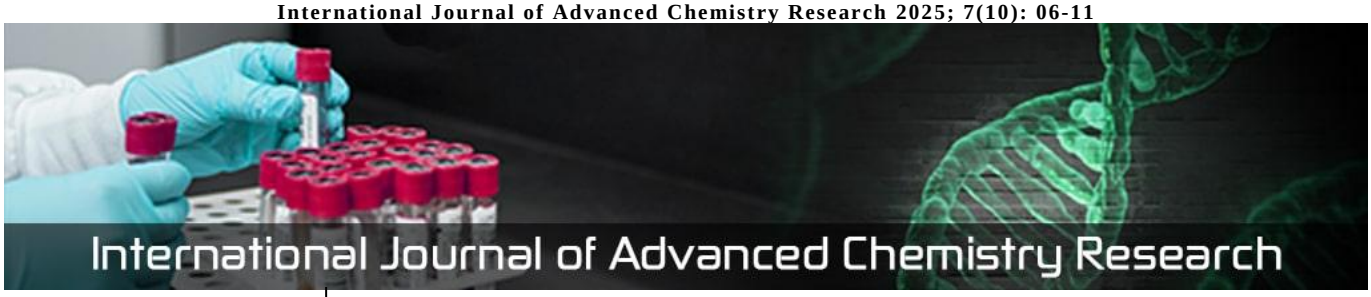

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Functionalization of silk fabric with madder dye and TiO_2 nanoparticles

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Abstract
The present study was carried out to assess the effect of TiO_2 nanoparticles treatment on functional (antibacterial and UV protection) properties of madder dyed silk fabric. The nanoparticle treatment was applied to degummed silk fabric using optimized concentrations and conditions and dyed simultaneously with selected madder dye through exhaust method in IR beaker dyeing machine. FE-SEM analysis of untreated dyed and nanotreated dyed fabric samples was done. FTIR of madder dye, untreated dyed and nanotreated dyed fabric samples were performed. The functional (ultra violet protection and antimicrobial) properties of treated dyed silk fabric samples were tested to analyze the effect of nano treatments on dyeing of silk fabric. Nanotreated dyed fabric showed 25.94 and 32.06 percent reduction in bacterial growth against *Staphylococcus aureus* and *Escherichia coli* and good (22.45%) UV protection.

Keywords: Antibacterial properties, madder dye, nanoparticle, silk, UV protection

1. Introduction
Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are obtained from plant sources such as roots, berries, bark, leaves, wood and other biological sources such as fungi. Natural dyeing presents an environmentally sustainable alternative to synthetic dyes, offering unique and vibrant colour outcomes while supporting the preservation of traditional dyeing practices. This method also minimizes the use of harmful chemicals, thereby reducing environmental pollution and contributing to ecological conservation. Whereas there are some disadvantages related to the application of natural dyes which reduced its applications i.e. poor colour fastness properties, poor reproducibility of shades, no standard colour recipes and methods available, use of metallic mordants for better dyeing, some of which are not eco-friendly [1]. The discovery of man-made synthetic dyes in the mid-19th century triggered a long decline in the large-scale market for natural dyes. In the early 21st century, the world is heading towards safer, less hazardous, recyclable technologies and the use of natural dyes for textile colouration can be a step towards minimal polluting textile processes and the market for natural dyes in the fashion industry is experienced a revival in market and for researcher [2].
Mordant is a substance which helps a chemical reaction to take place between the fibre and dye. During mordanting and dyeing process, attracts the dye and creates a coordinating bond and attaches the dye firmly to fibre matrix. Use of mordants in textile dyeing result in the generation of highly contaminated wastewater containing non-biodegradable and persistent substances, posing a threat to the environment and human health. As a result, researchers are now shifting their focus towards eco-friendly methodologies that enhance the colour characteristics of natural dyed textiles without causing environmental pollution [2]. Nanoparticles of metal oxide are progressively gaining global attention because it is widely perceived as offering vast potential in a broad array of end uses. Due increment in surface area of nano-sized particles attracted attention of scientists and research personnel to utilize nanoparticles for improving functional properties to various textile materials [3, 5].
Silk is a luxurious, natural protein fibre produced by silkworms that is renowned for its smooth texture, lustrous, and exceptional drape.

Widely used in high-end fashion and textiles, silk has been prized for centuries for its elegance and comfort, making it a timeless choice for both clothing and home decor. Silk, animal protein filament, comprising of two varieties of proteins: fibroin (70–80%) and sericin (20–30%). Fibroin, composed of amino acids constitutes the foundation of silk filament and is enclosed by sericin serving as an adhesive. Silk filament contains amino (-NH2) and carboxylic (-COOH) groups, at either extremity of its chemical composition, this combination makes it feasible to dye with natural, acidic, reactive and metal complex dyes. Silk is the most popular and upscale textile material due to its excellent performances such as good moisture absorbance, satisfactory mechanical properties and air permeability. However, silk proteins are nutrients for the growth and reproduction of microorganisms, which undoubtedly limit the application of silk in the medical textile field. Furthermore, the propagation of microorganisms on silk results in decrease in its aesthetic look and strength. Because of light and thin nature, silk fabric has high UV light transmittance, resulting in poor UV protection property.[5] Therefore, it is necessary to improve the antibacterial and UV protection properties of silk in order to make silk materials more attractive and broaden their application fields.

Hence, the present study was planned in order to use nanoparticles for imparting functional properties with the objective to evaluate the effect of colour strength of nanotreated dyed silk fabric.

2. Materials and Methods

2.1 Materials

- **Fabric:** The plain weave silk fabric, commonly used for apparel purpose was procured from the local market of Hisar, Haryana.
- **Enzyme:** For degumming of greige silk fabric, papain enzyme was procured from the Aum Enzymes, Ahmedabad, Gujarat, India.
- **Natural dye:** The natural dye obtained from root of madder (*Rubia cordifolia*) was taken for the study.
- **Nanoparticles:** The nanoparticles of TiO_2 were procured from Central Drug House (P) Ltd., New Delhi, India.

2.2 Method

2.2.1 Enzymatic degumming of silk fabric: To remove the gum and increase the absorbency of selected silk fabric and make the process eco-friendly, enzymatic degumming was carried out using papain enzyme. The enzymatic degumming bath was prepared using 3g/l enzyme solution keeping 1:50 material to liquor ratio at pH 6, 85±2 ℃ temperature and treated for 60 minutes with intermittent stirring [4].

2.2.2 Nanoparticles treatment and dyeing of silk fabric: The nano treatment and simultaneous dyeing of silk fabric with madder dye was carried out in the treatment solution containing 1.00 percent concentration of TiO_2 nanoparticles, maintaining MLR 1:50 at pH 5.0, 80 ℃ temperature for 50 minutes in IR beaker dyeing machine. After dyeing, fabric samples were allowed to cool in the solution and then rinsed with hot water followed by soaping with 2g/l non-ionic detergent using MLR 1:20 at 60 ℃ temperature for 15-20 minutes. The nano treated madder dyed samples were washed thoroughly in cold water, squeezed and dried in shade at ambient temperature.

2.2.3 FTIR Analysis: The FTIR analysis of untreated dyed and nano TiO_2 treated dyed silk fabric samples was carried out using Nicolet iS50, Thermo Scientific. FTIR spectrum was recorded for transmittance in the range of 400-4000 cm^{-1} and 16 scans (Resolution 4) were performed for each sample.

2.2.4 FE-SEM Analysis: FE-SEM of dyed samples were performed on JSM-IT800 at an acceleration voltage of 15 kV with the magnification ranging from 100-1500X.

2.2.5 Testing of Functional Properties: Antibacterial and ultra-violet protection properties of nano treated madder dyed silk fabric were examined to analyze the effect of nanoparticles treatment and simultaneous dyeing on silk fabric.

- **Antibacterial property:** The fabric samples of untreated and nanoparticle treated dyed silk fabric were examined for antibacterial property using standard quantitative test method i.e. AATCC Test Method 100. The bacterial resistance of untreated dyed (control) and nanoparticle treated dyed samples was tested against gram-positive, *Staphylococcus aureus* and gram-negative, *Escherichia coli* bacteria.
- **Ultra-violet protection property:** The UV protection category was determined by the UPF values described by Australia/ New Zealand Standards AS/NZS4399 (1996).

3. Result and discussion

3.1 FTIR analysis of nano TiO_2 treated and madder dyed silk fabric: FTIR analysis of untreated madder dyed and nano titanium dioxide treated madder dyed silk fabric was done for identification of the organic and inorganic groups present in the fabric sample by securing an infrared absorption spectrum. The table reflect the details of various wave numbers at which peaks were observed in fabric samples and various functional groups associated to them. The FTIR spectra of untreated dyed and nano treated dyed silk fabric samples are given in Figure 1.

Table 1: FTIR analysis of nanoparticle treated and madder dyed silk fabric

Wave numbers (cm-1)	Functional groups	Peak positions of nanoparticle treated dyed samples	
		Untreated	TiO_2 treated
1000–1200	C-N stretch primary amine	1064, 1164	1007, 1064, 1165
1200–1400	C-O stretch alkyl aryl ether	1227	1227
1400-1600	N-O stretch nitro compound	1442, 1513	1441, 1513
1600–2000	C=C/C=O stretch alkene/amide	1619, 1982	1619, 1982
2000–3000	C-H stretch methane	2053, 2083, 2112, 2192, 2926	2052, 2108, 2198, 2928
3200–3400	OH/N-H stretch alcohol/ amine	3072, 3278	3071,3277

The Table 1 shows that the peaks at 1007, 1064 and 1165 cm^{-1} in nano titanium dioxide treated dyed samples are associated with the presence of C-N stretch primary amines. The appearance of a strong broad band at 1227 cm^{-1} in untreated madder dyed silk fabric and nano titanium dioxide treated dyed silk fabric exhibited the characteristics of C-O stretch alkyl aryl ether groups. Peaks at 1442 and 1513 cm^{-1} in untreated dyed and 1441 and 1513 cm^{-1} in nano titanium dioxide treated dyed silk fabric samples reflected the presence of N-O stretch nitro compound. Similarly, peaks at 1619 and 1982 cm^{-1} in untreated dyed as well as in nano titanium dioxide treated dyed samples attributed to the presence of C=C/C=O stretch alkene/amide group. Whereas peaks at 2053, 2083, 2112, 2192 and 2926 cm^{-1} in untreated dyed and peaks at 2052, 2108, 2198 and 2928 cm^{-1} in titanium dioxide nanoparticle treated dyed samples is the characteristic of C-H stretch methane. Further, peak at 3072 and 3278 cm^{-1} in untreated dyed and 3071 and 3277 cm^{-1} in nano titanium dioxide treated dyed silk fabric samples depicted the characteristic of O-H/N-H stretch alcohol/amine. Hence, FTIR analysis of nanoparticle treated dyed fabrics indicated the presence of amine groups and addition of -OH group which are active sites for many chemical reactions. In suitable conditions, the nanoparticle treatment and dyeing imparted the secondary amine characteristics of silk fabric which provided maximum percent dye absorption; hence these groups get protonated form and attract more anionic dye. Tangkawanit and Keawsri [6], Haijuan *et al.* [12] also noticed the slight shift in peaks from untreated to nano TiO_2 treated silk fabric.

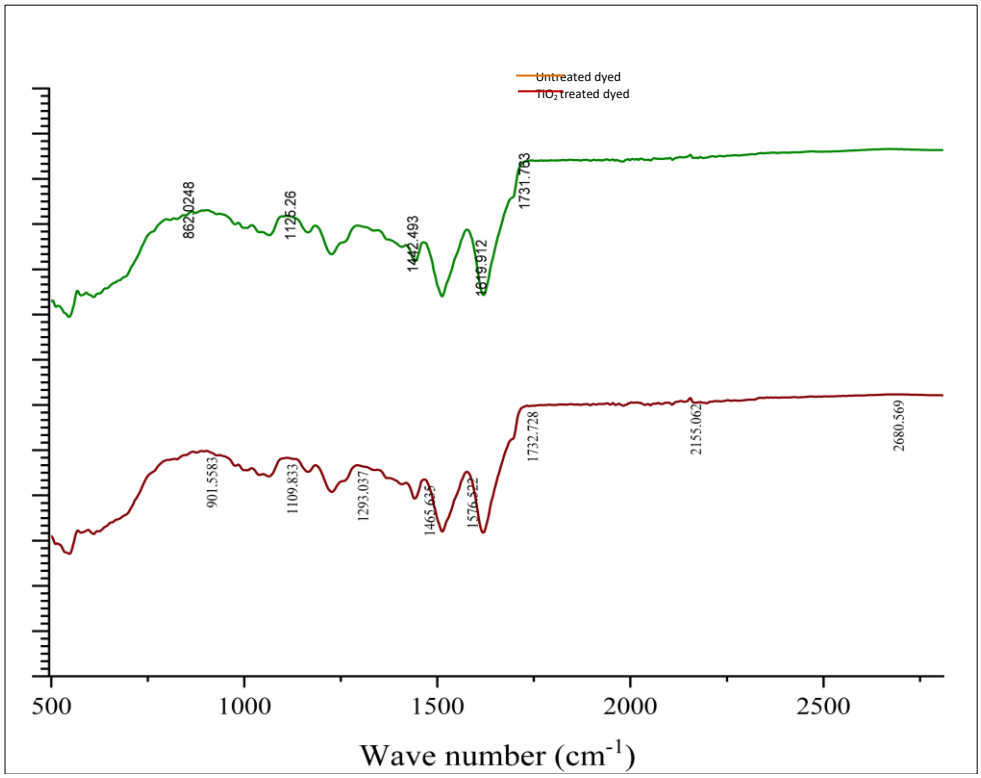


Fig 1: FTIR spectra of untreated and titanium dioxide nanoparticle treated madder dyed silk samples

3.2 FE-SEM Analysis of Nanoparticle Treated Dyed Silk Fabric

The FE-SEM analysis enables to reveal the correlation between elemental composition and morphological changes in the resultant substrate. Hence, it was carried out to check the effect of nanoparticle treatment on surface morphology of dyed silk fabric samples and confirmed the presence of nanoparticles onto the fibre matrix as the particles were observed to be well dispersed on the fibre surface. The morphological structures of untreated dyed and treated dyed silk fabric samples are depicted in Plate 1. The FE-SEM analysis of treated sample provide information about the topography and elements present on a surface. Similar findings were reported by Tangkawanit and Keawsri [6], Cheng *et al.* [5] and Zou *et al.* [11].

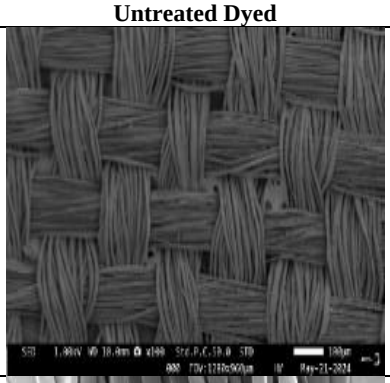
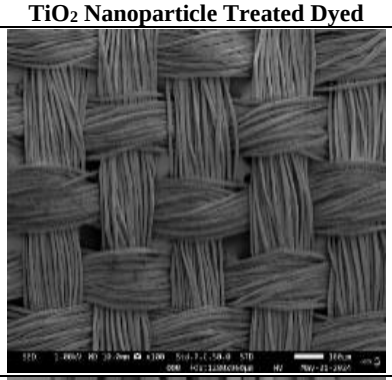
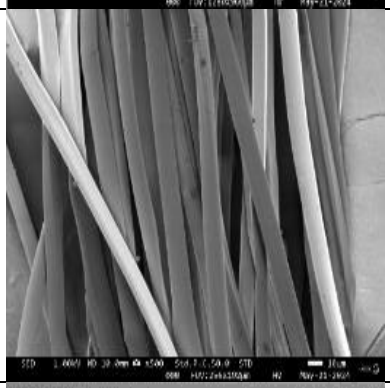
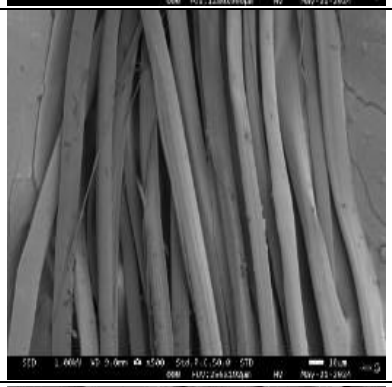
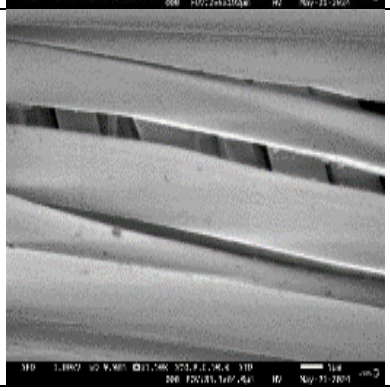
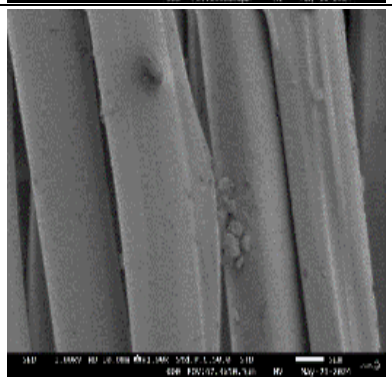
Samples Magnifications	Untreated Dyed	TiO_2 Nanoparticle Treated Dyed
100X		
500X		
1500X		

Plate 1: FE-SEM images of Untreated and Nano Treated Madder Dyed Silk Fabric

3.3 Effect of nanoparticle treatments and dyeing on functional properties of silk fabric

3.3.1 Effect of nano TiO_2 treatment and natural dyeing on antimicrobial properties of silk fabric: The data incorporated in Table 2 depict the antibacterial activity of untreated and nanoparticle treated silk fabric dyed with madder dye against *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) bacteria. The table showed that the antibacterial property of nano TiO_2 treated dyed silk fabric was found good in terms of reduction of growth percent as compared to untreated dyed silk fabric. It was found that the untreated madder dyed silk fabric had 8.48×10^7 CFU/ml for *Staphylococcus aureus* bacteria and 10.48×10^7 CFU/ml for *Escherichia coli* bacteria. The growth of more number of bacteria on untreated dyed silk fabric might be due to the fact that silk protein are nutrients for the growth and reproduction of microorganisms [5]. The nano titanium dioxide treated dyed fabric exhibited bacterial count of 6.28×10^7 CFU/ml for *Staphylococcus aureus* and 7.12×10^8 CFU/ml for *Escherichia coli* with 25.94 and 32.06 percent reduction in bacterial growth of *Staphylococcus aureus* and *Escherichia coli* respectively. -The results are in line with the findings of Shahin *et al.* [8], Zhang *et al.* [10] and Khatib *et al.* [9] that improvement in antibacterial activity on nano treated dyed silk fabric than untreated dyed silk fabric. The images of bacterial growth on untreated dyed and nano titanium dioxide treated dyed silk fabric samples are given in Plate 2.

Table 2: Antimicrobial properties of nanoparticle treated and madder dyed silk fabric

Treated dyed samples	*Staphylococcus aureus*		*Escherichia coli*	
	Bacterial count (CFU/ml)	Reduction in bacterial growth (%)	Bacterial count (CFU/ml)	Reduction in bacterial growth (%)
Untreated	8.48×10^7	-	10.48×10^7	-
Titanium dioxide	6.28×10^7	25.94	7.12×10^7	32.06

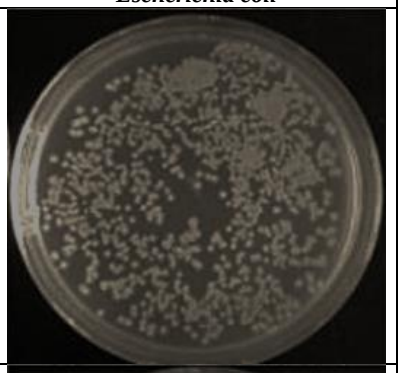
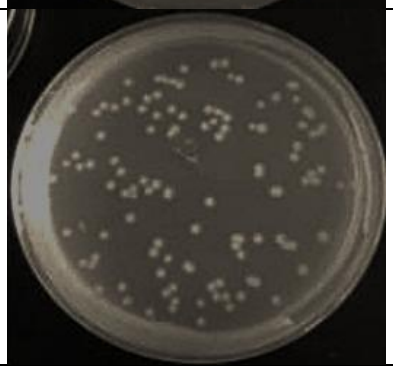
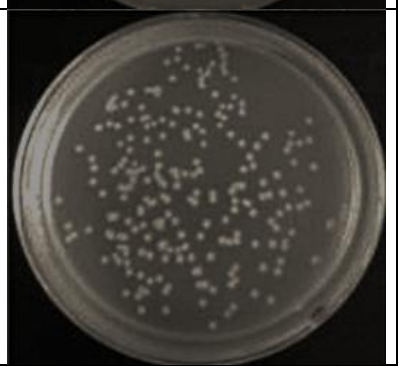
Test bacteria Fabric Samples	Bacterial Growth	
	Stayphlococcus aureus	*Escherichia coli*
Untreated		
Titanium dioxide		

Plate 2: Bacterial Growth on Treated Dyed Silk Fabric

3.3.2 Effect of nanoparticle treatments and dyeing on ultra-violet protection property of silk fabric: The data presented in Table 3 describe the ultra-violet protection property of untreated dyed and nanoparticle treated and madder dyed silk fabric samples. It is found that UPF value of untreated madder dyed silk fabric was 12.34 which came under no protection category which is due to light and thin nature, silk fabric has high UV light transmittance, resulting in poor UV protection property. After treatment of silk fabric with nano titanium dioxide and dyeing with madder dye, UPF values of treated dyed fabric sample was observed to be increased to 22.45 which represented the good protection category due to deposition of nanoparticles in the fibre matrix which create the hindrance to penetrate the UV radiation. The results of the study are supported by the findings of Tangkawanit and Keawsri[6] and Chitichotpanya *et al.* [7] the nano treatment of silk fabric can increase the UPF value of silk fabric.

Table 3: Ultra-violet protection property of nanoparticle treated and madder dyed silk fabric

Treated dyed samples	UVA Transmission (%)	UVB Transmission (%)	UPF	Protection Category
Untreated	17.21	8.56	12.34	No category
Titanium dioxide	4.21	3.41	22.45	Good

UPF Rating: Good protection: 15, 20; Very good protection: 25, 30, 35; Excellent protection: 40, 45, 50, 50+

4. Conclusion

The TiO_2 nanoparticles treatment and simultaneous dyeing of silk fabric with madder root dye and to ascertain the effect of nanoparticles on its functional properties. FE-SEM analysis exhibited the presence of nanoparticles on surface matrix of silk fabric which showed the successfully deposition of nanoparticles. The FTIR analysis showed the presence of different functional group at different peaks in nanotreated dyed silk fabric which show the interaction between chemical groups that are present in fabric and nanoparticles. UV protection property of nano treated dyed and untreated dyed silk fabric were also evaluated and found to be in good category (22.45) from the no category (12.34) of UPF value. The antibacterial property of samples was also examined and it was concluded that nanotreatment on dyed silk fabric can be also used to reduce percent reduction in bacterial growth of *Staphylococcus aureus* and *Escherichia coli*. Hence, nanoparticles for treatment during the dyeing of silk fabric can be used for imparting functional properties on the silk fabric.

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Conflicts of Interest/Competing Interests

The author declares that there are no conflicts of interest or competing interests.

Ethics Approval

Ethical approval was not required for this study as it did not involve human participants or animal experimentation.

Consent to Participate/ Consent for Publication

All authors consent to participate in this work

Availability of Data and Material

The data generated and analyzed during the study are available from the corresponding author on reasonable request.

Code Availability
Not applicable.

Authors' Contributions
Pratibha Pratibha: Conceptualization, Methodology, Investigation, Data Curation, Writing and Original Draft Preparation.
Saroj Yadav Neelam M. Rose and Shalini Rukhaya: Supervision, Review & Editing.

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