeing, the degradation of polyester and dye is accelerated; however, this research was carried out by exhaustion dyeing at a maximum temperature of 100^0C. It is thought that dye exhaustion is related to dye molecular interaction due to Van der Wa'als forces between the disperse dye and polyester fabric. This might have contributed greatly to dye adsorption.

Wash Fastness Rating Of the Dyes

TABLE 7: Wash, Light and Perspiration fastness of dyes derived from 4-Amino-3-Nitrobenzadehyde on polyester fabrics

Dye	Fastness to Wash		Fastness to Light	Fastness to Perspiration			
				ACID		ALKALI	
	CHS	STN		CHS	STN	CHS	STN
1	4-5	3-4	6	3	3-4	5	4-5
2	4	4	5	5	4	5	4-5
3	4-5	4-5	7	5	4	5	4-5
4	4-5	4-5	7	4	3-4	4-5	4-4
5	5	5	7	3	2-3	4	3-4
6	5	5	7	5	4	5	4-5
7	4-5	4-5	6	4	4-5	5	4-5

KEY: CSH ------- Change in shade, STN ------- Staining of white

From Table 7 above, **dyes 5and 6** have excellent fastness to wash and light while **Dyes 1, 2, 3, 4** and **7** have very good fastness to both wash and light. Fastness to washing is dependent on diffusion as it is unlikely during the limited time of a washing cycle or test that an equilibrium between the dye inside and outside the fibre will be reached. Consequently, the fastness will be subject to kinetic control [9].

Dyes 2, 3 and **6** show very good resistance to acid and alkali whereas **Dyes 1, 4, 5** have moderate to good resistance and **Dye 7** has moderate to very good resistance to both acid and alkali on the perspiration test.

Satisfactory fastness to light, washing, perspiration, rubbing, sublimation and burnt gas fumes is particularly significant for disperse dyes [14].

From the results shown in Table 7 it is obvious that the dyes under investigation have good to very good resistance to both acids and alkalis.

Generally, however, there was no significant change in fastness properties of the dyes under investigation

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as a result of variation in time, temperature, liquor ratio, carrier concentration or pH.

I. CONCLUSION

The disperse dyes applied on 2% o.w.f. polyester fabrics were treated at different, times, temperatures, carrier concentrations, liquor ratios and pH. The results showed that the percentage exhaustion increased with increase in time, temperature, carrier concentration while decrease in liquor ratio increased percentage exhaustion.

On the other hand, lower pH resulted to higher percentage exhaustion and vice – versa.

The results obtained for changes in pH are slightly different from literature as generally, in the commercial dyeing of polyester with disperse dye, dyeing is carried out within the pH range 5.5 to 6.5. Strongly alkaline or acidic conditions, such as higher than pH 9 and lower than pH 4,induced hydrolysis of the fibre as well as decomposition of azo disperse dyes [13].

Based on the results obtained, the fastness properties of these dyes have been examined and found to be very good and satisfactory irrespective of the changing variables that were investigated. The changes in the various dyeing conditions that were investigated however, did not result in much significant changes in shade and fastness. In the reaction which was largely exothermic, Van der Wa'als forces are thought to have played significant role in dye – fibre attraction since the monoazo disperse **dyes 1- 7** are non – ionic.

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