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Synthesis of a Novel Acid Dye to Impart Mosquito Repellency and UV Protection to Nylon

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ABSTRACT

Novel routes are continuously innovated in the textile industry to obtain high-performance products, and the development of functional textiles using functional dyes is an attractive alternative to existing methods. In this context, the current study reports the synthesis of a new acid dye to develop mosquito-repellent and UV-protective nylon. The acid dye was synthesized by reacting a diazotized derivative of ethyl anthranilate (ethyl 2-aminobenzoate) with H-acid (4-Amino-5-hydroxy-2,7-naphthalenedisulfonic acid). The synthesized dye was thoroughly characterized through Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H NMR),^{13}C NMR (Carbon-13 NMR) spectroscopy, elemental analysis (CHN analyzer), and UV-Vis spectroscopy. The dye was used to dye nylon, and dyeing characteristics (exhaustion and fixation) were examined. The functional effects and coloring properties of dyed fabrics were further investigated. The dyed fabrics were also characterized by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The dyed fabrics were imparted with 100 % mosquito repellency and excellent UV protection. Prog. Color Colorants Coat. 16 (2023), 207-219© Institute for Color Science and Technology.

1. Introduction

Recently, the development of new routes to generate functional textiles has been increasingly reported [1-9]. Functional dyes are an important tool for imparting color and functional effects. Functional dyes can compete with commercially available dyes and finishing agents to combine both operations (dyeing and finishing). An azo chromophore is mainly utilized to synthesize textile dyes [10-12], and exploring the different classes of azo dyes is an interesting research area. Various studies on functional dyes were found [13, 14]. Naphthalene-based azo dyes were synthesized, and the dyeing performance of the dyes on polyester fibers was studied [15]. Dyeing of polyester using naphthalimide azo dyes was done [16, 17].

Acid dyes are important dyes used to dye polyamide fibers (wool, silk, and nylon). Acid dyes are applied to the textiles through an acidic to neutral medium, and they form an electrostatic bonding, producing brilliant shades with overall satisfactory fastness. Diazotized amino benzene sulfonic acid was reacted with amino benzoic acid to synthesize acid dyes; the dyed wool and silk showed an excellent UV protection rating and good antibacterial activity [18]. Cowper et al. prepared azulene-containing acid dyes and studied electrochemical and crystallographic natures [19]. The acid dyes based on surfactants were synthesized; these dyes' substantivity, levelling, and exhaustion properties on wool were studied [20]. Blus synthesized disazo acid dyes, and the coloration of polyamide fiber was performed using synthesized acid

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dyes [21].

Protection against harmful living species, such as mosquitoes, is a worldwide concern. Various products (lotions, creams, electrical devices) are available to counter mosquito bites; however, these products showed limited efficiency and non-durable mosquito repellency. On the other hand, mosquito-repellent textiles can provide better results by covering a large part of the human body. There is a growing interest in synthesizing non-toxic mosquito repellents, and ethyl anthranilate (ethyl 2-aminobenzoate) could be a safe option [22]. A mosquito repellent patch loaded with ethyl 2-aminobenzoate showed no acute oral and dermal toxicity, and it can be used without any health hazard [23]. The toxic action of ethyl 2-aminobenzoate against *Aedes albopictus skuse* was evaluated [24]. Mosquito repellent activity of ethyl 2-aminobenzoate against *Aedes aegypti*, *Anopheles stephensi*, and *Culex quinquefasciatus* [25] was explored. Comparative mosquito-repellent efficacy of ethyl 2-aminobenzoate against methyl N,N-dimethyl anthranilate, and butyl anthranilate was studied by Afify et al. [26].

Mosquito-repellent dyes tend to repel mosquitoes, and textiles dyed with these dyes generate a wash-durable, mosquito-repellent-colored textile. Researchers [27] used Bronner's acid, DEET (N,N-Diethyl-meta-toluamide), and cyanuric chloride to synthesize mosquito-repellent dyes. Azoic colorants for imparting mosquito repellent and antibacterial actions to cotton were prepared by *in-situ* azo coupling using DEET-NH_2 [28]. Singh & Sheikh prepared mosquito-repellent disperse dyes [8]; in their work, two mosquito repellents (ethyl 2-aminobenzoate and 4-hydroxy coumarin) were reacted to form azo disperse dyes. Recently, a multifunctional mosquito-repellent azoic dye was developed on cotton by reacting diazotized ethyl 2-aminobenzoate with *Terminalia chebula* [7]. A cold brand reactive based on DEET was synthesized for imparting UV protection and mosquito-repellent action to nylon [29].

After reviewing the literature on mosquito-repellent textiles, acid dyes, and mosquito-repellent dyes, limited studies were found on mosquito-repellent dyes. Interestingly, no report was found on mosquito-repellent acid dye. As acid dyes are widely utilized for the coloration of nylon, one of the most widely used fibers for preparing apparel and technical textiles, the synthesis of mosquito-repellent acid dye is highly desirable. Very few studies utilized ethyl 2-aminobenzoate for imparting mosquito-repellent protection to textiles. Hence, exploring the ethyl 2-aminobenzoate in synthesizing novel acid dye molecules is interesting.

In the present work, ethyl 2-aminobenzoate was diazotized and reacted with H-acid to prepare a novel acid dye. The acid dye was thoroughly characterized by its chemical structure and organic purity. The dye was applied to nylon, and dyed fabrics were explored for coloration (L*, a*, b*), mosquito repellent, and UV protection properties. The dyed fabrics were further studied for wash-durability of functional properties.

2. Experimental

2.1. Materials

TCI (Tokyo Chemical Industry) supplied ethyl 2-aminobenzoate, H-acid, hydrochloric acid (36 %), Naphthalene-2-ol, ethyl acetate, dimethylformamide, and sodium nitrite. Ready-for-dyeing Nylon-6 woven fabric having a GSM of 81.3, EPI of 80, and PPI of 64, was used. TLC (Thin layer chromatography) silica plate was used to evaluate the organic purity of the dye. FTIR Nicolet 6700 (Thermo) was used to assess the presence of functional groups in the dye. ^{1}H and ^{13}C NMR spectra of the dye were recorded with the help of Bruker DMX500 MHz NMR spectrometer in a DMSO (Dimethyl sulfoxide)-d6 solvent using tetramethyl-silane (TMS) as a standard. The UV-visible spectrum of acid dye was recorded using a spectrophotometer (UV-1900i, Shimadzu). An elemental analyzer (PerkinElmer) was utilized to measure the elemental ratio of the dye. The dyed fabrics were evaluated for thermogravimetric analysis (TGA) using a nitrogen atmosphere at a heating rate of 20 °C/min in the temperature range of 50-800 °C. X-ray diffraction analysis of dyed fabric was done using XRD X'Pert PRO (PANalytical, Netherlands).

2.2. Methods

2.2.1. Synthesis of novel acid dye

12 mmol (1.98 g) of ethyl 2-aminobenzoate was dissolved in 3 mL of hydrochloric acid (36 %) and allowed to cool (0-5 °C). 12 mmol sodium nitrite (0.83 g) was reacted with the ethyl 2-aminobenzoate solution. The diazotization was performed for the desired time (negative test on starch iodide paper) at 0-5 °C. The excess HCl was neutralized to pH=5-6 using a sodium acetate solution.

12 mmol (5.13 g, 80 %) of H-acid was dissolved in 100 mL of water at pH (7-8). The diazotized solution

was reacted with the H-acid solution at a pH of 7-8, maintained by adding 10 % sodium carbonate solution at 0-5 °C. The coupling reaction was performed for 4 h when no colour development was observed with a naphthalene-2-ol solution. The coupling solution was heated to 60 °C, and 12 g of dry powder of sodium chloride was added in small lots. The stirring of the mixture was performed for 30 min. The mixture was kept for 2 h to attain room temperature. The precipitated dye was filtered, washed with brine, dried, and dissolved in dimethylformamide solvent. Salt-free dye was obtained by filtering the dye solution and reprecipitating it in ethyl acetate. The dye was given a washing treatment with ethoxyethane solvent for further purification. The obtained dye was pink-red. Figure 1 shows the synthesis procedure, the dye solution's appearance, and the compounds' chemical structures.

2.2.2. Dyeing of nylon with acid dye

The dye was applied to nylon in an Infra-Red laboratory dyeing machine using a material-to-liquor ratio of 1:10 and pH of 3-4 at 90 °C for 1 h. The obtained dyed fabric was given a cold wash (room temperature, 5 min), hot wash (60 °C for 20 min), and dried to get the final dyed fabric. Figure 2 records the dyeing cycle of acid dyeing of nylon.

2.2.3. Colour measurement, exhaustion, and fixation analysis

A spectrophotometer (Premier Colorscan, SS5100H) was used to determine dyed nylon's color parameters (L*, a*, b*, and K/S).

The dyeing characteristics, like exhaustion (%) and fixation (%), were calculated using the following formulas (Eqs. 1 and 2):

$$\text{Exhaustion (\%)} = \frac{(\text{Absorbance of dyebath solution before dyeing} - \text{Absorbance of dyebath solution after dyeing})}{\text{Absorbance of dyebath solution before dyeing}} \times 100 \quad (1)$$

$$\text{Fixation (\%)} = \frac{(\frac{K}{S}\text{ value before hot washing} - \frac{K}{S}\text{ value after hot washing})}{\frac{K}{S}\text{ value before hot washing}} \times 100 \quad (2)$$

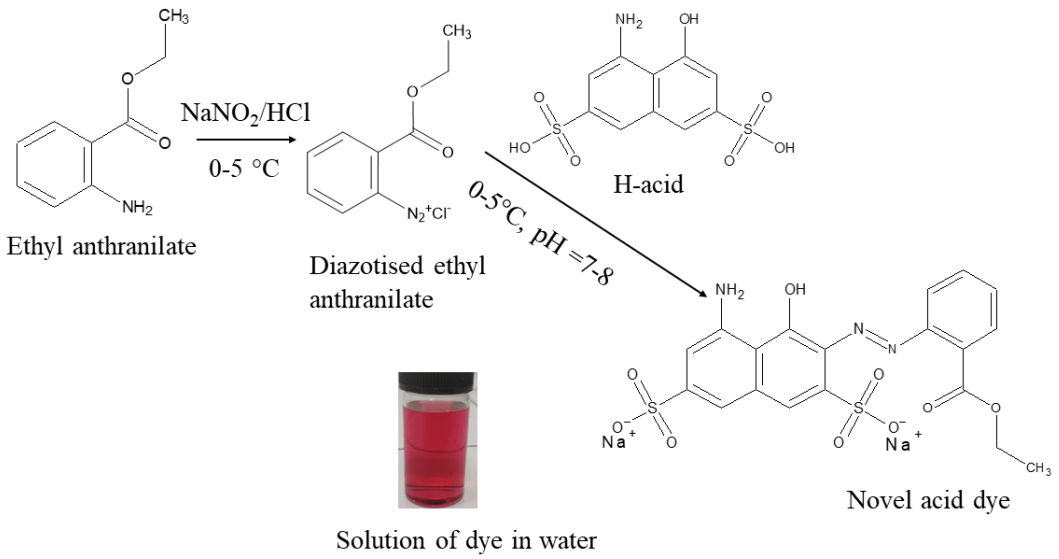


Figure 1: Preparation procedure for novel acid dye.

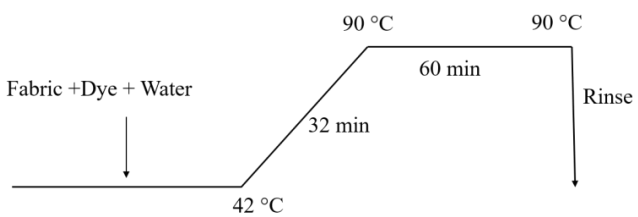


Figure 2: Dyeing cycle of acid dyeing of nylon.

2.2.4. Evaluation of fastness of dyed fabrics

ISO 105- C06, ISO 105-X12, ISO 105 E04, and ISO 105 BO2 methods [30] were used to evaluate the washing fastness, rubbing fastness, perspiration fastness, and lightfastness of dyed samples, respectively.

2.2.5. Evaluation of mosquito repellent and UV protection activities

Mosquito repellency and UV protection of dyed samples were evaluated using the "Arm in cage method" [8] and AS / NZS 4399 (1996) methods, respectively [31].

2.2.6. Laundering treatment of dyed fabrics

The dyed fabrics were washed as per AATCC-61A [32] to assess the durability of functional performance against laundering treatments.

3. Results and Discussion

3.1. Characterisation of acid dye

An eluent system (2-butanol: ethanol: ethyl acetate: water =2:4:1:3) was used to determine the organic purity of the acid dye on the TLC (thin layer chromatography) plate, which was confirmed by a single spot.

The FTIR spectra of acid dye are recorded in Figure 3. OH and N-H stretching at 3444 cm^{-1}, =C-H stretching at 3090 cm^{-1}, asymmetric C-H stretching at 2982 cm^{-1}, symmetric C-H stretching 2972 cm^{-1}, C=O stretching at 1709 cm^{-1}, N-H bending at 1625 cm^{-1}, N=N stretching at 1586 cm^{-1}, and C=C stretching at 1492 cm^{-1} were obtained [33]. Hence, various functional groups and successful coupling reactions were confirmed through FTIR analysis.

^{1}HNMR spectrum of dye is recorded in Figure 4. A triplet with a coupling constant of 7.1 Hz at 1.42 ppm due to CH_3, and a quartet with a coupling constant of 7.1 Hz at 4.47 ppm to CH_2 and benzene ring hydrogens in the 6.87 to 8.42 ppm region were obtained. The presence of the OH group in the dye was confirmed through a singlet peak at 15.83 ppm. The summary of all hydrogens is mentioned below.

^{1}H NMR (500 MHz, DMSO-d6): δ=1.42 (t, 3H, CH_3, J=7.1Hz), 4.47(q, 2H, -CH_2, J=7.1 Hz), 6.87 (d, 1H, ArH, J=1.5 Hz), 7.09 (d, 1H, ArH, J=1.6Hz), 7.20 (t, 1H, ArH, J=7.4 Hz), 7.32 (s, 1H, ArH), 7.67 (t, 1H, ArH, J=7.8 Hz), 8.00 (d, 1H, ArH, J=7.9Hz), 8.42 (d, 1H, ArH, J=8.5Hz), 15.83 (s, 1H, OH).

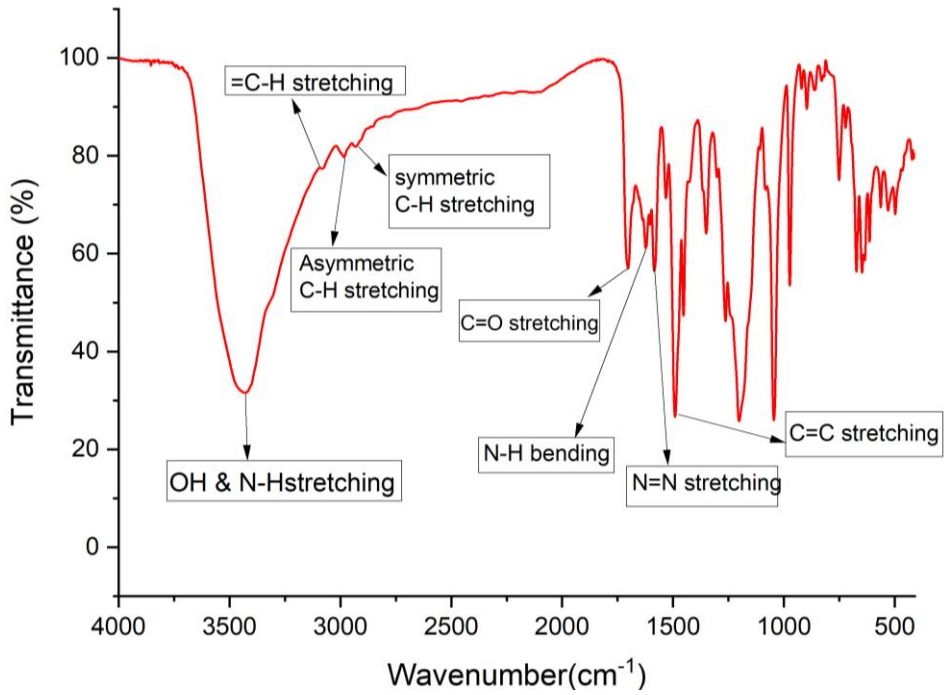


Figure 3: FTIR spectra of acid dye.

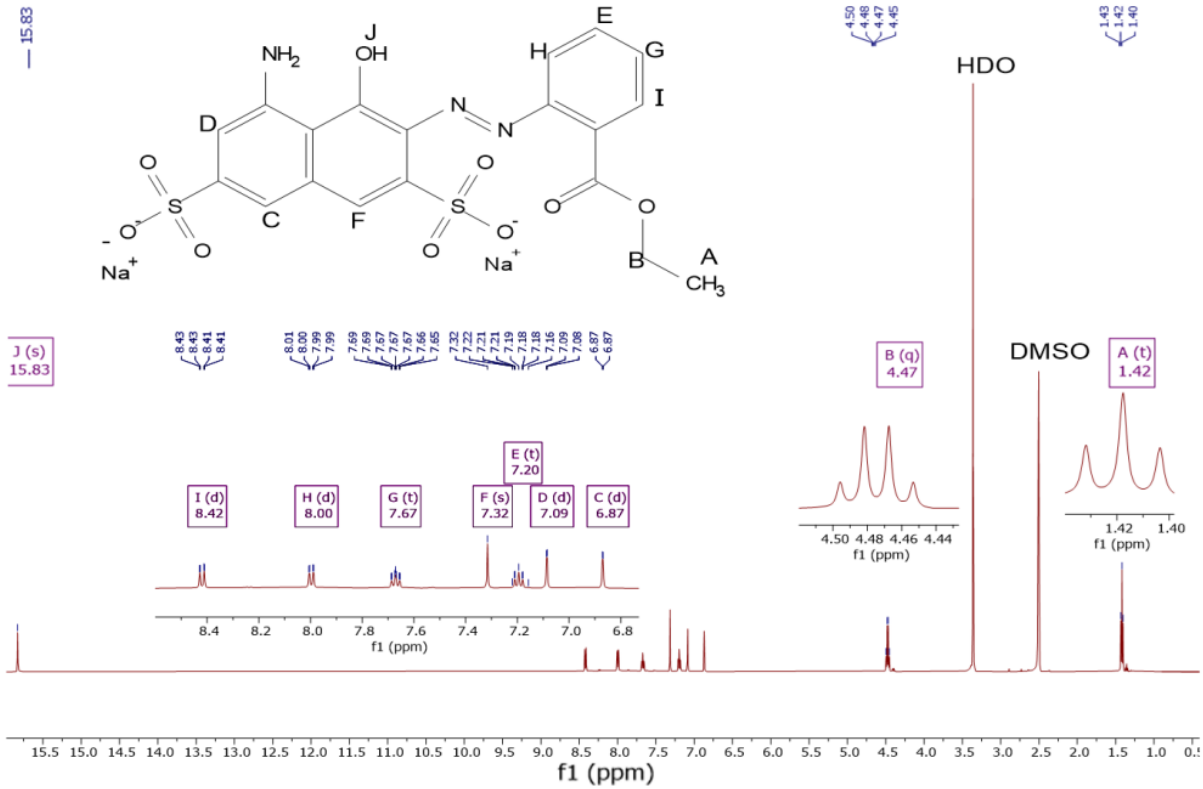


Figure 4: ^{1}HNMR spectrum of acid dye.

Figure 5 shows the ^{13}C NMR spectrum of the acid dye. A peak at 14.69 ppm due to methyl and a peak at 61.70 ppm due to methylene were obtained. Various peaks due to aromatic carbon atoms were observed in the region of 112.04 to 154.02 ppm. The Carbonyl group showed a peak at 181.69 ppm. The summary of all carbons is mentioned below.

^{13}C NMR (126 MHz, DMSO-d6, ppm): δ =14.69 (1C, CH_3), 61.70 (1C, OCH_2), 112.04 (1C), 113.10 (1C), 114.22 (1C), 114.89 (1C), 117.72 (1C), 123.46 (1C), 124.55 (1C), 130.21 (1C), 130.89 (1C), 131.13 (1C), 134.99 (1C), 136.74 (1C), 143.37 (1C), 145.13 (1C), 153.86 (1C), 154.02 (1C), 181.69 (1C, C=O)

Thus,^{1}H NMR and ^{13}C NMR analysis confirmed the chemical structure of the dye.

Elemental composition, molecular formula, and coupling reaction yield are recorded in Table 1. The values calculated on the theoretical formula are indicated by the subscript "cal," and the values obtained from the CHN analyzer are indicated as "Ob". Both values were very close, which confirmed the molecular formula of the synthesized dye. The coupling reaction yield of more than 80 % was obtained. The molecular formula of the dye was obtained as $C_{19}H_{15}N_3O_9S_2Na_2$.

The aqueous solutions of the dye in various concentrations (5, 10, 20 and 30 mg/L) were used to evaluate the UV-vis characteristic. Two peaks were obtained in the scanned region (Figure 6 (A)). The peaks at 528 and 237 nm were obtained. The calibration of absorbance with the concentration of dye (mg/L) at 528 nm is recorded in Figure 6(B). The slope of absorbance vs. concentration gives the extinction coefficient of the dye [34]. The extinction coefficient of the dye was found as 47.5 L g^{-1} cm^{-1} (25,623.73 L mol^{-1} cm^{-1}).

Table 1: Elemental analysis, molecular formula, and coupling reaction yield.

Molecular formula	Yield (%)	C_{cal} (%) /C_{ob} (%)	H_{cal} (%) /H_{ob} (%)	N_{cal} (%) /N_{ob} (%)
$C_{19}H_{15}N_3O_9S_2Na_2$	80.13	42.30/42.10	2.80/2.41	7.79/7.63

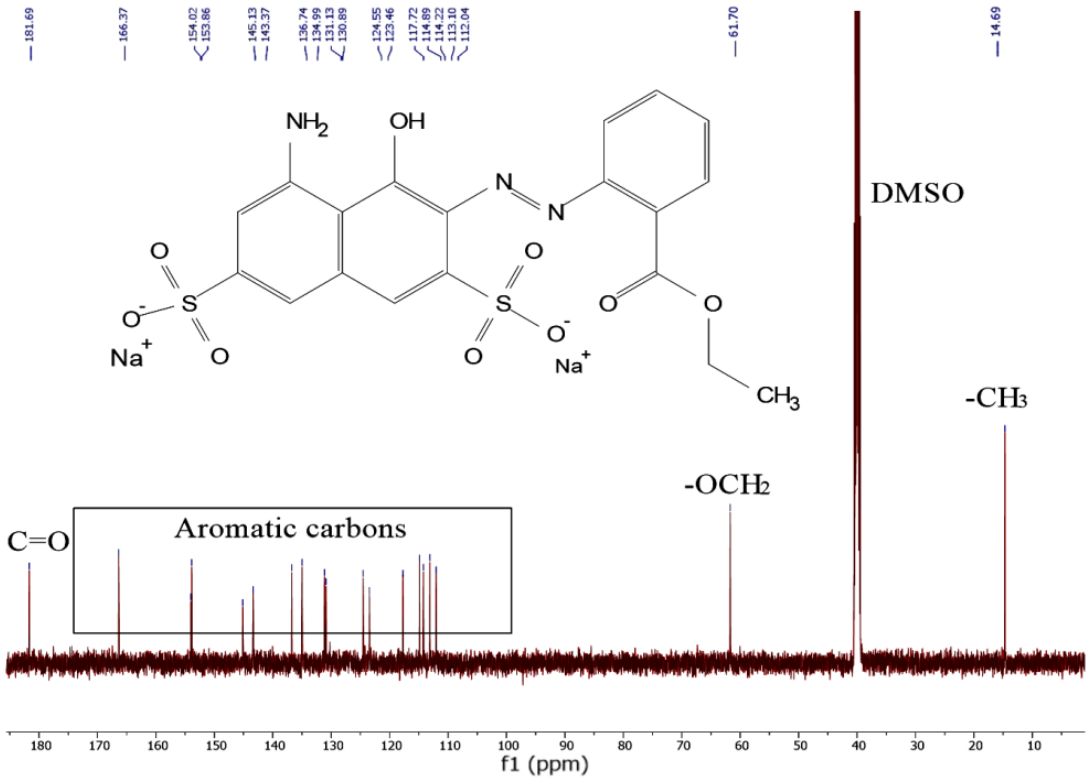


Figure 5: ^{13}C NMR spectrum of acid dye.

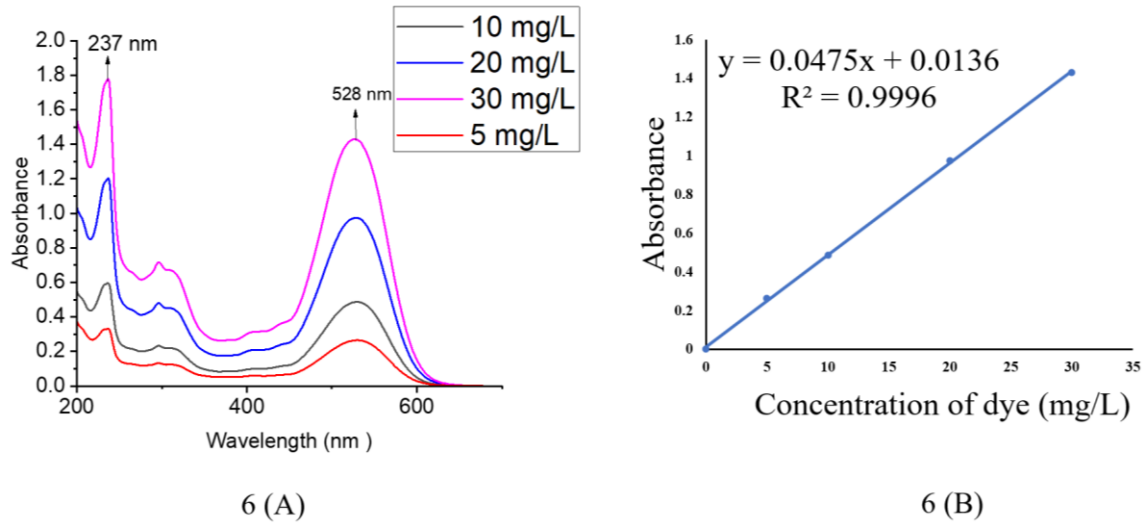


Figure 6: (A): UV-Vis spectra of dye and (B): Calibration plot of the dye.

3.2 Color values, color strength, exhaustion, and fixation values

Table 2 shows the color values and appearance of dyed fabrics. L* values were in the range of 29 to 46. The a* values varied from 28 to 46, while the b* values varied from -4 to -11. Colour appearance also suggested the increased darkness in the shade with an increasing amount of dye on the fabric. The colour strength (K/S) values of more than 4 were obtained. A gradual improvement in colour strength (K/S) with increasing shade (%) of dye on fabric was also observed, confirming the presence of a higher quantity of acid dye with increasing shade (%) (Figure 7).

Table 2: Colour values and appearance of the dyed nylon

Sample name	Colour values$			Colour appearance
	L*	a*	b*	
0.1 % shade	46.551	28.042	-4.795	
0.5 % shade	44.107	46.115	-9.584	
1 % shade	38.376	39.781	-11.858	
1.5 % shade	35.784	37.168	-6.858	
2 % shade	36.680	41.835	-11.163	
2.5 % shade	29.209	29.146	-7.819	

$ Represents the average value of three determinations

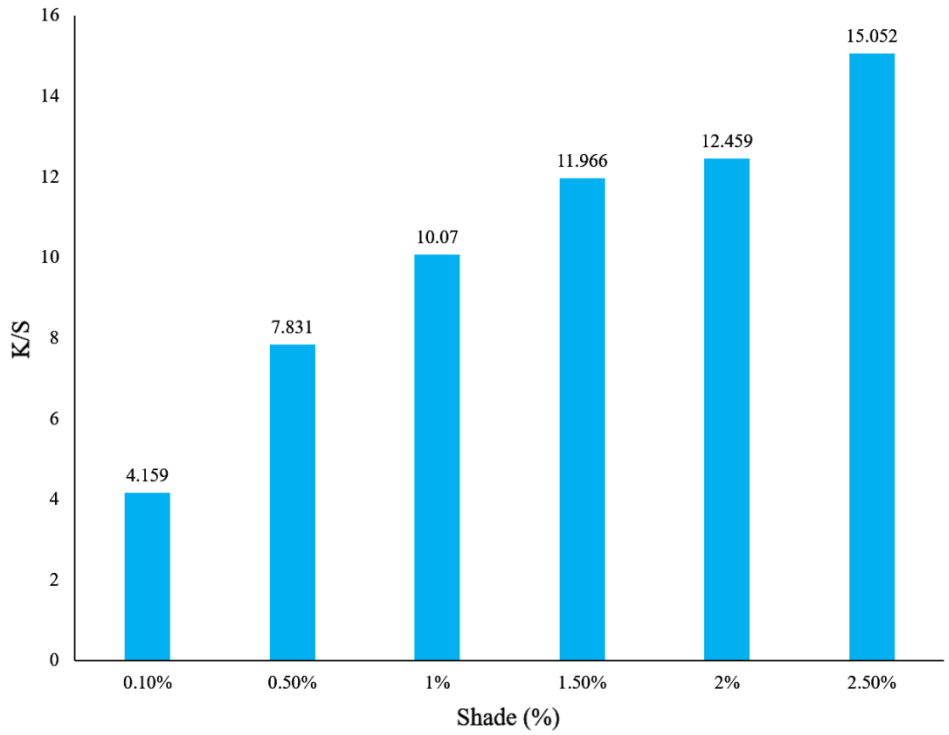


Figure 7: Build-up characteristic of the dye on nylon.

The exhaustion and fixation of dye on nylon and the fastness ratings of the dyed fabrics are recorded in Table 3. "Good" to "excellent" washing and rubbing fastness ratings were obtained. Light fastness ratings were in the range of 5 to 6. Perspiration fastness of dyed fabric, in both acidic and alkaline perspirations, was found in the range of 4 to 5. In some cases, the rubbing and washing fastness ratings of fabrics dyed in darker shades were lower than those dyed in lighter shades (%), and such outcomes are well established in the literature [35, 36]. The concentration of dye molecules is higher in darker shades, and the

possibility of loosely held dye molecules is also greater. This can result in dye bleeding from dyed fabrics during washing and abrasive rubbing resulting in lower fastness ratings. However, the fastness of such darker fabrics was in the range of "good" to "very good." Moreover, in darker shades, the light fastness of dyed fabrics was improved.

More than 62 % exhaustion (%) and fixation (%) were observed. A gradual decrease in exhaustion and fixation was also seen by increasing the shade (%). Similarly, authors also reported the reduction of exhaustion with increasing shade (%) of disulfonated acid dye on silk [37]. At lower shade (%), the protonated amino sites of nylon were quickly occupied with the acid dye. With increasing shade (%), the availability of free cationic sites was reduced, which resulted in the reduction of exhaustion and fixation.

3.3. Dye-fiber interaction between acid dye and nylon

An acid dyeing was done at acidic pH of 3-4, and this condition generates $^{+}NH_3$ groups on nylon fiber. One molecule of the dye is expected to react with two end amino groups of the nylon. This is well established that acid dye interacts with nylon through ionic linkage. Moreover, satisfactory fastness ratings confirmed this phenomenon, and Figure 8 shows the expected interaction between the synthesized dye and nylon.

Table 3: Exhaustion and fixation of the dye on nylon and fastness ratings of dyed fabrics.

Sample name	Washing fastness	Rubbing fastness		Light fastness	Perspiration fastness		Exhaustion (%)$	Fixation (%)$
		Dry	Wet		Acid	Alkaline		
0.1 % shade	4-5	4	3-4	5	5	5	85.75	78.31
0.5 % shade	4-5	3-4	3-4	5	4-5	4-5	80.77	77.35
1 % shade	4	3-4	3-4	5-6	4-5	4-5	75.67	72.14
1.5 % shade	4	3-4	3	5-6	4	4	70.65	68.91
2 % shade	3-4	3	3	6	4	4	63.44	65.12
2.5 % shade	3-4	3	3	6	4	4	62.29	62.93

$ represents the average value of three determinations

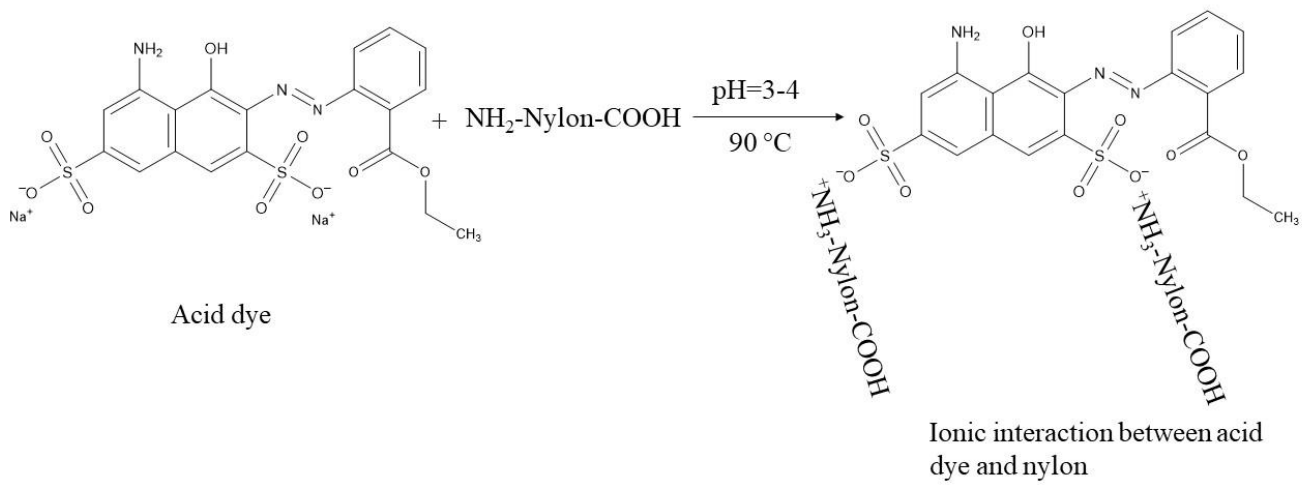


Figure 8: Ionic interaction of the acid dye with nylon.

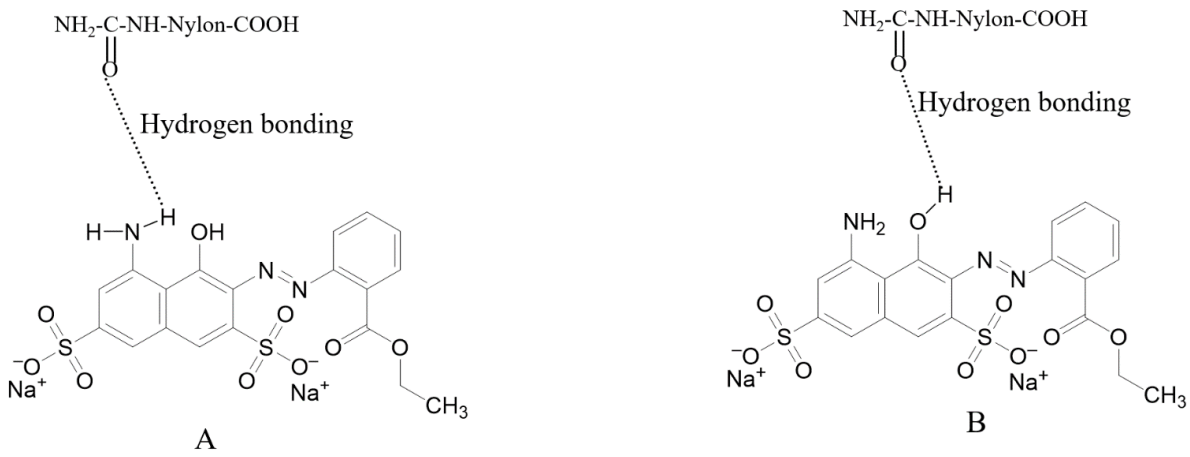


Figure 9: Hydrogen bonding of the dye to nylon.

Besides ionic bonding, the acid dye can also interact with the fiber by forming hydrogen bonds [38]. Figure 9 shows the possible mechanism of the interaction of the dye with nylon through hydrogen bonding. The amide group of the nylon can easily bond hydrogen with the dye's amino and hydroxyl groups.

3.4. Functional properties of dyed nylon

Table 4 indicates the mosquito repellency of dyed nylon. The dyed nylon showed 100 % repellent action at 0.1 % shade, and this was constantly retained with increasing % shade. The dyed fabrics also confirmed a wash-durable repellent action. The acid dye is a modified repellent molecule, making the nylon a mosquito-repellent substrate. Hence, the synthesized acid dye can be considered an efficient mosquito-repellent dye.

Figure 10 shows a transmittance and wavelength plot in the UV region (ultraviolet transmittance spectra). Undyed fabric showed higher transmittance values than dyed fabrics. The electronic transition property of the dye in the UV region caused the absorption of the UV rays, thus, preventing UV rays from passing through the fabric. UV protection values also supplemented the UV protection activity (Table 5). Undyed nylon showed a UPF value of 13.77, which indicates a "poor" UV protection rating. A lower amount of dye on the fabric (0.1 % shade) was sufficient to provide an excellent UPF rating (UPF value of 44.69). Such fabric, after 20 washes, retained an excellent UPF rating. Due to an efficient UV absorption of the dye, the UV protection activity was imparted to the dyed nylon. The absorption of the UV rays is directly proportional to the amount of the dye on the fabric; thus, the UPF values increased with increasing shade (%). With the washing treatments, some dye molecules get washed away from the fabric, reducing the UPF value. However, the UPF ratings were excellent even after 20 washes. Hence, the acid dye provided wash-durable and excellent UV protection to the nylon fabric.

Table 4: Mosquito-repellent efficacy of dyed nylon fabrics.

Sample name	Mosquito repellency (%)[$]
0.1 % shade	100
0.5 % shade	100
1 % shade	100
1.5 % shade	100
2 % shade	100
2.5 % shade	100
2.5 % shade after 20 washes	100

$ Represents the average value of three determinations

Table 5: UV protection activity of nylon fabrics.

Sample name	UPF value[$]	Rating
Undyed nylon	13.77	Poor
0.1 % shade	44.69	Excellent
0.5 % shade	71.72	Excellent
0.5 % shade after 20 washes	49.27	Excellent

$ Represents the average value of three determinations

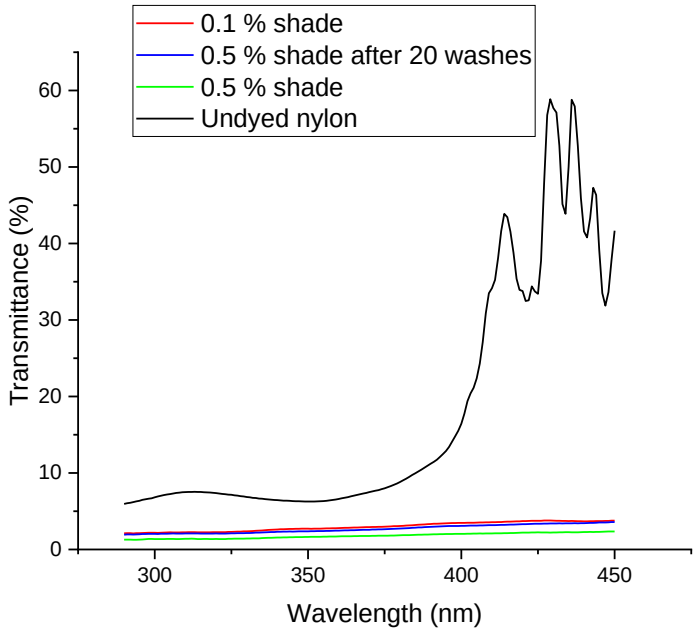


Figure 10: Ultraviolet transmittance spectra of fabrics.

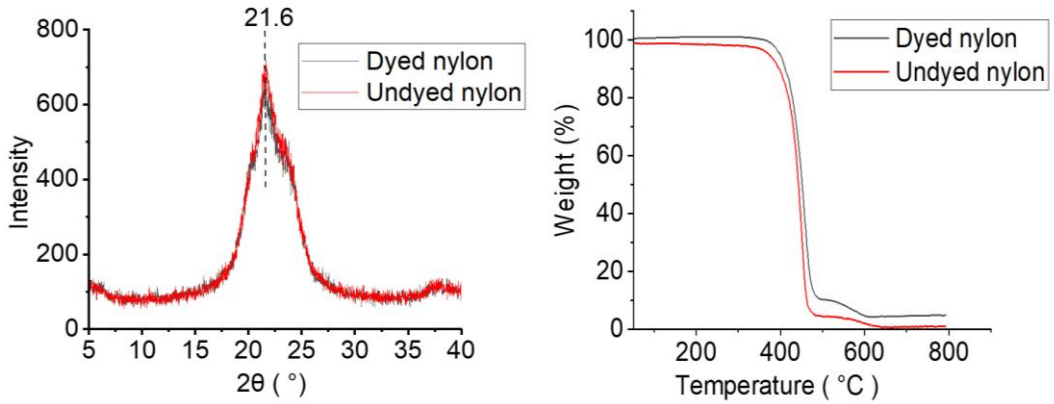
3.5. Characterization of dyed nylon

Figure 11 (A) indicates the XRD patterns of undyed and dyed nylon. Diffractograms of undyed and dyed nylon showed a similar pattern with no significant changes. A semicrystalline nature was observed for the nylon fabrics due to the presence of γ -a form of crystals. It appeared in Figure 11(A) at 2θ (theta) of 21.6. Similar outcomes were also documented in the literature [39-41]. Thermal gravimetric analysis (TGA) of the undyed and dyed nylon is recorded in Figure 11 (B). Insignificant differences in thermal behavior were observed for dyed and undyed nylon. Main weight loss was obtained at 400-600 °C; similar results were also found in the literature [42, 43].

Table 6 indicates the various weight loss temperatures; for example, T_{10} represents the temperature at 10 % weight loss. Dyed nylon showed insignificantly higher thermal stability than undyed nylon; however, the residues obtained at 800 °C for undyed nylon and dyed nylon were 1.2 and 5 %, respectively.

Table 6: Thermal data obtained from TGA thermograms of nylon.

Sample name	T10 (°C)	T25 (°C)	T50 (°C)	T75 (°C)
Undyed nylon	394	433	442	454
Dyed nylon	410	425	452	465



11 (A) 11 (B)

Figure 11: (A): XRD and (B): TGA analysis of undyed and dyed nylon.

4. Conclusions

Novel acid dye was prepared by coupling reaction of diazotized ethyl 2-aminobenzoate and H-acid. FTIR, ^{1}H NMR,^{13}C NMR, CHN analysis, and UV-Vis spectroscopy confirmed the successful synthesis of the acid dye. The dyed nylon demonstrated satisfactory fastness, 100 % mosquito repellency, and excellent UV protection. Characterizations of dyed fabric suggested no significant changes occurred in the backbone of nylon due to the dyeing with the synthesized dye. The obtained results indicated the development of wash-durable functional nylon, which can be efficiently utilized to manufacture mosquito-repellent and UV-protective garments. Hence, the novel acid dye demonstrated interesting results that can be utilized to protect humankind from mosquitoes and UV rays.

5. References

1. A. G. Rodrigues, P. J. Romano de Oliveira Gonçalves, C. A. Ottoni, R. de Cássia Ruiz, M. A. Morgano, W. L. de Araújo, I. S. de Melo, A. O. De Souza, Functional textiles impregnated with biogenic silver nanoparticles from Bionectria ochroleuca and its antimicrobial activity, *Biomed. Microdevices*., 21(2019), 56.
2. Q. Qiu, S. Chen, Y. Li, Y. Yang, H. Zhang, Z. Quan, X. Qin, R. Wang, J. Yu, Functional nanofibers embedded into textiles for durable antibacterial properties, *Chem. Eng. J.*, 384(2020), 123241.
3. A. Bashari, A. H. S. Koohestani, N. Salamatipour, Eco-friendly dual-functional textiles: green water-repellent & anti-bacterial, *Fibers Polym.*, 21(2020), 317-323..
4. A. Asar, M. S. Irfan, K. A. Khan, W. Zaki, R. Umer, Self-sensing shape memory polymer composites reinforced with functional textiles, *Compos. Sci. Technol.*, 221(2022), 109219.
5. M. Gupta, J. Sheikh, Annu, A. Singh, An eco-friendly route to develop cellulose-based multifunctional finished linen fabric using ZnO NPs and CS network, *J. Ind. Eng. Chem*., 97(2021), 383-389.
6. A. Singh, J. Sheikh, Cleaner functional dyeing of wool using Kigelia Africana natural dye and Terminalia chebula bio-mordant, *Sustain. Chem. Pharm*., 17(2020), 100286.
7. A. Singh, J. Sheikh, Development of mosquito repellent, antibacterial, Antioxidant and UV protective cotton using a novel method of azoic dyeing with terminalia chebula, *J. Nat. Fibers.*, 19(2021), 1-14.
8. A. Singh, J. Sheikh, Development of multifunctional polyester using disperse dyes based through a combination of mosquito repellents, *J. Mol. Struct.*, 1232(2021), 129988. h
9. S. Tambi, A. Mangal, N. Singh, J. Sheikh, Cleaner production of dyed and functional polyester using natural dyes vis-a-vis exploration of secondary shades, *Prog. Color. Color. Coatings.*, 14(2021), 121-128.
10. V. Selvaraj, T. Swarna Karthika, C. Mansiya, M. Alagar, An over review on recently developed techniques, mechanisms and intermediate involved in

the advanced azo dye degradation for industrial applications, *J. Mol. Struct.*, 1224(2021), 129195.
11. A. Pielesz, The process of the reduction of azo dyes used in dyeing textiles on the basis of infrared spectroscopy analysis, *J. Mol. Struct.*, 511-512 (1999), 337-344.
12. F. Eyduran, N. Süleymanoğlu, R. Ustabaş, Synthesis, spectroscopic and computational investigation of N1,N4-bis(3-oxobutanoyl)benzene-1,4-dicarbohydrazide as a coupling component for azo dyes from waste poly(ethyleneterephthalate) bottle, *J. Mol. Struct.*, 1244(2021), 130985.
13. H. Shaki, A. Khosravi, K. Gharanjig, Novel cationic dye based on naphthalimide: Part 1: Synthesis, characterization and evaluation of biology efficacy as antimicrobial agent, *Prog. Color. Colorant Coatings.*, 9(2016), 261-268.
14. A. Mohammadi, H. Ghafoori, M. Rassa, Aryl azo 5-arylidene-2,4-thiazolidinone dyes as novel antioxidant and antibacterial compounds, *Prog. Color. Colorant Coat.*, 8(2015), 145–152.
15. A. Mohammadi, H. Ghafoori, Naphthalene-based azo dyes: Synthesis, characterization and dyeing performance on polyester fibers, *Prog. Color Colorant Coat.*, 8(2015), 317-327.
16. K. Gharanjig, F. Ameri, F. S. Dadras, A. Khosravi, Novel naphthalimide based azo disperse dyes for dyeing of polyester fabrics, *Prog. Color Colorant Coat.*, 4(2011), 27-37.
17. A. Khosravi, S. Moradian, K. Gharanjig, F.A. Taromi, Synthesis and spectroscopic studies of some naphthalimide based disperse azo dyestuffs for the dyeing of polyester fibres, *Dyes Pigm.*, 69(2006), 79-92.
18. S. Bait, S. Shinde, R. Adivarekar, N. Sekar, Multifunctional properties of benzophenone based acid dyes: Synthesis, spectral properties and computational study, *Dyes Pigm.*, 180(2020), 108420.
19. P. Cowper, A. Pockett, G. Kociok-Köhn, P.J. Cameron, S.E. Lewis, Azulene – Thiophene – Cyanoacrylic acid dyes with donor-π-acceptor structures. Synthesis, characterisation and evaluation in dye-sensitized solar cells, *Tetrahedron*, 74(2018), 2775-2786.
20. J. Sun, H. Wang, C. Zheng, G. Wang, Synthesis of some surfactant-type acid dyes and their low-temperature dyeing properties on wool fiber, *J. Clean. Prod.*, 218(2019), 284-293.
21. K. Blus, Synthesis and properties of disazo acid dyes, *Dyes Pigm.*, 43(1999), 183-188.
22. A. M. Api, D. Belsito, S. Bhatia, M. Bruze, P. Calow, M.L. Dagli, W. Dekant, A.D. Fryer, L. Kromidas, S. La Cava, J.F. Lalko, A. Lapczynski, D.C. Liebler, Y. Miyachi, V.T. Politano, G. Ritacco, D. Salvito, J. Shen, T.W. Schultz, I.G. Sipes, B. Wall, D.K. Wilcox, RIFM fragrance ingredient safety assessment, ethyl anthranilate, CAS registry number 87-25-2, *Food Chem. Toxicol.*, 82(2015), 97-104.
23. J. Islam, K. Zaman, S. Chakrabarti, P. Chattopadhyay, Exploration of toxicological impacts following acute and sub-chronic exposure to ethyl anthranilate-loaded mosquito repellent patch, *Regul. Toxicol. Pharmacol.*, 97(2018), 209-224.
24. Z. Ruizhen, W. Rulin, Z. Lianshun, Z. Yating, W. Lizhi, Z. Fei, H. Babar, X. Yijuan, Toxicity and repellency of two anthranilates against Aedes albopictus Skuse (Diptera: Culicidae), *Acta Trop*., 200(2019), 105171.
25. J. Islam, K. Zaman, V. Tyagi, S. Duaraha, S.Dhiman, P. Chattopadhyay, Protection against mosquito vectors Aedes aegypti, Anopheles stephensi and Culex quinquefasciatus using a novel insect repellent, ethyl anthranilate, *Acta Trop.*, 174(2017), 56-63.
26. A. Afify , B. Horlacher, J. Roller ,C.G Galizia ,, Different repellents for Aedes aegypti against blood-feeding and oviposition, *PLoS One*., 9(2014), e103765.
27. M. D. Teli, P. P. Chavan, Synthesis of reactive dye to impart mosquito repellency to nylon, *J. Text. Inst*., 108(2017), 226-232.
28. M. D. Teli, P. P. Chavan, Dyeing of cotton fabric for improved mosquito repellency, *J. Text. Inst.*, 109(2018), 427-434.
29. A. Singh, J. Sheikh, Synthesis and application of a novel cold brand reactive dye to impart colouration, mosquito repellency, and UV protection to nylon, *Arab. J. Chem*., 15(2022), 104339.
30. ISO manual 2006. ISO Technical manual ,Geneva, switerzland. (2006).
31. AS/NZS,4399.1996-AS/NZS 4399.Sun protective clothing evaluation and classification. (1996)
32. AATCC technical manual 2007. Association of Textile Chemists and Colorists; AATCC technical manual.Research Triangle Park. (2007).
33. R. M .Silverstein, R. M., G. C. Bassler,T. C. Morrill. Spectrometric Identification of Organic Compounds. 3rd ed. New York: John Wiley & Sons. (1974).
34. A. N. M. A. Haque, M. A. Islam, The contribution of different vinyl sulphone-reactive dyes to an effluent, *J. Taibah Univ. Sci.*, 9(2015), 594-600.
35. M. Rahman, A.K.M. A.H Asif, Md. A. B. Siddiquee, M.d. Rokonuzzaman, Effect of shade percentage on various properties of cotton knitted fabric dyed with reactive dyes, *Int. J. Res. Eng. Technol.*, 03(2014), 339-343.
36. S. M. Burkinshaw, O. Kabambe, Attempts to reduce water and chemical usage in the removal of bifunctional reactive dyes from cotton: Part 2 bis(vinyl sulfone), aminochlorotriazine/vinyl sulfone and bis(aminochlorotriazine/vinyl sulfone) dyes, *Dyes Pigm.*, 88(2011), 220-229.
37. Y. Wang, B. Tang, W. Ma, S. Zhang, Synthesis and UV-protective properties of monoazo acid dyes based on 2-hydroxy-4-methoxybenzophenone, *Procedia Eng.*, 18(2011), 162-167.

38. N. J. Bhatt, E. H. Daruwalla, Studies in the mechanism of dyeing of polyamide fibers with acid dyes, *Textile Res. J.*, 34(1964), 435-444
39. T. M. Ting, M. M. Nasef, K. Hashim, Modification of nylon-6 fibres by radiation-induced graft polymerisation of vinylbenzyl chloride, *Radiat. Phys. Chem.*, 109(2015), 54-62.
40. H. R. Pant, W. Il Baek, K.T. Nam, I.S. Jeong, N.A.M. Barakat, H.Y. Kim, Effect of lactic acid on polymer crystallization chain conformation and fiber morphology in an electrospun nylon-6 mat, *Polymer.*, 52(2011), 4851-4856.
41. C. B. Giller, D. B. Chase, J.F. Rabolt, C. M. Snively, Effect of solvent evaporation rate on the crystalline state of electrospun Nylon 6, *Polymer.*, 51(2010), 4225-4230.
42. S. Pashaei, Siddaramaiah, M. M. Avval, A. A. Syed, Thermal degradation kinetics of nylon6/gf/crysnano nanoclay nanocomposites by TGA, *Chem. Ind. Chem. Eng. Q.*, 17(2011), 141-151.
43. K. Liu, Y. Li, L. Tao, R. Xiao, Preparation and characterization of polyamide 6 fibre based on a phosphorus-containing flame retardant, *RSC Adv.*, 8(2018), 9261-9271.

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