iLetters An Open Access Journal of Innovations

Original Article - RC (Research Complete)

Green approach to the creation of naturally dyed nylon and polyester with antimicrobial properties

Anjali Agrawal[1*], Deepali Rastogi[2]

[1] *Department of Textile Design, National Institute of Fashion Technology, Kolkata*

[2] *Department of Fabric and Apparel Science, Lady Irwin College, University of Delhi*

Received: 20 March 2023; Revised: 2 May 2023; Accepted: 27 May 2023; Available online: 09 June 2023

Abstract:

The recent pandemic has increased the interest in discovery of new health and hygiene-related products. The growth of synthetic fabrics like nylon and polyester has been propelled over the last years, because of their excellent strength and resiliency. At the same time, the demand for natural colourants for the dyeing of these fabrics is gradually increasing due to a greater emphasis on a cleaner and greener production process. The dyeing of nylon and polyester with Ratanjot (Arnebia nobilis), a natural dye, is a novel process that has been extensively studied in this article. The dyeing of systhetic fabrics with Ratanjot was conducted without using hazardous metallic mordants. The dyeing performance was investigated in terms of depth of shade and colour fastness. The antimicrobial properties of dyes fabrics were also studied. The findings suggested that dyeing polyester and nylon with Ratanjot dye gives a good depth of shade even without any metallic mordants. At the same time, it is a promising approach to get excellent antimicrobial activity, thus opening up the avenue for green dyeing and medical textiles.

Keywords: Green, nylon, polyester, natural dyes, antimicrobial, Ratanjot, Naphthoquinones

1.0 Research Gap addressed:

- The naphthoquinones present in Ratanjot are responsible for colour and therapeutic efficacy. However, there are limited dyeing studies with the crude dye extracted from Ratanjot. This study presents an in-depth understanding of the behaviour of the dye extracted from Ratanjot at different pH and temperature and its affinity towards synthetic textile substrates viz. nylon and polyester.
- Mostly metallic mordants are used to increase the affinity of natural dyes for fabric. This study proposes a green process, without using hazardous metallic mordants.
- Despite the therapeutic properties of Ratanjot, the dyed textile substrates have not been fully exploited with respect to their bioactive potential. This paper assesses the antimicrobial property of dyed synthetic fabrics.

2.0 Key Findings:

- The dye solution showed the maximum absorption wavelength (λ_{max}) at 526 nm at pH 3 - 8. With the increase in pH, the λ_{max} shifted to 618 nm and the colour changed from red to dark blue. Because of this pH sensitivity of the dye, the liquor used for subsequent dyeing studies was buffered and colourimetric estimations were conducted at 526 nm.
- The dye extracted from Ratanjot was found to be the most stable at pH 4.5 at temperature 70^0 - 80^0C.
- The dye was applied under different pH values to study the effect of pH on dye uptake. Nylon was found to have K/S of 2.1 and Polyester of 2.57 when dyed at 80^0C and 130^0C respectively.
- Ratanjot dyed nylon sample in blue colour whereas polyester fabric showed pink colour.
- Nylon and polyester dyed with 0.5% and 5% dye, didn't show any zone of inhibition against bacteria. Ratanjot dyed polyester showed 100% activity against *S. aureus* and 80% activity against *E. coli* at 5% shade, whereas no activity was observed at 0.5% shade. Nylon showed no antimicrobial activity at both the concentrations.
-

3.0 Method /Experiments

1. Extraction of Dye

Roots of *A. nobilis* were ground to a coarse powder and extracted with *n*-Hexane in soxhlet apparatus at 50°C till the entire colour was extracted. A deep red viscous residue amounting to about 5% on the dry weight basis of roots was obtained after evaporation of the solvent.

2. Effect of pH on Colour Value

The effect of pH on the colour value of the dye was determined by recording the visible spectra of the dye solution at different pH values ranging from 3 to 12. Sodium acetate and acetic acid buffer was used to maintain pH in the range of 3-7 while glycine and sodium hydroxide buffer was used to maintain pH in the range of 8-12. Spectra were recorded on Lambda 25 (Perkin Elmer, US).

3. Effect of Temperature on Dye Stability

A dye bath containing a dye solution having 0.05 g/L dye was prepared from the stock solution (0.2 %) in 20 mL water. Sodium lauryl sulphate (SLS) (1 g/L) was also added to the dye bath. The dyebath was heated continuously in a high-temperature high-pressure (HTHP) beaker dyeing machine (R. B. Electronic and Engg. Private Ltd, India) at temperatures ranging from 70°C to 130°C for 60 min at pH 4.5, 7 and 10 (selected based on the effect of pH on dye extract as shown in Fig. 1). The absorption spectra were recorded before and after the treatment.

4.Dyeing of Textile Substrates*:* Fabrics were dyed at pH 4.5, 7 (adjusted with sodium acetate and acetic acid buffer) and 10 (adjusted with glycine and sodium hydroxide buffer). The substrates were dyed with 0.5 % shade (owf) for 60 mins. The dyebath also contained 1 g/L sodium lauryl sulphate (SLS) as dispersing agent and liquor-to-goods ratio was maintained at 30:1. Polyester was dyed at 130°C. Nylon was dyed at 80°C. The dyed samples were then cold rinsed and soaped. The depth of shade was determined in terms of *K/S* values.

5. Fastness tests: For assessing the fastness to light, wash, rub and perspiration, fabrics were dyed at pH 4.5 with 0.5 % (owf) shade. Light fastness was assessed in accordance with AATCC 16: 2004 on Xenotest alpha high energy light fastness tester. Fastness to washing was assessed in launder-O-meter in accordance with the method prescribed in IS 3361:1984 (ISO–II); rubbing on a crockmeter as per AATCC 8: 2007; and perspiration on a perspirometer in accordance with the method prescribed in AATCC 15: 2007.

6. Assessment of the antimicrobial activity: Qualitative assessment of the dyed fabrics for their antimicrobial activity was done using AATCC 30. The samples were tested against both Gram positive and Gram negative bacteria. Undyed samples were taken as a positive control. A quantitative assessment was conducted by colony counting method. Samples were dyed with 0.5% and 5% owf dye. Dyed sample swatches were exposed to 20µl of bacterial inoculums containing 10 cfu/ml of bacteria using the modified agar-plate method. After incubation, the bacterial colonies were counted and BR% was calculated.

4.0 Results & Discussion

1. Effect of pH on colour uptake

The absorbance value was low (0.78) at pH 3-6, according to the visible spectra of the dye solution at various pH levels (Fig. 1). The hue of the solution deepened from neutral to alkaline conditions (pH 7-12), as seen by an increase in absorbance value (0.95). This may be due to the limited solubility of the naphthoquinone dyes, which are non-polar in nature in acidic environments. The hydroxyl group is ionised in the pH range of 7-12, which results in greater solubility and, consequently, an increase in absorbance value.

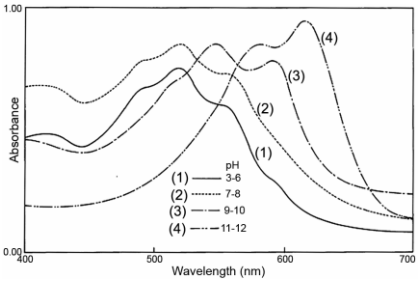

Fig 1: Effect of pH on dye extract

The dye solution exhibited λ_{max} at 526 nm in the pH range of 3 to 8 (Fig. 1), and there is no shifting in the λ_{max} value. However, as the pH of the dye solution rises, the electron donor groups imposed a significant bathochromic shift (red end), resulting in a λ_{max} of 574 nm. Additionally, the dye solution's colour gradually shifts from red to purple. The colour of the dye solution changes to

dark blue with a λ_{max} at 618 nm as the pH is raised to 12. According to Indrayan et. al. (2004), the active coloured ingredient in *Arnebia nobilis* is present in a quinonoid form in an acidic medium. In an alkaline medium, the phenolic proton of the quinonoid form gets dissociated from the naphthoquinone nucleus and is converted to a benzenoid form which is responsible for the blue colour.

2. Effect of temperature on dye stability

The thermal stability of the dye was studied by recording the absorbance spectra of the dye solution before and after heating.

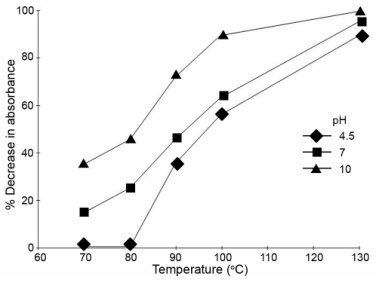

Fig 2: Effect of temperature on dye stability

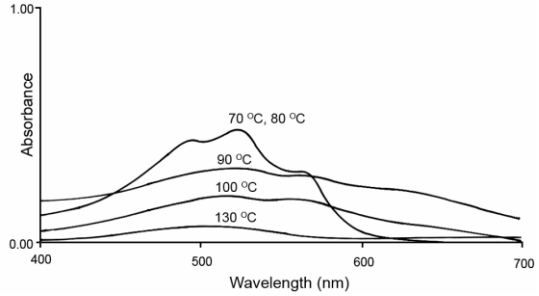

Fig 3: Spectra of dye at pH 4.5

When the dye solutions at different pH (4.5, 7 and 10) were subjected to various temperature treatments from 70°C to 130°C, it was found that the dye is most stable under pH 4.5 at 70°C and 80℃. On the other hand, an appreciable decrease in absorbance was observed for the dye solutions having pH 7 and 10 at temperature ≥ 80℃ (Fig. 2). At 130°C, there is almost 90 % loss in colour of the dye solution at pH 4.5, and ~ 95 % and 100 % loss in colour at pH 7 and 10 respectively. This may be due to the decomposition of the dye molecule to give colourless products at higher temperature.

To ascertain that the dye has decomposed at a higher temperature and does not modify into a different chromophore (as is observed at alkaline pH), the λ_{max} was determined after treating the dye solution at higher temperatures at a particular pH. It was observed that λ_{max} of the dye remained the same at various temperatures (Fig. 3), although the absorbance decreased with the increase in temperature. Moreover, no new peaks were observed, thus confirming that the dye decomposed and did not convert into a different chromophore when exposed to a higher temperature.

3. Dyeing of nylon and polyester with dye extracted from Ratanjot

Affinity of the dye extracted from *A. nobilis* towards nylon and polyster was studied. The dye was applied under different pH values to study the effect of pH on dye uptake (measured in terms of *K/S*) and the results are summarised in Table 1. It was found that the dye uptake decreased with increasing pH of application. This may be because the dye decomposed at pH 7 and 10 (Fig. 3). Substrates dyed at pH 4.5 yielded the highest *K/S* values.

An experiment was conducted to determine the reason of obtaining different colours on nylon and polyester under the same dyeing conditions. One set of dyed nylon was treated for 60 minutes at 90°C with a 30% w/v H_2O_2 solution, while the second set of fabric was treated for 20 minutes at 80°C with a solution comprising 2 g/L sodium dithionite and 2 g/L sodium hydroxide. After being treated with sodium dithionite and sodium hydroxide solution, nylon remained blue, but the hue intensified. The samples turned pink after the H_2O_2 treatment, indicating that the dye had oxidised on these substrates. These oxidised samples once more turned blue when they were exposed to sodium hydroxide and sodium hydrosulphite. Thus, this confirmed that the dye gets reduced in nylon.

Table 1: Colorimetric data showing the effect of pH

Fabric	pH	L*	a*	b*	C*	h^0	K/S
Nylon	4.5	53.06	4.61	-13.2	13.98	289.24	2.1
	7	56.78	5.32	-11.87	13.01	294.12	1.6
	10	64.39	5.22	-9.76	11.07	298.12	0.81
Polyester	4.5	53.2	18.76	-3.87	19.16	348.35	2.15
	7	55.19	3.69	-4.9	6.13	306.94	1.4
	10	60.56	3.31	-3.55	4.86	313.02	0.97

This may be because the quinonoid form of the dye gets converted to benzenoid form (reduced form) (Fig. 4).

Polyester fabric was also treated with sodium dithionite and sodium hydroxide and it was found that the colour of the sample remained pink. It seemed that the dye stabilized in the quinonoid form in the compact structure of polyester and hence is not available for reduction.

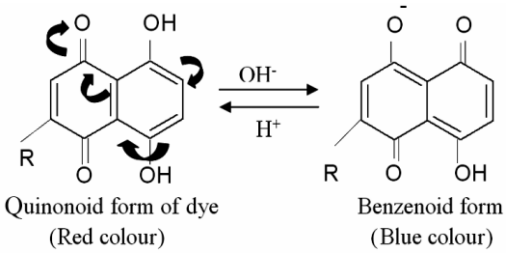

Fig 4: Potential conversion

4. Assessment of fastness activity

The dyed samples exhibited poor light fastness with rating of 1-2. The wash fastness rating of dyed nylon and polyester was 4/5 – 5 The fabrics exhibited excellent colour fastness to rubbing and perspiration with the rating of 4/5 - 5. It is interesting to note that though the dye exhibits acute sensitivity to different pH solutions, there is no change in hue of the dyed fabrics in the acidic and alkaline perspiration solutions.

5. Assessment of antimicrobial property

Table 1: Bacteria reduction percentage of Ratanjot dyed fabrics

Substrate	Bacteria reduction %			
	E. coli		*S. aureus*	
	0.5% shade	5% shade	0.5% shade	5% shade
Nylon	0	0	0	0
Polyester	0	80	0	100

With a ten-fold increase in dye concentration, the bactericidal property of dyed polyester increased from 0% to 100% reduction against S. aureus and 80% reduction against E. coli (Table 1). Inactive at both dye concentrations was nylon fabric. The chemical reactions between the dye and the fibre are responsible for this. Polyester, a nonpolar fibre that is hydrophobic, has a strong attraction for dye molecules that are also hydrophobic. It dissolves small dye molecules and holds them there due to hydrophobic forces of attraction. In the fibre, the molecules are unaltered and chemically free. Because it is an ionic fibre, nylon can react with dye. This is taking place in this instance, as shown by the fact that while the dye gives a pink colour on polyester, it gives a blue colour on nylon indicating that nylon may be reducing the dye.

5.0 Theoretical Background

With India's 2-3% share of global medical textile consumption, it is one of the fastest-growing segments in technical textiles market in India (Saha, C., 2019). The growing medical tourism, technological advancements, and ongoing pandemic are some of the factors expected to boost the

growth of the antimicrobial medical textiles market (Anonymous, 2021). Synthetic fibres like nylon and polyester possess high tenacity and have found applications in the field of medical textiles. One of the essential requirements becomes antimicrobial property. Although the studies report the usage of synthetic compounds to impart this property, there is a need for natural antimicrobial agents (Gulati et al., 2022).

The natural dyes have moved from back to front stage owing to the growing concern for the environment and green processes. The natural dyes are rich in phytochemicals, which provide distinctive functional finishing to the textiles (Kamboj et. al., 2021). Ratanjot, botanically referred to as *Arnebia nobilis* Rech.f., is a rich source of hydroxynaphthoquinones, commonly known as alkannin and shikonin. It is imported from Afghanistan and can be procured easily in the form of crude rootstocks and leafy bark in markets (Arora et. al., 2012). These naphthoquinones form the main active constituent of this plant and are responsible for its colour and therapeutic efficacy (Khatoon et. al., 2003). These are biologically extremely potent compounds with a well-established and wide spectrum of wound healing, antimicrobial, anti-inflammatory, antioxidant and anticancer properties (Spyros, et al., 2005; Akkol, et al., 2009). Despite the colour and therapeutic properties, the roots of *A. nobilis* have not been fully exploited regarding the dyeing of synthetic fabrics and their bioactive potential.

Author Contribution: DR is the supervisor

Conflict of Interest: N/A

References

Akkol, E.K., Koca, U., Pesin, I., Yilmazer, D., Toker, G., Yesilada, E., (2009) Exploring the wound healing activity of *Arnebia densiflora* (Nordm.) Ledeb. by in vivo models, Journal of Ethnopharmacology, 124, 137 - 141.

Anonymous (2021) Global Antimicrobial Medical Textiles Market Size by Fabric (Polyester, Polyamide, Cotton), by Application (Medical Textiles, Home Textiles, Apparel) by Geographic Scope and Forecast, Report ID 14421, available onlien at *(accessed on 9 June 2023)* https://www.verifiedmarketresearch.com/product/antimicrobial-medical-textiles-market/

Arora, A., Rastogi, D., Gupta, D. and Gulrajani, M.L. (2012) Dyeing parameters of hydroxynaphthoquinones extracted from *Arnebia nobilis* Rech.f , Indian Journal of Fibre and Textile Research, 37, 91 – 97.

Gulati, R., Sharma, S. and Sharma, R. K. (2022) Antimicrobial textile: recent developments and functional perspective, Polymer Bulletin, 79, 5747–5771.

Indrayan, A.K., Yadav, V., Kumar, R. and Tyagi, P.K. (2004) 'Isolation of the colourant from the roots of *Arnebia nobilis* and its use as a new neutralization indicator', Journal of Indian Chemical Society, 81, 717 – 720.

Kamboj, A., Jose, S. and Singh, A. (2021) Antimicrobial Activity of Natural Dyes – A comprehensive Review, Journal of Natural Fibres, https://doi.org/10.1080/15440478.2021.1875378

Saha, C. (2019) Medical Textiles- A beginning of new era, opens new vistas, Medical Textiles Market size, Share & Trend Analysis 2019-2025. Available online at https://www.textilesphere.com/2021/01/medical-textile.html *(accessed on 9 June 2023)*

Spyros, A., Assimopoulou, A.N., Papageorgiou, V.P., (2005) Structure determination of oligomeric alkannin and shikonin derivatives, Biomedical Chromatography, 19, 498- 505.