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Solvent free fluorescein dye and its application use Microwave

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Abstract: Fluorescein dye is a synthetic organic compound available as a dark orange/red powder soluble in water and alcohol. Fluorescein dye has an absorption maximum at 494 nm and emission maximum of 521 nm (in water), the color of its aqueous solution varies from green to orange.
In this study, fluorescein dye has been synthesized by the condensation of phthalic anhydride with resorcinol through a novel route of microwave irradiation technique under solvent free condition in high yields within a period of minutes in the presence of zinc chloride via the Friedel-Crafts reaction.
The light fastness of the dyes was found to depend on the mobility of electrons through conjugated system from donating electron (OH) to electron withdrawing in
(COO-) afforded a good value of light fastness. The structure of the dye is characterized and confirmed by melting point, elemental analysis, infrared, ultraviolet-visible spectroscopy (UV/VIS) and nuclear magnetic resonance (^{1}H-NMR) data. This dye was used for dyeing wool and nylon 6 in microwave. Dyeing wool and nylon 6 with the prepared fluorescein dye using microwave irradiation was investigated. Moreover fastness properties of the dyed fabrics were found to be better as comparable with conventional dyed fabrics which saving time, energy and decreasing liquor ratio in both synthesis of dye and its application to dye wool and nylon 6 were achieved.
Keywords: Fluorescein dye; microwave; structure elucidation; dyeing; wool; nylon 6.

1. Introduction

Phthaleins are an important class of organic compounds which have many applications which have many applications[1]. Some methods were reported[2,3,4] .The inherent drawbacks of described synthetic methods are long heating time (upto 10-15hrs), high temperature, low yield and consumed many solvent. in the presence of acidic catalyst necessary for high yield reactions[5]. Microwave irradiation presents a powerful tool toward organic reactions. Solvent-free microwave irradiation is well known as environmentally benign method, which offers several advantages including shorter reaction times, cleaner reaction profiles and simple experimental/product isolation procedures procedures[6].

It is known that acid dyes and their metal complexes are used for textile fibres dyeing, due to their high affinity to textile fibres, high strength and stability, bright colours and a variety of possible shades[7,8,9] .This property depends on the number and position of the sulphonic groups, and their attraction to positive groups of the textile substrate[10,11]. Furthermore, amino groups on the untreated fibres are capable of forming hydrogen bonds with the groups – OH and – CO of the dye molecules, therefore creating bridges between fibre and dye, consequently, increasing the affinity of dye to wool fibre[12] . These structural changes which taking place between dye and textile fibre have attracted the attention of researchers in the past two decades, leading to the development of a range of dyes application in textile fibres dyeing[13,14,15].

The aim of the present work is to synthesize Fluorescein dye using microwaves irradiation which saving time, energy and free from solvent reaction were achieved. The synthesised dye was applied to wool and nylon 6 fabrics in microwaves which saving time, energy and decreasing liquor ratio cotton and wool fabrics under exhaust dyeing conditions and their dyeing properties were investigated. The structures of this dye was characterised and confirmed by melting point, elemental analysis, infrared, ultraviolet-visible spectroscopy (UV/VIS) and nuclear magnetic resonance (1H-NMR) data. Characterization of this prepared dye was investigated.

2. Experimental

2.1. Materials

Fabrics

Wool fabric, 100% was twill weave fabric (2/2) of equal warp and weft (26x24 threads/cm, yarn count Nm 44/2). Scoured and bleached nylon 6 knitted fabric (El-Shourbagy Co., Egypt) weighing 114 g/m^2 was used.

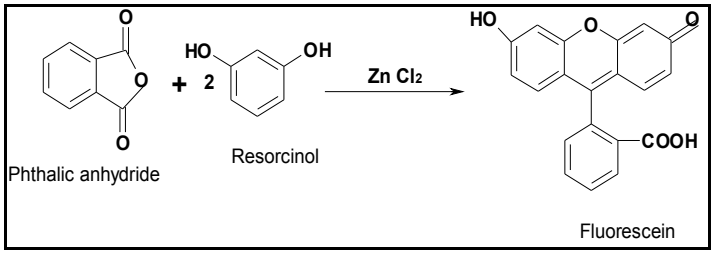
Fabrics, supplied from Misr El-Mahala Co. Egypt, were treated in an aqueous solution containing 2 g/L Hostapal CV for 1 h at 80°C and a 50:1 liquor ratio (LR), then washed thoroughly in water and air dried at room temperature.

Chemicals

Phthalic anhydride and resorcinol were obtained from Fluka Chemie AG. All other chemicals used in the study were of reagent grade and applied without further purification

2.2. Synthesis of Dye

Fluorescein dye was prepared by conventional method as well as[16,17] . In this work we prepared this dye in microwave by using a mixture of phthalic anhydride **1** and resorcinol **2** with zn cl_2 as a catalyst. The reaction mixture was irradiated in a microwave oven at 800W for 10 Minutes at 90 ^oC without solvent (Scheme 1). After usual work up it offered the pure compound **3**. The reaction takes place in a single step. In this reaction we decreased the time, the temperature and the liquor ratio also we increased the yield of products.



(Scheme 1)

Flourescence dye : Yellow, λ_{max} 460 m.p. > 300 ^oC, yield 90%

$C_{19}H_{12}O_5$ (336) [M^+-1] = 335 Calcd.: C,67.85; H, 3.57 %, Found: C; 67.88; H, 3.60; % (IR (ν, cm^{-1}): 3747 ,3713 (2OH), 1685 (C=O carboxylic acid), 1594 (C=O). ^{1}HNMR (δ, ppm): 6.77-6.87(t, 2H, naphthyl), 7.01-7.23(d, 6H, naphthyl), 7.77-7.87 (s, 2H, naphthyl) 11.15-11.30 (s,2H, 2OH).

2.3. Dyeing Procedures

Wool and nylon 6 fabrics were dyed using fluorescence dye by convential method at optimum condition 2% owf in an Ahiba dyeing machine at a 50:1 LR. The dyebath was prepared at pH 4 using acetic acid. Dyeing was started at 40°C and then the temperature raised to 100°C over 45 min. Also, we can dye Wool and nylon 6 by the same prepared dye in microwave and we can compare between two methods in dyeing time, liquor ratio and temperature. Dyeing in microwave 800 w was carried at a 20:1 LR, different concentration of dye (1-5% owf), different PH (3-7) diferent temperature (70-100) over (5-30minutes). Dye exhaustion on wool and nylon 6 fabrics

were evaluated spectrophotometrically. After dyeing, all dyed samples were rinsed with water and air dried. Dye exhaustion on wool and nylon 6 fabrics were evaluated spectrophotometrically.

2.4. Measurements and Testing

2.4.1. Dye Exhaustion

dye Uptake by the wool and nylon 6 fabrics was calculated by measuring the dye bath concentration before and after dyeing on a Shimadzu UV-2401PC UV/V is spectrophotometer at the λ_{max} value using a calibration curve was defined using known dye concentrations (g/L). The percentage of dyebath exhaustion (%E) was calculated using Eq. 1.

$$\%E = \left[1 - \left(C_2 / C_1\right)\right] \times 100 \qquad (1)$$

Where C_1 and C_2 are the dye concentrations in the dyebath before and after dyeing, respectively.

2.4.2. Colour Measurements

The colour parameters of the un-dyed and dyed wool, and nylon fabrics were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 10° standard observer[18,19] .

2.4.3. Fastness Testing

Dyed wool and nylon samples, the fabric was treated with a liquor ratio 50:1 solution containing 5 g/l nonionic detergent (Hostapal CV, Hoechst) and 2 g/l sodium carbonate at 60 °C for 30 min, thoroughly washed in water and air dried at room temperature. Wash fastness (ISO 105-C02 (1989), crock fastness (ISO 105-X12 (1987), and fastness to perspiration (ISO 105-E04 (1989) were evaluated using the visual ISO Gray Scale for both color change (AATCC Evaluation Procedure (EP) 1-similar to ISO 105-A02) and color staining (AATCC EP 2—same as ISO 105-A03). Light fastness (carbon arc) was evaluated using ISO 105-B02.

3. Results and Discussion

3.1. Effect of Time Using Microwave Radiation

In conventional method the optimum time of dyeing in an Ahiba dyeing machine is around one hour and half. We study the effect of time in microwave at pH 4, dye concentration 2% owf and temperature is 90 ˚C through interval time from 5-30 min. From the results given in figure 1, it is apparent that the suitable time is 15 min. which gives higher exhaustion after that the exhaustion is approximitaly fixed. From results we can reduce the time of dyeing and saves the energy.

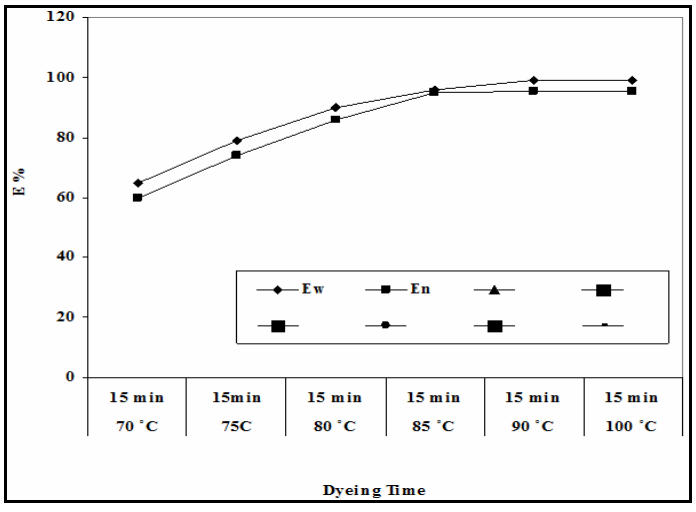


Figure 1. Effect of dyeing time on the exhaustion values (E) of dye (2% owf) on wool(w) and nylon 6(n) fabric at pH 4.

3.2. Effect of Temperature Using Microwave Radiation

In conventional method the optimum temperature of dyeing in an Ahiba dyeing machine was performed at 40°C, allowing the temperature of the dye bath to raise to the boiling temperature 100 °C, but in microwave when we study the effect of temperature for dyeing wool and nylon 6 from 70-100 °C at pH 4, dye concentration 2% owf and15 min. The results indicate that the higher exhaustion at 90°C after that the exhaustion is approximitaly fixed figure 2, so we can reduce the temperature which used in microwaves than conventional method.

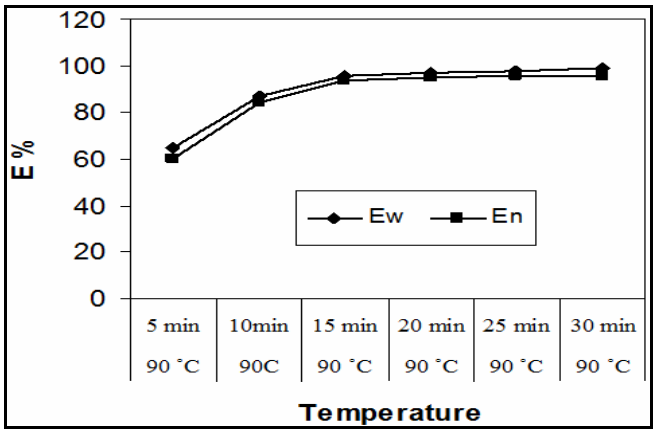


Figure 2. Effect of temperature on the exhaustion values (E) of dye (2% owf) on wool(w) and nylon 6(n) fabric at pH 4.

3.3. Effect of Liqour Ratio

In convencial method we used 50:1 LR in an Ahiba dyeing machine but when dyeing in microwave we decreased liquor ratio to 1:20 so we can save the water which used.

3.4. Effect of Dye Concentration

The exhaustion of the dye on wool and nylon 6 fabric were examined in microwave using different depth of shades (1-5% owf) at pH 4 and 90 ˚C at 15 min. The exhaustion percentage of wool fabric lies at 98.9, whereas exhaustion dyes on nylon lies at 97.3. There are a large number of amino groups present in the wool fibre. As a guide, there are approximately twenty times as many amino groups on wool as on nylon and five times as many amino groups on wool as on silk. Dark shades can be readily obtained on wool because of the highly amorphous nature of the fibre, which results in relatively easy penetration of the fibre polymer by the dye molecule and because of the presence of amino groups, as shown in figure 3. Increasing the dye concentration reduces the exhaustion on wool and nylon 6 fabrics.

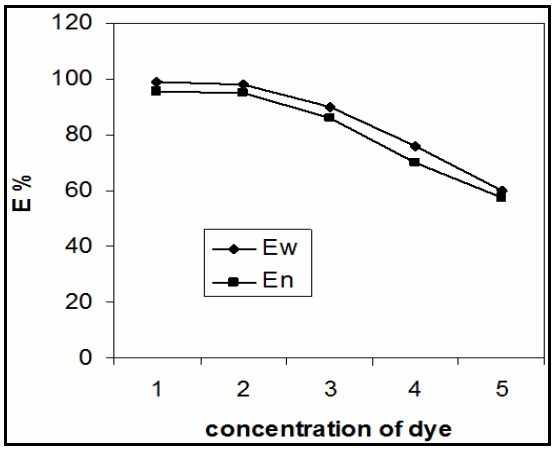


Figure 3. ***Exhaustion (E) values at different concentrations of dye (90°C for 15 min and pH 4) on wool (w)*** **and nylon 6 (n)fabric**

3.5. Effect of Dyebath Ph

The protein and polyamide fibres produce cationic sites in water under acidic conditions, as the acidity of the solution is increased more cationic sites are produced under these strongly acidic conditions. These cationic sites are thus available for the acid dye anions to combine with through hydrogen bonding, vander waals forces or ionic bonding. These linkages are strong enough to break, and thus dyeing produced is fast. Dyeing was carried out using 2% owf dye concentration at 90 ˚C at 15 min. by varying the dye bath pH from 3 to 7 to examine dye exhaustion.

The results obtained from the investigations regarding colour intensity are transformed into indices K/S, as presented in Table 1. It is observed that the best results occurred when dyeing in acetic acid medium, recorded maximum values in pH 4 intervals. In the case of dyeing in acetic acid medium, the results revealed an average affinity of the dyes for wool fibres and nylon 6. In the case of dyeing in neutral medium, the affinity of dye is lower. Chromatic parameters were determined in comparison for samples dyed with all dyes figure 4

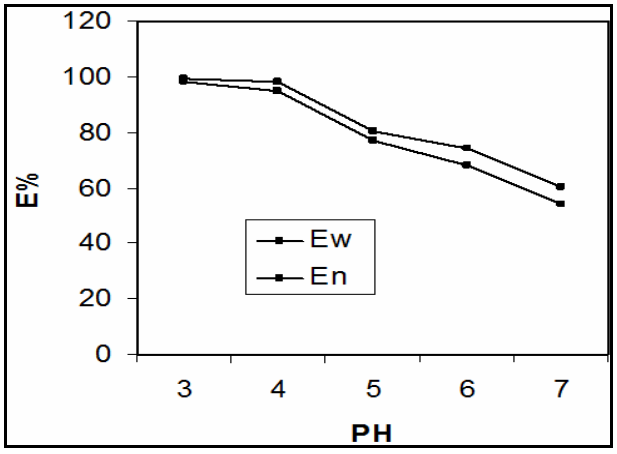


Figure 4. Effect of pH on the exhaustion values of flourescence dye (2% owf) on wool (w), Nylon 6 (n)

3.6. Colorimetric and Fastness Properties

The colorimetric CIE L*a*b*C*h^{o} data of the dyed wool and nylon 6 using the dye are shown in **table 1, 2.** It can be seen that K/S values obtained for dyeing at pH 6 and pH 4 are better at pH 4 than pH 6 according to all previous study. The colour parameters were evaluated by means of the Cielab system and the modified CIE L* C * h^{o} (D65/10^{o}) system. The following colour parameters for the dyed samples were obtained by the digital Cielab system: L* – lightness, a* – redness if positive coordinate, or greenness if negative coordinate, b* – yellowness if positive coordinate, or blueness if negative coordinate, h – hue of the colour, X – coordinate x, Y – coordinate y, Z – coordinate z. As shown in table 3, the fastness to washing, rubbing and perspiration of all samples dyed with the fluorescence dye in microwave radiation were excellent to very good irrespective to the fabric used.

Table 1: Colorimetric data of the dyed wool and nylon 6 fabrics using fluorescence dye (2% owf) at 90°C and at pH 6.

Fabric	Δ E	K/S	L*	a*	b*
W	115.40	15.91	74.24	16.92	86.72
N	98.62	1.79	84.38	-5.58	50.74

Table 2: Colorimetric data of the dyed wool and nylon 6 fabrics using fluorescence dye (2% owf) at 90°C and at pH 4.

Fabric	Δ E	K/S	L*	a*	b*
W	108.13	20.21	67.98	21.36	81.32
N	99.36	2.53	82.31	-5.19	55.43

Table 3: Fastness properties of dyed wool and nylon 6 fabrics using fluorescence dye (2% owf) at 90°C and at pH 4.

Fabric	Fastness to rubbing		washfastness			Fastness to Perspiration						Light
						Alkaline			Acidic			
	Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
W	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**5**
N	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4-5**	**4**

Alt. colour change of dyed sample; SC, staining on cotton; SW staining on wool**.**

4. Conclusion

Fluorescence dye can prepare in microwave which suitable for saving time to 15 min., decrease temperature to 90 ˚C and also decrease the solvent which used in common way. Also, in dyeing of polyamide fibre and wool were carried in small liquor ratio, shortage in time of dyeing to 10 min. and without adding any additives The dye have very good fastness to water, washing, perspiration, and rubbing. Light-fastness of the dyes varied from 5-4, and was considerably affected by the nature of the coupling component. The study analyses the behaviour of the wool fibres in the dyeing process using acid dyes synthesized at molar ratios (1:20) and pH 4. The dye recorded maximum values in pH 4 interval. In the case of dyeing in acetic acid medium, the results revealed an average affinity of the dyes for wool fibres and in the case of dyeing in neutral medium, the affinity of dyes is lower. Chromatic parameters were determined in comparison for samples dyed with all dyes. The light fastness of the dyes was found to depend on the mobility of electrons through cogugated system from donating electron (OH) to electron withdrawing in (COO-) afforded a good value of light fastness. The visible absorption spectra of all dyes showed that colours of dyes is fluorescence yellow. The fastness of dyed knitted polyamide fabrics to water, washing, alkaline and acid perspirations and rubbing were found to be very high irrespective of degree of sulphonation in the coupling component.

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