



Synthesis, Characterization, and antimicrobial investigations of a novel Heterocyclic disperse dyes based on Chromene moieties



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Hagar Fathy¹, M.H.Helal², Dina Abbas¹, Fatma A. Mohamed^{1*}

¹Dyeing, printing and auxiliaries department, Institute for Textile Research and Technology, National Research Center 33
El Buhouth St., Dokki, Giza, Egypt Postal code: 12622

²Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt

Abstract

New azo Schiff base disperse dyes were synthesized based on the chromene moiety through a condensation reaction of resorcinol, malononitrile, and 4-chlorobenzaldehyde in ethanol, yielding 2-amino-4-(4-chlorophenyl)-7-hydroxy-4H-chromene-3-carbonitrile, which contains a free amino group. The produced chromene primary amine can react to form new Schiff bases when they interact with vanillin as an aldehyde and ninhydrin as a ketone. Next, we diazotized 2-chloro-para-nitro aniline and coupled it with our recently produced Schiff bases to obtain novel azo disperse dyes. The structures were validated using ¹HNMR, mass spectrometry (MS), and Fourier Transform Infrared Spectroscopy (FTIR). Our recently developed azo disperse dyes assessed all color attributes and antimicrobial activity against *Staphylococcus aureus* ATCC 6538-P the gram-positive bacteria, *Escherichia coli* ATCC 25933 as the gram-negative bacteria, *Candida albicans* ATCC 10231 as yeast, and the filamentous fungus *Aspergillus Niger* NRRL-A326 on nylon and polyester textiles. The K/S values of the dyed samples were measured, and the results indicated that the investigated dyes imparted excellent color fastness properties. The dyed samples exhibited strong resistance to fading when exposed to light, washing, rubbing, and perspiration.

Keywords: Disperse dyes; antimicrobial activity; Chromene; Nylon; Polyester

1. Introduction

Chromene-based disperse dyes have garnered significant attention in the textile industry due to their unique chemical structure and excellent dyeing performance [1]. Chromenes, also known as benzopyrans, are chemical compounds characterized by their distinctive structure: a benzene (phenyl) ring fused to a six-membered heterocyclic pyran ring containing an oxygen atom. This fusion creates a bicyclic system that serves as the core scaffold for many naturally occurring and synthetic compounds [2]. This chromene core, when integrated into disperse dyes, enhances the dye's color properties, making it vibrant and long-lasting on synthetic fibers such as polyester and nylon. The interaction between the chromene moiety and azo groups (–N=N–), commonly found in disperse dyes, enhances both dyeing performance and biological functionality [3]. Additionally, chromene-based disperse dyes are well-known for their excellent color fastness to washing, light, and perspiration [4]. "Methoxyphenyl-4H-chromene-3-carbonitrile derivatives represent an important class of chromene azo dyes that are well-known for their extensive use as functional colorants [5]. Azo groups in dye structure are well-known chromophores that provide a wide range of bright colors [6], from yellow to deep red and violet. When azo dyes are combined with Schiff-base structure, these dyes exhibit excellent dyeing properties and enhanced molecular interaction with fibers [7]. Also, the unique molecular structure of these dyes

including chromene moiety gives the dye structure an additional action besides enhancing their dyeing by their heterocyclic systems [8]. The incorporation of chromene with an azo linkage enhances the biological performance of synthesized dyes [9] and that of other useful chemotherapeutic agents such as anti-tuberculosis [10], anti-diabetic [11], anti-cholinesterase [12], antiepileptic [13], anti-HIV activity [14] in addition to the similar characteristics of heterocyclic compounds like anti-bacterial [15], anti-viral [16], anti-cancer [17], anti-fungal [18], pesticide [19] and anti-Alzheimer [20]. The unique qualities and adaptability of Schiff bases in the dye structure offer numerous benefits across various industries, especially in analytical chemistry, medicines, and textiles [21]. Furthermore, because of their biocompatibility and functionalization potential. Besides having demonstrated promise in biomedicine, particularly in drug transport and imaging. Overall, Schiff base dyes are significant in both industrial and scientific contexts [22] as they are particularly suited for dyeing hydrophobic synthetic fibers due to their small molecular size and their ability to penetrate the fiber under high-temperature conditions besides their multifunctional uses [23]. According to the significant role of chromene moiety in the dye industries of heterocyclic dyes, herein, we present the synthesis, characterization, and antimicrobial activity of some new Schiff-base azo disperse dyes based on chromene moiety [24-33]. The synthesized compounds were applied as dyes to polyester and nylon fabrics using three different dyeing methods. Ultrasonic dyeing was

*Corresponding author e-mail: fatmaali1811@gmail.com; (Fatma A. Mohamed).

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used for both fabrics, while conventional dyeing was specifically employed for nylon, and a high temperature-high pressure technique was used for polyester [34-40]. We evaluated the dyed samples for their color properties and fastness characteristics. The dyed fabrics also demonstrated antimicrobial properties, suggesting their potential application as novel antimicrobial textiles in medical settings.

2. Experimental

2.1. Materials

2.1.1. Fabrics

Two types of fabric were used in this study: polyester (160 g/m²) sourced from Misr El-Mahalla Co., Egypt, and nylon (149 g/m²) obtained from El Mahalla El-Kubra Company. Both fabrics underwent a pre-treatment process prior to dyeing. They were cleaned in a solution containing nonionic detergent (Hostapal CV, 5 g/L) and sodium carbonate (2 g/L), using a 50:1 liquid-to-fabric ratio. The treatment was conducted at 60°C for 30 minutes, followed by thorough water rinsing and air-drying at room temperature.

2.1.2. Chemicals

The study used Hostapal CV (Clariant, Egypt) as a nonionic detergent. The main chemical reagents, obtained from Sigma-Aldrich, included: 4-chlorobenzaldehyde, Malononitrile, Resorcinol, Vanillin, Ninhydrin, 2-chloro-4-nitroaniline. All other chemicals were laboratory-grade and used as received.

2.1.3. Instruments

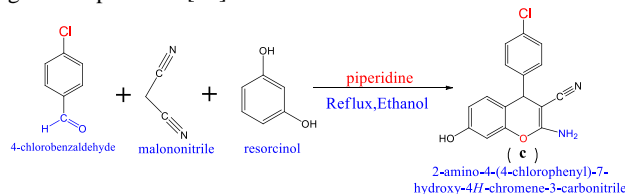
The following instruments were used for analysis: Melting points: Gallenkamp apparatus

Infrared spectra: Nicolet 5000 FT-IR spectrophotometer, Nuclear Magnetic Resonance: Bruker WP 400 MHz spectrometer (using DMSO-d₆ as solvent) and Mass spectrometry: Thermo Scientific Focus/DSQII Quadrupole GC/MS (operating at 70 eV)

2.2. Synthesis of dyes

2.2.1. Synthesis of Chromene moiety: -

A mixture of 4-Chlorobenzaldehyde (1.41 g, 0.01 mol), malononitrile (0.66 ml, 0.01 mol), resorcinol (1.1 g, 0.01 mol), ethanol (20 ml), and drops of piperidine were stirred and refluxed until the reaction was completed 2 hours (Scheme 1). The product precipitated when the reaction cooled at room temperature. The crude product was filtered, dried, and recrystallized from ethanol to give compound **C** [30].



Scheme (1)

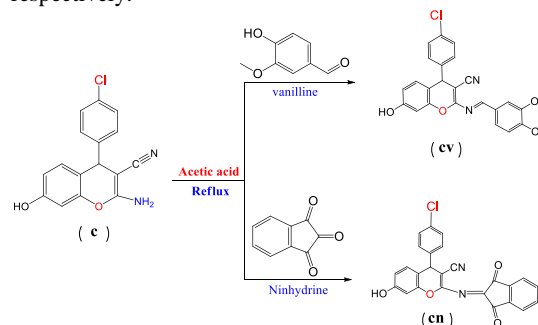
2.2.1.1. 2-amino-4-(4-chlorophenyl)-7-hydroxy-4H-chromene-3-carbonitrile (c):-

yellow crystals m.p.237°C, yield(74%), C₁₆H₁₁ClN₂O₂, m/z 298 M⁻¹ [293] percent, calcd: C, 64.33; H, 3.71; N, 9.38 percent, found: C, 64.30; H, 3.70; N, 9.30 percent. FT-IR (cm⁻¹) 3411 (OH), 3335(-NH₂-), 3220 (C-H, aromatic), 2188 (CN), 1587 (C=C, aromatic), 1400 (C-O of chromene);¹HNMR (d, ppm), 4.534 (s, H, CH

chromene), 6.370-7.057 (m, 7H, C₆H₄, C₆H₃), 7.60 (s, 1H, NH₂), 9.72(s, 1H, OH).

2.2.2. Synthesis of Schiff base: -

A mixture of **c** (2.99 g, 0.01 mol), Vanillin (1.52 g, 0.01 mol), or Ninhydrin (1.8 g, 0.01 mol), ethanol (30 ml), and drops of acetic acid was stirred and refluxed until the reaction was completed 4 hours, and 5 hours respectively (Scheme 2). The product precipitated when the reaction cooled at room temperature. The crude product was filtered, dried, and recrystallized from ethanol to give yellow crystals (cv), and yellow crystals (cn) respectively.



Scheme (2)

2.2.2.1 Synthesis of (E)-4-(4-chlorophenyl)-7-hydroxy-2-((4-hydroxy-3-methoxy benzylidene)amino)-4H-chromene-3-carbonitrile(cv)

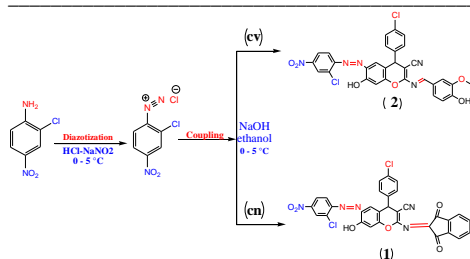
yellow crystals. P. 228°C, yield (75%), C₂₄H₁₇ClN₂O₄ MS, m/z 432 M⁺ [432] percent, calcd: C, 66.60; H, 3.96; N, 6.47 percent, found: C, 66.62; H, 4.09; N, 6.50 percent. FT-IR (cm⁻¹)3345 (2OH), 2220 (CN), 1558 (C=N, Schiff base); ¹HNMR (d, ppm), 3.424 (s, 3H, OCH₃), 4.50 (s, H, CH chromone), 6.37-7.157 (m, 10H, C₆H₄, 2C₆H₃), 7.44 (s, 1H, C=N), 9.75 (s, 2H, 2OH).

2.2.2.2. Synthesis of 4-(4-chlorophenyl)-2-((1,3-dioxo-1H-inden-2(3H)-ylidene)amino)-7-hydroxy-4H-chromene-3-carbonitrile(cn)

yellow crystals m.p. 220°C, yield(70%), C₂₅H₁₃ClN₂O₄ MS, m/z 440 M⁺ [440] percent, calcd: C, 68.11; H, 2.97; N, 6.35 percent, percent, found: C, 71.50; H, 3.80; N, 6.44 percent. FT-IR (cm⁻¹) 3342 (OH), 2190 (CN), 1614 (2C=O) 1588 (C=N), 1402 (C-O); ¹HNMR (d, ppm), 3.310 (s, 3H, OCH₃), 4.191 (s, H, CH chromone), 6.82-7.96 (m, 9H, 3C₆H₃), 11.30 (s, H, OH).

2.2.3. General procedure for the synthesis of azo disperse dyes:

To an ice-cold solution of the appropriate aromatic amine (2-chloro-4-nitroaniline) (1.72g, 0.01 mmol) in a concentrated hydrochloric acid (30 mL), a cold aqueous solution of sodium nitrite (1g), was added dropwise through 15 min at 0 -5°C. The solution was stirred vigorously with traces of sulfamic acid to remove any excess nitrous for 30 min to yield the diazonium salt solution. The diazonium salt solution was then added drop wisely to the pre-cooled solution of compound cv, and cn (0.01 mol, in 20 mL ethanol and 5 mL of 10% NaOH) over 1 hour with vigorous stirring and adding sodium acetate to collect the dye particles. Following the reaction's conclusion, the products were filtered out, cleaned in water to remove any remaining acid, and then dried at room temperature to yield dyes **1** and **2**, which were recrystallized from the appropriate solvent (Scheme 3).



Scheme (3)

Dye 1:- 6-((2-chloro-4-nitrophenyl)diazenyl)-4-(4-chlorophenyl)-2-((1,3-dioxo-1H-inden-2(3H)-ylidene)amino)-7-hydroxy-4H-chromene-3-carbonitrile

Brown powder, m.p. 120 °C, yield (82%), $C_{31}H_{15}Cl_2N_5O_6$ MS, m/z 623 M^{+1} [624] percent, calcd: C, 59.63; H, 2.42; N, 11.22 percent, percent, found: C, 59.60; H, 2.20; N, 11.02 percent. FT-IR (cm^{-1}) 3357 (OH), 2192 (CN), 1720 (2C=O), 1580(C=N), 1512 (N=N), 1489 (C-O); 1H NMR (d, ppm), 3.72 (s, 3H, OCH₃), 4.77 (s, H, CH chromone), 6.18-7.95 (m, 13H, 2C6H4, C6H3, C6H2), 10.13 (s, 1H, OH).

Dye 2:- 6-((2-chloro-4-nitrophenyl)diazenyl)-4-(4-chlorophenyl)-7-hydroxy-2-((E)-(4-hydroxy-3-methoxybenzylidene)amino)-4H-chromene-3-carbonitrile

Dark red powder, m.p. 124 °C, yield (65%), $C_{30}H_{19}Cl_2N_5O_6$ MS, m/z 616 M^{+1} [617] percent, calcd: C, 58.46; H, 3.11; N, 11.36 percent, found: C, 58.40; H, 3.10; N, 11.30 percent. FT-IR (cm^{-1})3279 (2OH), 2192 (CN), 1589 (C=N), 1517 (N=N), 1460 (C-O); 1H NMR (d, ppm), 3.63 (s, 3H, OCH₃), 4.51 (s, H, CH chromone), 6.37-7.14 (m, 12H, C6H4, 2C6H3, C6H2), 7.16 (s, 1H, Sciff base C=N), 9.77 (s, 2H, 2OH).

2.3. Dyeing Procedures, Color Measurements, and Fastness Testing of the Dyed Fabrics

The dyeing process is performed using two different techniques for polyester fabric as ultrasonic and high temperature-high pressure (IR) Also, using ultrasonic and conventional dyeing techniques for Nylon fabric. The dyeing procedures of the two dyes for two fabrics used were applied at liquor ratio 1:50 .

2.3.1. High temperature-high pressure dyeing technique (HTHP) and Conventional Dyeing

A dispersion of the two dyes **1**, **2** were produced by dissolving the appropriate amount of dye in drops of DMF (Liquor ratio 1:50) while studying the other dyeing factors such as dispersing agent, concentration, pH, time, and temperature for Polyester or nylon.

2.3.2. Ultrasound dyeing

The two dyes **1**, **2** were applied at 80°C at liquor ratio 1:50, with studying the other dyeing factors dispersing agent, shade, pH, and time for both fabrics, in addition to studying carrier as a factor for dyeing polyester fabric.

2.4. Colour measurements

Using barium sulphate as the standard blank and a D65/108 source, A CE 7000A reflectance

spectrophotometer (Gretag Macbeth, UK) was used to calculate the colour strength (k/s) values, reflectance (%), and CLE $L^*a^*b^*$ value. These values indicate the colour depth and colour strength of dyed samples that were assessed based on their k/s values and CLE $L^*a^*b^*$ coordinates. Three average settings from repeated measurements and UV elimination were used to incorporate the specular component. The colour values were expressed using the CIE 1976 Colour Space method. L^* for lightness, a^* for greenness (negative value) and redness (positive value), b^* for blueness (negative value) and yellowness (positive value), C^* for chroma, and h^* for hue angle were the coordinates used to establish the colour values. We can measure the reflectance and colour strength from equation 1:

$$K/S = (1-R) / 2R \quad (\text{eq. 1})$$

where K act as absorbance, S for scattering, and R for reflectance. Different samples' colour strengths were assessed using the equation above.

2.5. Fastness testing

According to ISO standard procedures, the coloured samples were evaluated for wash fastness, light fastness, rub fastness, and perspiration fastness after being cleaned off with 2 g/l non-ionic detergents at 80 °C for 30 minutes. For both colour change (AATCC Evaluation Procedure (EP) 1-similar to ISO 105-A02) and colour staining (AATCC EP 2—same as ISO 105-A03), the ISO Grey Scale was used to visually assess wash fastness (ISO 105-C02 (1989), crock fastness (ISO 105-X12 (1987), and perspiration fastness (ISO 105-E04 (1989)). Light fastness was evaluated using ISO 105-B02 (carbon arc). [41-43].

2.6. Evaluation of antimicrobial activity

The antimicrobial activities of treated fabrics have been studied using colony forming technique (CFU) against *Staphylococcus aureus* ATCC 6538-P was used as the gram-positive bacteria, *Escherichia coli* ATCC 25933 as the gram-negative bacteria, *Candida albicans* ATCC 10231 as yeast, and the filamentous fungus *Aspergillus niger* NRRL-A326. Bacterial stocks (10 μ l) of stock of CFU value of about 10⁸ were inoculated into a 10ml freshly prepared liquid nutrient broth containing 5g/l peptone; 3g/l beef extract at pH 6.8 in 100 ml-volume of Erlenmeyer flasks, and incubated for 24h. but for the fungus potato dextrose broth was used. Fabrics (1cm²/250mg) were added to the inoculated flasks (with 10 μ l of inoculums) leaving the control (inoculated flasks without samples). After 24h incubation at 28 and 37°C (for the fungus and bacteria, respectively), the reduction (R %) in growth was measured by detecting the reduction in the absorbance of the inoculated flasks related to the untreated controls. The growth reduction was calculated from the following equation:

$$R (\%) = A - B / A \times 100$$

Where A is the no. of colonies of the culture control but B is the no. The colonies of treated samples. The absorbance of treated samples was measured (at 600 nm) compared to the textile-treated samples [37, 44].

3. Result and Discussion

3.1. Synthesis and spectroscopic characterization

Scheme (1) shows the structures of investigated compounds **c**, which were confirmed by elemental analysis (experimental section), FT-IR, and 1H NMR. FTIR spectra **c** revealed the absorption bands localized 1400 cm^{-1} correspond to CO of chromene aromatic

stretching. These stretching vibrations of C=C aromatic appeared at 1587 cm^{-1} , a sharp CN absorption around 2188 cm^{-1} , NH₂ and OH stretching band at 3335 and 3411 cm^{-1} respectively. Compounds **c** display singlet signals at 4.53 ppm are due to the CH of chromene protons. Multiple signals are due to aromatic rings. A singlet signal is due to NH₂ at 7.60 . A singlet signal at 9.72 is due to OH. Scheme (2) shows that the Schiff base is formed by the structures of the investigated compounds **av**, **bv**, **an**, and **bn**. Mass spectra of the Schiff base compounds revealed molecular ions at m/z 432 [M⁺] and 440 [M⁺] for compounds **cv** and **cn**, respectively. All structures were illustrated by elemental analysis (the experimental part). The IR spectra of all compounds showed C=N stretching modes of the Schiff base in 1588 . Compounds **cv** and **cn** are characterized by the appearance of stretching mode OH. Also, **cn** is characterized by the appearance 2C=O of ninhydrin at 1614 . ¹HNMR spectra of compounds were observed at their respective fields. The singlet signal of NH₂ disappears, and the presence of a singlet signal of Schiff base in compounds **cv** and **cn**. Scheme 4 shows the structure of dyes **1** and **2** confirmed by elemental analysis (exp. Part). IR spectra of all dyes showed the presence of N=N stretching mode of azo dyes at 1517 - 1512 cm^{-1} .

3.2. Dyeing of Polyester

3.2.1. High temperature-High pressure (HTHP) & ultrasonic technique

3.2.1.1. Effect of dispersing agent

The experiment involved applying disperse dyes **1** and **2** at a pH of 4, for 1 hour at a temperature of 120°C in

HTHP or at temperature of 80°C in Ultrasonic Technique, with and without the use of dispersing agents. According to Figures 1, 2, the results show that dye exhaustion reached higher values when no dispersing agent was used, indicating more effective dye uptake under these conditions. Additionally, the data confirm that dye 2 exhibited higher exhaustion than dye 1 due to chemical Structure of Dye 2 which contains functional groups such as hydroxyl (-OH) and methoxy (-OCH₃). These groups enable hydrogen bonding between the dyes and the fibers, enhancing the dye-fiber affinity and leading to greater exhaustion.

3.2.1.2. Effect of Concentration

A series of dyeing experiments were performed using disperse dyes **1** and **2** at varying shade concentrations (1%, 2%, and 3%). These dyeings were conducted at a pH of 4, at a temperature of 120°C in IR or at temperature of 80°C in Ultrasonic Technique, for a duration of 1 hour, without the use of dispersing agents. The results, as illustrated in Figure 3,4, revealed that Dye 2 exhibited greater exhaustion compared to dye 1 across all shade concentrations. This increased exhaustion is related to the structural characteristics of dye 2, which enhance its affinity and uptake by the fibers. Also, further the data indicate that lower dye concentrations (1%) resulted in a higher extent of exhaustion. This trend can be attributed to the saturation behavior of dye uptake, where lower dye levels allow more efficient absorption and distribution within the fiber, whereas higher concentrations may lead to less efficient exhaustion due to limited sites or saturation effects.

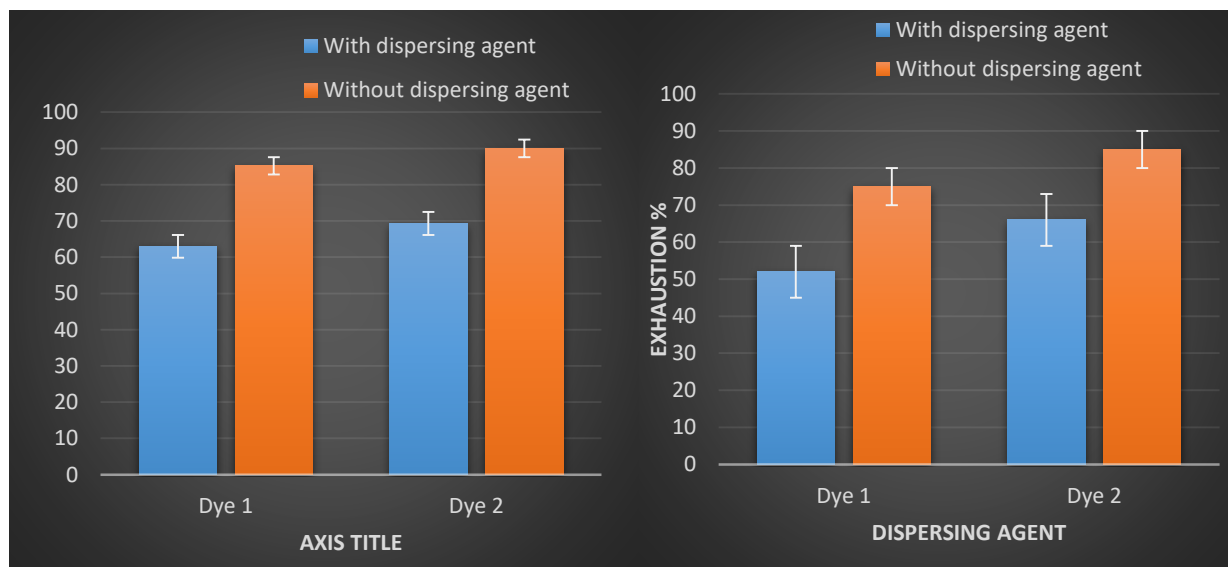


Figure 1: Effect of dispersing agent with Exhaustion values in IR dyeing at pH = 4 for 1 hour at 120°C for dyes 1, and 2.

Figure 2: The effect of dispersing agents with Exhaustion values in Ultrasonic dyeing at pH = 4 for 1 hour at 80°C for dyes 1, and 2.

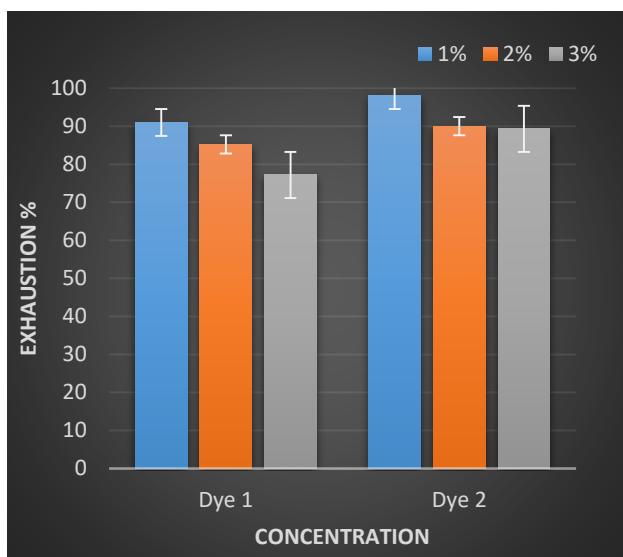


Figure 3: The effect of Concentration with Exhaustion values in IR dyeing at pH = 4 for 1 hour at 120 °C for dyes 1, and 2.

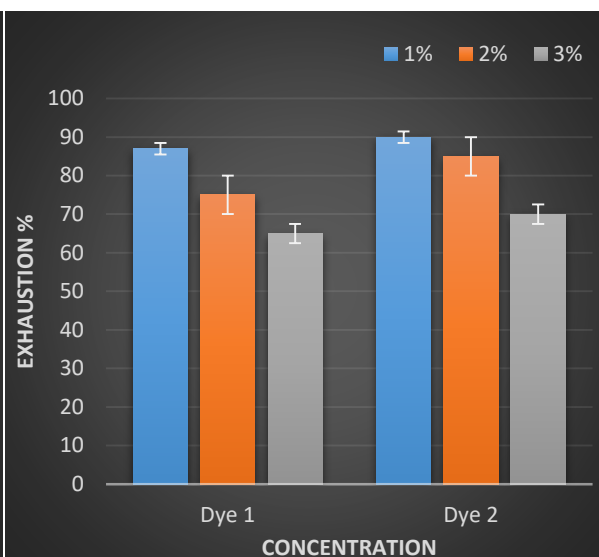


Figure 4: The effect of Concentration with Exhaustion values in Ultrasonic dyeing at pH = 4 for 1 hour at 80 °C for dyes 1, and 2.

3.2.1.3. Effect of pH

A series of dyeing experiments were conducted using disperse dyes 1 and 2, with dyebath pH levels ranging from 3 to 5, at a temperature of 120°C in IR or at temperature of 80°C in Ultrasonic Technique for 1 hour, and without the use of dispersing agents. The results presented in Figures 5,6 demonstrate that pH 3 yielded the highest exhaustion values compared to pH 4 and pH 5. This observation suggests that a more acidic environment (pH 3) enhances the uptake of the dye by

the fibers, likely due to the increased protonation of functional groups on the fiber or dye, which could facilitate stronger dye-fiber interactions. Despite pH 3 showing higher exhaustion, a pH of 4 was selected for all subsequent investigations. This choice was made to ensure the stability and integrity of both the fibers and the dyes under high-temperature conditions. At pH 4, there is a reduced risk of fiber or dye degradation, maintaining the quality and safety of the dyeing process.

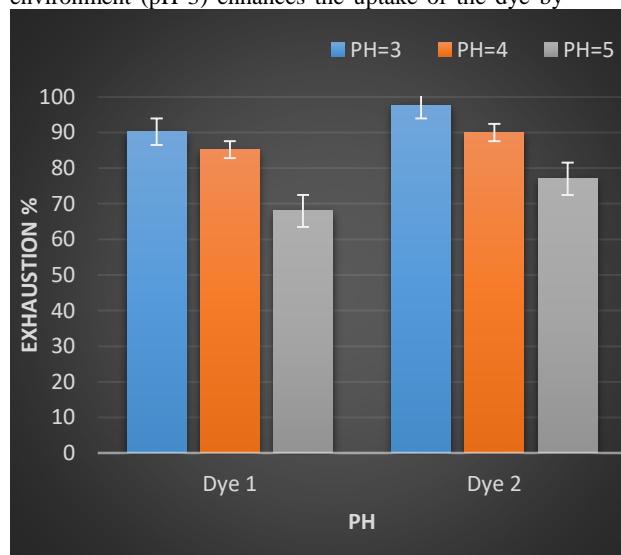


Figure 5: The effect of pH with Exhaustion values in IR dyeing without dispersing agent for 1 hour at 120 °C.

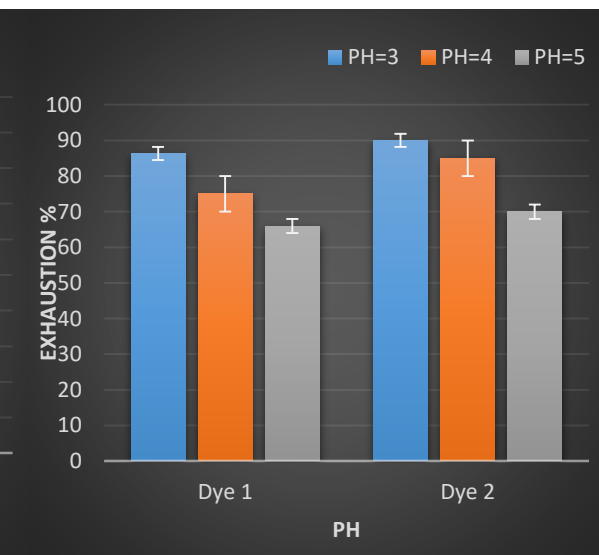


Figure 6: The effect of pH with Exhaustion values in ultrasonic dyeing without dispersing agent for 1 hour at 80 °C.

3.2.1.4. Effect of temperature

The study was extended to examine the dyeing behavior of disperse dyes 1 and 2 at various temperatures: specifically, 110°C and 120°C in infrared (IR) dyeing, and 60°C and 80°C in ultrasonic dyeing, for 1 hour at pH 4 without dispersing agents. As shown in Figures 7 and 8, a temperature of 120°C in IR dyeing yielded higher exhaustion values on polyester compared to 110°C. Similarly, in ultrasonic dyeing, 80°C produced higher

exhaustion values than 60°C. This increase in dye exhaustion at elevated temperatures can be attributed to the physical and chemical properties of polyester fibers, along with the enhanced solubility of disperse dyes at higher temperatures. At elevated temperatures, the polyester structure becomes more receptive to dye molecules, enabling greater dye uptake and resulting in more intense coloration.

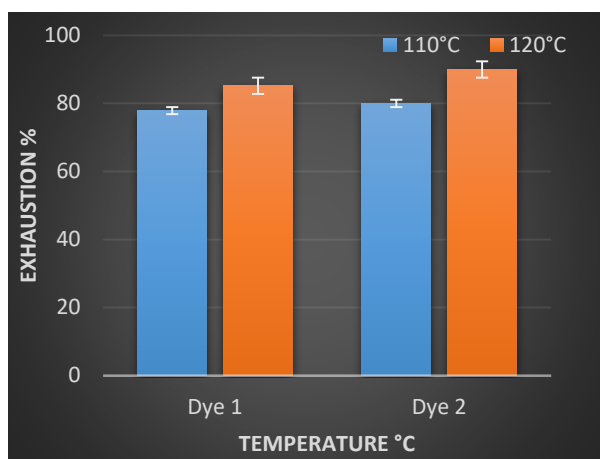


Figure 7: The effect of temperature with Exhaustion values in IR dyeing without dispersing agent for 1 hour at pH 4 for dyes 1 and 2.

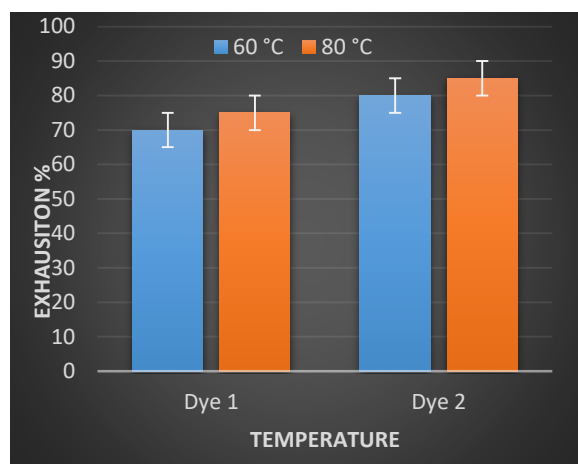


Figure 8: The effect of temperature with Exhaustion values in Ultrasonic dyeing without dispersing agent for 1 hour at pH 4 for dyes 1 and 2.

3.2.1.5. Effect of time

Figures 9,10 illustrates the dyeing behavior of disperse dyes 1 and 2 at different dyeing durations (30 and 60 minutes) at a temperature of 120°C in IR or at temperature of 80°C in Ultrasonic Technique and pH 4, without dispersing agents. The results show that both dyes exhibit a high dyeing rate within the first 30

minutes, indicating rapid initial exhaustion. By 60 minutes, exhaustion values reach equilibrium, as the dye uptake tends to stabilize. This suggests that most dyeing occurs within the initial period, with equilibrium reached at 60 minutes, beyond which there is minimal additional dye absorption.

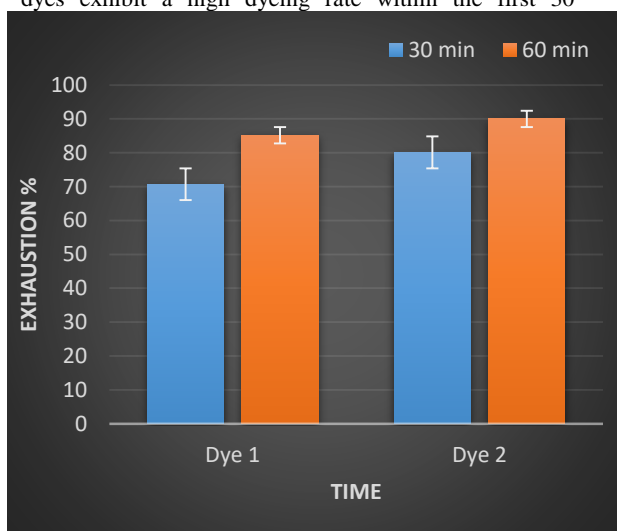


Figure 9: The effect of time with Exhaustion values in IR dyeing without dispersing agent for 1 hour at pH 4 for dyes 1 and 2.

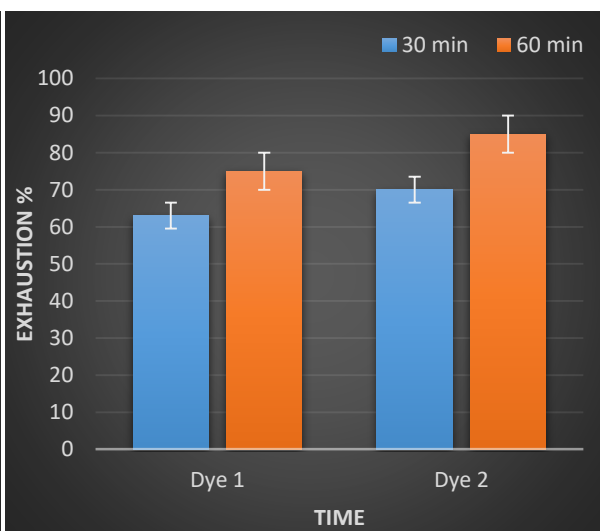


Figure 10: The effect of time with Exhaustion values in Ultrasonic dyeing without dispersing agent for 1 hour at pH 4 for dyes 1 and 2.

3.3. Dyeing of Nylon:-

3.3.1. Conventional dyeing & Ultrasonic technique

3.3.1.1. Effect of dispersing agent

The experiment involved applying disperse dyes 1, 2 at pH 4, for 1 hour at a temperature of 100°C in dye bath at Conventional dyeing or at temperature of 80°C in Ultrasonic Technique, with and without the use of dispersing agents. According to Figures 11, 12, the results show that dye exhaustion reached higher values

when no dispersing agent was used, indicating more effective dye uptake under these conditions. Additionally, the data confirm that dye 2 exhibited higher exhaustion than dye 1 as mentioned previously. The data indicate that the ultrasonic dyeing technique achieves higher exhaustion levels than conventional dyeing. This suggests that ultrasonic dyeing is more efficient, offering savings in time, temperature, and energy.

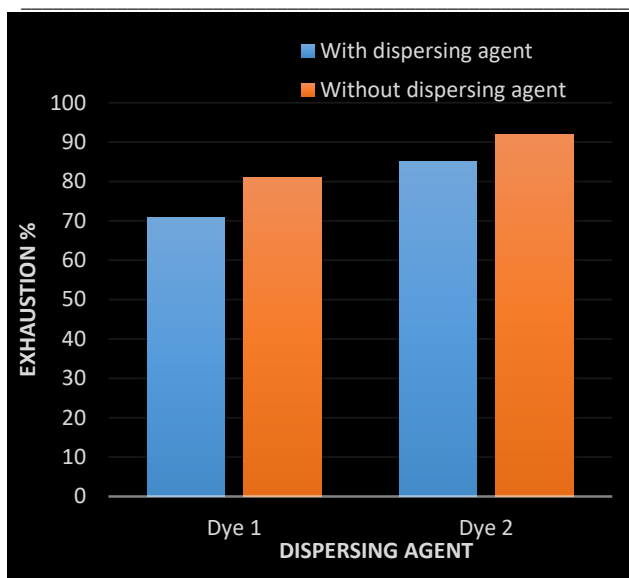


Figure 11: Effect of dispersing agent with Exhaustion values in conventional dyeing at pH 4, 2% shade for 100 °C and 1 hour for dyes 1, and 2.

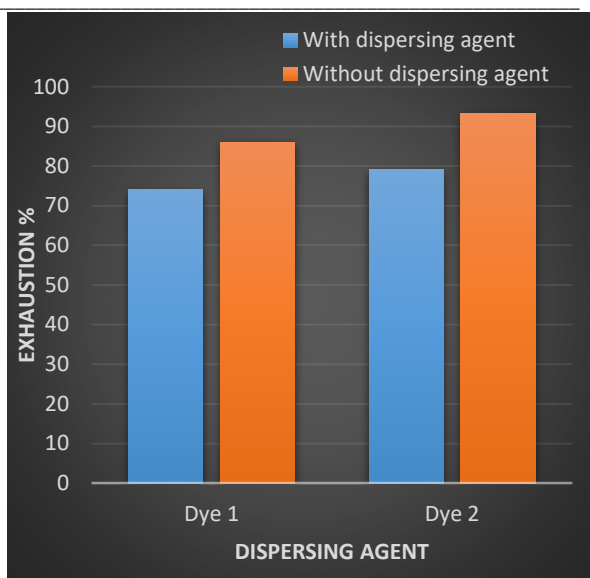


Figure 12: The effect of dispersing agents with Exhaustion values in Ultrasonic dyeing at pH 4, 2% shade for 1 hour at 80 °C for dyes 1, and 2.

3.2.1.2. Effect of Concentration

Disperse dyes 1 and 2 at varying shade concentrations (1%, 2%, and 3%) were performed at a pH of 4, at 100°C using conventional dyeing and at 80°C with the ultrasonic technique, each for a duration of 1 hour without dispersing agents. The results, as shown in Figures 13 and 14, indicate that Dye 2 achieved greater exhaustion than Dye 1 across all shade concentrations.

This increased exhaustion can be attributed to the structural characteristics of Dye 2, which enhance its affinity for and uptake by the fibers. Additionally, the data show that lower dye concentrations (1%) resulted in a higher extent of exhaustion, suggesting more efficient absorption and distribution within the fiber at reduced dye levels.

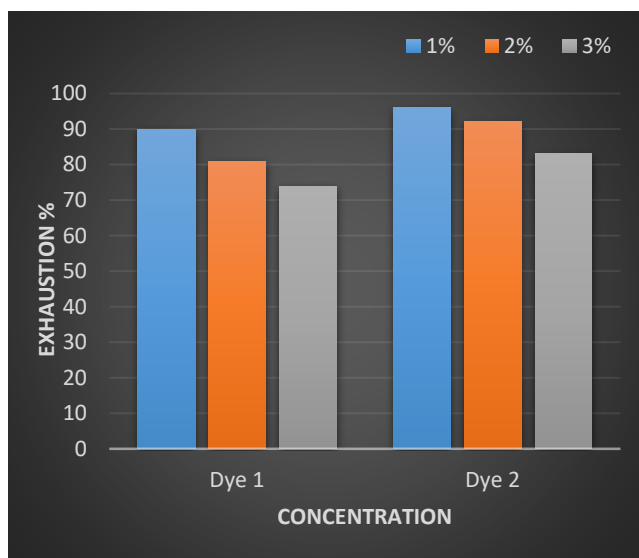


Figure 13: The effect of Concentration with Exhaustion values in conventional dyeing at pH = 4 for 1 hour at a temperature of 100 °C for dyes 1, and 2.

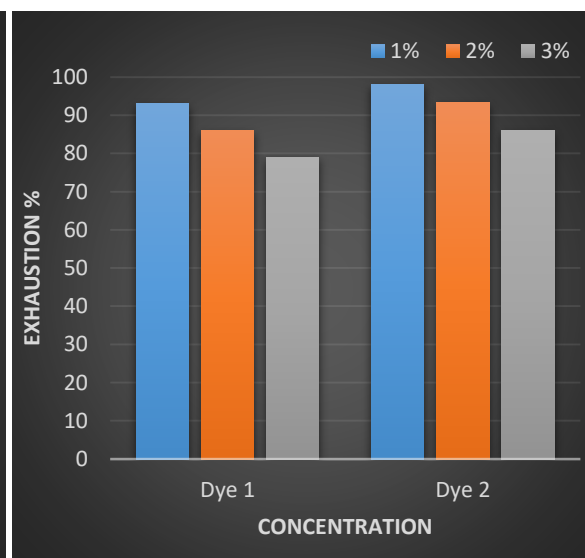


Figure 14: The effect of Concentration with Exhaustion values in ultrasonic dyeing at pH = 4 for 1 hour at a temperature of 80 °C for dyes 1, and 2.

3.3.1.3. Effect of pH

The data presented in Figures 14 and 15 highlights the relationship between dye bath pH levels and the dyeing performance of disperse dyes 1 and 2 on nylon under specified conditions. The study demonstrates that a more acidic environment, specifically at pH 3, produces the highest dye exhaustion values. This suggests that at pH 3, the protonation of functional groups on the nylon fibers or the dyes themselves is maximized, resulting in

stronger interactions between the dye and the fiber. Such conditions enhance dye absorption and fixation, leading to better dyeing performance. While dye exhaustion decreases at pH 4 and pH 5 compared to pH 3, these pH levels still maintain acceptable levels of dye uptake. Notably, pH 4 appears to strike a balance between maintaining good exhaustion values and reducing the risk of fiber or dye degradation, which might occur at more extreme acidic levels.

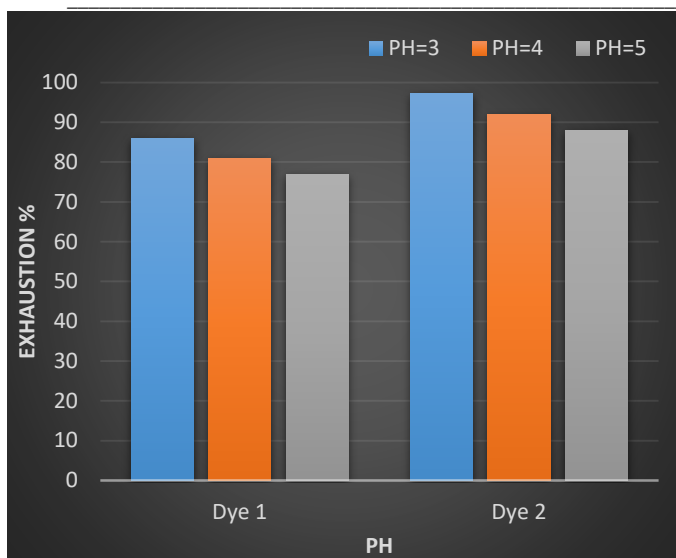


Figure15: The effect of pH with Exhaustion values in conventional dyeing at 100 °C, 2% shade and 1 hour for dyes 1, and 2

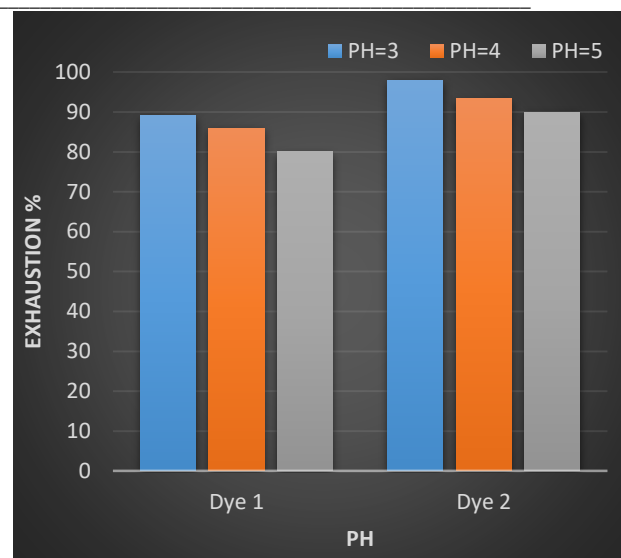


Figure16: The effect of pH with Exhaustion values in Ultrasonic dyeing at 100 °C, 2% shade and 1 hour for dyes 1, and 2

3.3.1.3. Effect of time

The dyeing behaviour of disperse dyes **1** and **2** is shown in Figures 17, 18 at various dyeing times (30 and 60 minutes), at pH 4, 2% shade, without dispersing agents, and at a temperature of 80°C using the Ultrasonic Technique or 100°C using the conventional method. The results show that both dyes exhibit a high dyeing exhaustion at 60 min. also, the dye **2** higher exhaustion than dye **1** due to function group. The use of ultrasonic energy at 80°C facilitates dye uptake, possibly due to the cavitation effect, which enhances the diffusion and interaction of dye molecules with the substrate, even at a lower temperature.

3.4. Colorimetric and Fastness properties:

According to the data, dyes **1** and **2** have high light fastness because they include carbonyl and hydroxyl groups, respectively, which raise electron resonance and, hence, light fastness. Additionally, polyester's inherent qualities that improve dye-fiber interaction and prevent photodegradation give it a higher light fastness than nylon. It should be noted that both wet and dry conditions produced very good wash fastness ratings (4-5) and very good rubbing fastness ratings (4-5), with no colour shift seen. Perspiration fastness properties (in both acidic and alkaline media) of dyed polyester and nylon samples in terms of ratings for staining of adjacent fabrics and changing in color were very good in (Table 1).

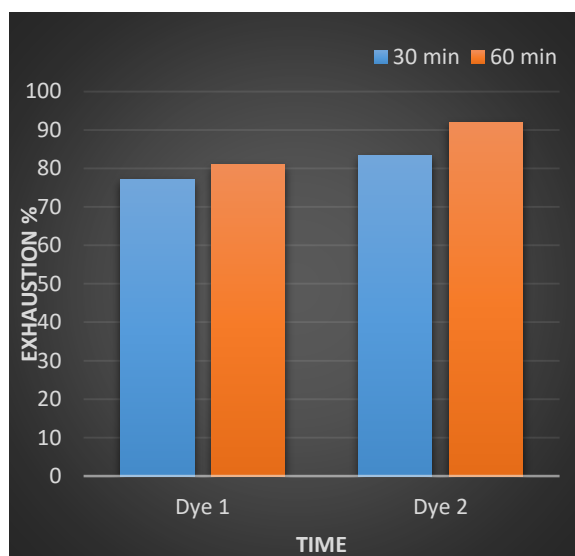


Figure17: The effect of time with Exhaustion values in conventional dyeing at 100 °C, 2% shade, pH 4 and 1 hour for dyes 1, and 2

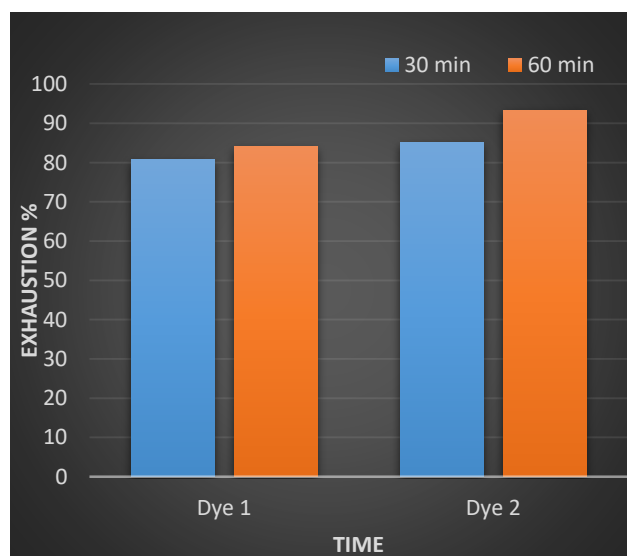


Figure18: The effect of time with Exhaustion values in Ultrasonic dyeing at 100 °C, 2% shade, pH 4 and 1 hour for dyes 1, and 2

Table 1: indicates the fastness properties of dyed polyester(P) in IR and ultrasonic techniques and dyed nylon(N) in conventional and ultrasonic techniques for dyes 1, 2 without dispersing agent, 2% shade and at pH 4

Dye	Fabric	Technique	Fastness to rubbing		Wash fastness	Fastness to perspiration						Light
			Dry	Wet		Alkaline			Acidic			
						Alt	Sc	Sw	Alt	Sc	Sw	
1	P	IR	4-5	5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
		ultrasonic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	N	conventional	4	4	4	4	4	4	4	4	4	4
		ultrasonic	4	4	4	4	4	4	4	4	4	4
2	P	IR	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
		ultrasonic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	N	Conventional	4	4	4	4	4	4	4	4	4	4
		Ultrasonic	4	4	4	4	4	4	4	4	4	4

C, Cotton; W, Wool; S, silk; Alt= alteration; Sc= Staining on cotton; Sw =Staining on wool.

Table 2 indicates the CIELAB and modified CIE LCh° systems are both standardized color measurement systems used to quantify and describe colors numerically in dyes 1 and 2. Here is a breakdown of the parameters mentioned: L* – lightness, a* – redness if positive coordinate, or greenness if negative coordinate, b* – yellowness if positive coordinate, or blueness if negative coordinate, C* – chromaticity, h – hue of the color, X – coordinate x, Y – coordinate y, Z – coordinate z.

3.5. Antimicrobial activity

Tables 3, 4 and Figure 19 demonstrate the Colony Forming Unit (CFU) values for dyed polyester and nylon fabrics against various microorganisms: *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* (yeast), and the filamentous fungus *Aspergillus niger*. The data represents samples dyed using infrared and ultrasonic procedures for polyester, and conventional and ultrasonic processes for nylon, using Dyes 1 and 2 without dispersion agents at 2% shade and pH 4. The presence of

hydroxyl and carbonyl groups in these dyes resulted in significant antimicrobial activity, with percentage reductions in CFU ranging from 56.8% to nearly 100%. The antimicrobial mechanism of Dye 1 involves the interaction between its positively charged nitrogen atoms and the negatively charged microbial cell membranes, with carbonyl groups playing a crucial role in growth inhibition. Notably, Dye 1 showed greater efficacy against *S. aureus* compared to *E. coli*. The infrared (IR) dyeing technique demonstrated marginally superior antimicrobial activity compared to ultrasonic dyeing across all synthesized dyes, likely due to enhanced dye molecule diffusion into the fabric, which increased the biological activity and antimicrobial efficacy of the treated samples. Overall, the antimicrobial performance was more pronounced against Gram-positive *S. aureus* compared to Gram-negative *E. coli* and the fungi *A. niger* and *C. albicans*, a difference attributed to variations in cell wall structures and compositions among these microorganisms.

Table 2: shows the colorimetric data of dyed polyester in IR and ultrasonic techniques and dyed nylon in conventional and ultrasonic techniques with dyes 1, 2 without dispersing agents, 2% shade and at pH 4

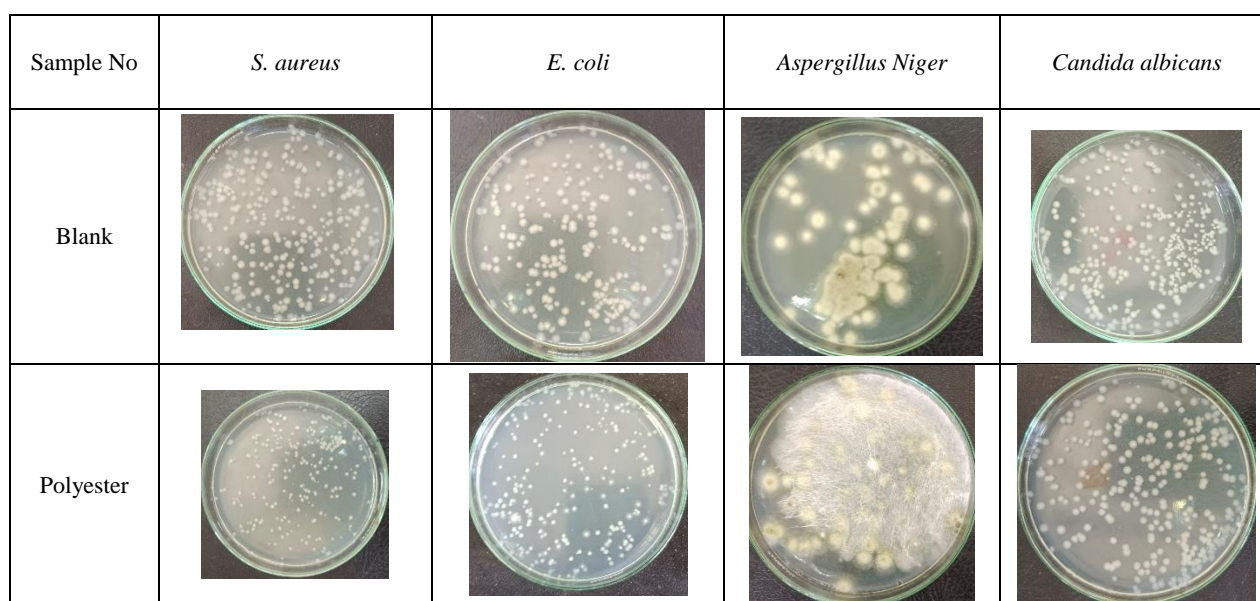
DYE	λ_{max}	Technique Of dyeing	fabric	K/S	L*	a*	b*	dE*	dH*
1	385	IR	polyester	25.73	48.01	31.32	47.39	66.42	56.54
		Ultrasonic		10.10	48.48	20.88	28.38	51.18	-11.90
2	380	IR		24.17	52.12	27.77	50.54	65.19	61.21
		Ultrasonic		10.56	51.32	22.87	35.24	54.41	-13.02
1	385	Conventional	Nylon	22.09	39.90	36.33	40.11	70.29	32.87
		Ultrasonic		27.94	41.63	39.39	41.95	73.43	37.17
2	380	Conventional		30.00	38.16	33.59	36.34	67.56	31.35
		Ultrasonic		27.13	36.89	33.88	34.76	67.41	32.85

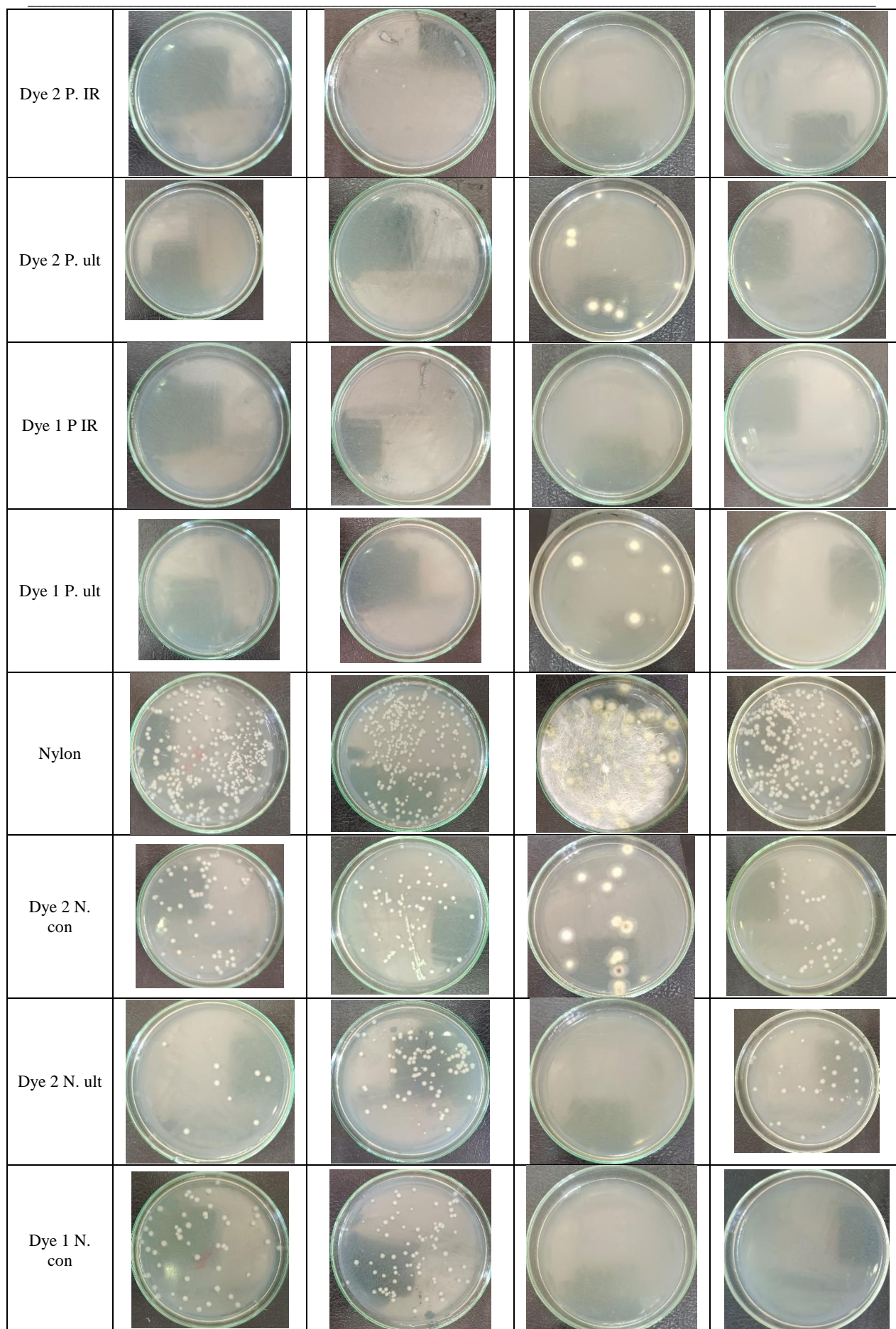
Table 3: show The CFU value at different dilutions of dyed polyester and nylon fabrics against *Staphylococcus aureus* and *Escherichia coli* bacteria.

Sample No	<i>S. aureus</i>				<i>E. coli</i>			
	Absorbance method (A at 600nm)		Counting method		Absorbance method (A at 600nm)		Counting method	
	Colonies No.	Reduction (R%)	Colonies No.	Reduction (R%)	Colonies No.	Reduction (R%)	Colonies No.	Reduction (R%)
Blank	2.159	-	233	-	2.216	-	177	-
Polyester	2.114	2.08	198	15.02	2.247	0.00	189	0.00
Dye 1 P. IR	0.042	98.05	0	100.00	0.018	99.19	0	100.00
Dye 1 P. ult	0.040	98.15	0	100.00	0.028	98.74	0	100.00
Dye 2 P IR	0.025	98.84	0	100.00	0.034	98.47	0	100.00
Dye 2 P. ult	0.010	99.54	0	100.00	0.019	99.14	0	100.00
Nylon	2.223	0.00	236	0.00	2.217	0.00	219	0.00
Dye 1 N. con	0.787	63.55	46	80.26	0.714	67.79	77	56.5
Dye 1 N. ult	0.033	98.47	0	100	0.021	99.05	0	100.00
Dye 2 N. con	0.841	61.05	59	74.68	0.717	67.64	55	68.93
Dye 2 N. ult	0.160	92.59	8	96.57	0.016	99.28	0	100.00

Table 4: indicates the CFU value at different dilutions of dyed polyester and nylon fabrics with dye 1, and 2 against *Candida albicans* as yeast, and the filamentous fungus *Aspergillus niger*.

Sample No	<i>Aspergillus Niger</i>				<i>Candida albicans</i>			
	Absorbance method (A at 600nm)		Counting method		Absorbance method (A at 600nm)		Counting method	
	Colonies No.	Reduction (R%)	Colonies No.	Reduction (R%)	Colonies No.	Reduction (R%)	Colonies No.	Reduction (R%)
Blank	1.468	-	88	-	2.137	-	231	-
Polyester	1.532	0.00	91	0.00	2.211	0.00	219	5.19
Dye 1P. IR	0.037	97.48	0	100.00	0.022	98.97	0	100.00
Dye 1 P. ult	0.360	75.47	4	95.45	0.028	98.69	0	100.00
Dye 2 P IR	0.009	99.39	0	100.00	0.031	98.55	0	100.00
Dye 2 P. ult	0.433	70.50	8	90.91	0.029	98.64	0	100.00
Nylon	1.467	0.00	101	0.00	2.187	0.00	199	13.85
Dye 1N. con	0.006	99.59	0	100.00	0.041	98.08	0	100.00
Dye 1 N. ult	0.007	99.52	0	100.00	0.519	75.71	37	83.89
Dye 2 N. con	0.225	84.67	11	87.5	0.603	71.78	42	81.82
Dye 2 N. ult	0.017	98.84	0	100.00	0.568	73.42	39	83.12





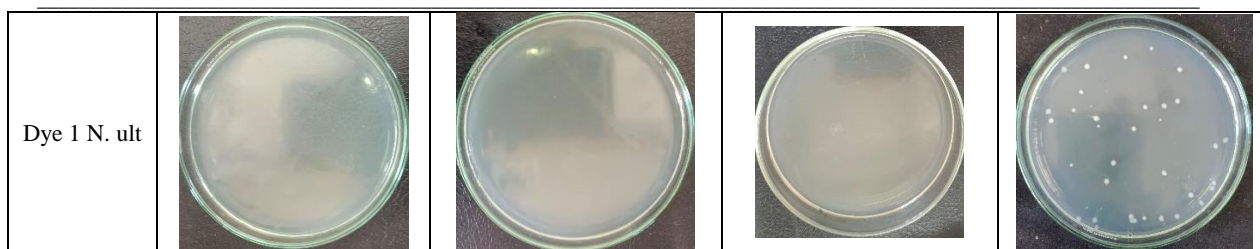


Figure 19: indicates antimicrobial screening of dyes 1 and 2 on *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus Niger* and *Candida albicans*

4. Conclusion: -

This study aimed to achieve simultaneous dyeing and antimicrobial finishing using novel heterocyclic disperse dyes incorporating chromene moiety. The K/S values of dyed samples demonstrated effective color yield under two conditions: high temperature-high pressure dyeing at 120°C and ultrasonic dyeing at 80°C. Both techniques were applied in continuous dyeing processes for 1 hour at pH 4 with 2% shade, without dispersing agents for polyester fabric, and under similar conditions using conventional and ultrasonic techniques for nylon fabric. The dyed samples exhibited excellent fastness properties, achieving ratings of 4-5 for both color change and staining of adjacent fabrics when tested against washing, light, perspiration, and rubbing. The presence of Schiff-base and chromene moiety in the dyes enhanced antimicrobial properties against both bacteria (*Pseudomonas aeruginosa* [Gram-negative] and *Staphylococcus aureus* [Gram-positive]) and fungi (*Aspergillus niger* and *Candida albicans*) when applied to nylon and polyester fabrics. The chromene-based dyes successfully integrated dual functionality in a single process, demonstrating their potential for industrial applications. The ultrasonic dyeing method proved to be an energy-efficient alternative to conventional techniques while maintaining comparable dye uptake and antimicrobial efficacy. Furthermore, the elimination of dispersing agents promotes environmentally friendly dyeing practices without compromising performance on either nylon or polyester fabrics. This research establishes a promising approach for sustainable and multifunctional textile treatments that combine aesthetic and protective properties in a single dyeing step.

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