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# Optimization of nanoparticle treatments for cotton fabric and dyeing with eco-friendly natural dyes

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**Abstract**
The revitalization of interest in green and sustainable materials and processes in textile dyeing is rising due to the increasing concern about environmental pollution in all spheres of life caused by the petrochemical based products and dyes. Natural dyes lack in shade reproducibility and fastness properties hence, mordants are required for better dye fixation of natural dyes on the textile substrate. The unique property of nanoparticles of higher surface to area ratio and more surface energy to react with the substrate can serve the purpose of mordant to enhance the dye uptake of natural dyes on the fabrics and thereby can replace the heavy metallic mordants. Therefore, the present study was undertaken to assess the effect of different nanoparticle treatments on dyeability of cotton fabris. Three different metallic nanoparticles with two natural dyes were explored to ascertain the effect of nano treatment on dye uptake of cotton fabric. Nano treatments for cotton fabric was optimized for different process parameters viz. treatment stage, nanoparticle concentration, treatment pH, time, temperature and M:L ratio of treatment bath on the basis of maximum dye absorption (%) and colour properties of treated dyed fabrics. The nanoparticle treatment was applied to scoured cotton and wool fabrics using optimized concentrations and conditions and dyed simultaneously with selected natural dyes through exhaust method in IR beaker dyeing machine. Nanoparticle treatments along with natural dyeing of cotton fabric demonstrated enhanced dye uptake and colour properties of nanotreated dyed fabrics. Hence, use of metallic nanoparticles in small amount can be successfully employed as viable approach to replace the conventional heavy metal based mordants used in large quantity for textile dyeing with natural dyes.

**Keywords:** nanoparticle treatments, cotton fabric, dyeing, eco-friendly natural dyes

## Introduction
Technological development in synthetic chemistry began in the middle of the 19$^{th}$ century and brought a revolution in the field of textile dyeing with the discovery of synthetic dyes. The first ever synthetic dye 'mauve' was discovered by Henry Perkin in 1856. Later many dyes were derived from different chemical compounds namely, naphthols, sulphur, triphenyl methane, nitroso, azoic, phthalocyanine, reactive based on cyanuric chloride, azo, anthraquinone, stilbene and others. Among these synthetic dyes, azo based dyes have the most toxic effects as these release harmful amines, allergens, carcinogens and other poisonous compounds that may cause cancer, allergy and are detrimental to health and environment. Consequently, during 1996-97 many countries around the globe including India imposed a ban on the import, stock and sale of commodities related to azo based dyes. Therefore, it became imperative to find the alternate sources to replace the synthetic dyes. To revive the art of natural dyeing, resurgence of natural dyes took place as these are known for their eco-friendliness and also benign to both mankind and environment. In the present times, an inclination towards the use of natural dyes has increased rapidly due to stringent environmental standards imposed by many countries in response to toxic and allergic reactions related with synthetic dyes. Therefore, the application of eco-friendly natural dyes on textiles is being reintroduced for dyeing of textile materials due to growing concern for the noxious effects of synthetic dyes (Singh and Bharti, 2014; Barani *et al*., 2017; Nimkar, 2018) [6, 3].
Natural dyes are having wide applications in the colouration of most of the natural fibres such as cotton, linen, wool and silk and to some extent to few synthetic fibres i.e. nylon and polyester. However, the major issues for natural dyes are reproducibility of shades, non availability of well-defined standard procedures for application and poor lasting performance of dye under wash and light exposure. As natural dyes have poor colour fastness and to achieve good fastness especially towards washing and light is a challenge for the researchers as well as dyers.

Therefore, an agent known as mordant is required to create an affinity between the fibres and colouring compound. The metallic mordants in the form of metal salts are frequently used for the improvement of dye uptake and retention of natural dyes in the dyed substrate. Hence, the final shade, their brilliance and fastness properties are not only dependent on the chemical composition of dye itself but are also determined by varying concentrations and skillful manipulation of the mordants. The use of heavy metal salts in large quantity generates very polluted waste water consisting of non-biodegradable and persistent chemicals which endangers the environment and human health. As a result, researchers have shifted their attention towards eco-friendly treatments which improve colour properties of natural dyed textiles without causing pollution (Singh and Bharti, 2014) [6]. For successful commercial use of natural dyes, appropriate and systematic procedures need to be standardized to obtain better colour yield with very good colour fastness properties and minimal pollution load on environment. The nanoparticles can be used for modification of fibre surface to enhance dye uptake and dye fixation to the substrates dyed with natural dyes for improving the colour properties. Therefore, the present study was carried out to ascertain the effect of metallic nanoparticles on the dye affinity and colour properties of cotton and wool fabrics towards natural dyes.

**Methodology**

1. **Procurement of nanoparticles:** To improve the dyeability of the cotton fabrics with natural dye, three different metal based nanoparticles (50-100nm) copper oxide (CuO), titanium dioxide ($TiO_2$) and zinc oxide (ZnO) were used as mordant. All the nanoparticles were procured from Sigma-Aldrich, India.
2. **Procurement of natural dye**: Eucalyptus (*Eucalyptus globulus)* bark and Madder (*Rubia tinctorum*) root dyes were taken for the study. The dye materials were collected, washed to remove the impurities, shade dried and then crushed and ground into fine powder.
3. **Phytochemical analysis of the selected dye extracts:** For identification of active chemical components present in the selected natural dyes, phytochemical screening of the dye extracts was done following the standard procedures given by Verma, 2017 [7]; Pandey *et al.,* 2018 and Samant *et al.,* 2020 [4].
4. **Preparation of Cotton and Wool Fabrics:** To make the cotton fabric ready for nanoparticle treatments and subsequent dyeing with natural dyes, it becomes necessary to remove the undesired inherent or added impurities and foreign materials for uniform wetting and absorbency of the dye extracts. Desizing followed by scouring of selected cotton fabric was carried out to make the fabrics more absorbent and free from the extraneous substances by adopting the methods given by Vigneshwaran *et al.,* 2013 and Sawada *et al.,* 2003 [5].
5. **Standardization of Nanoparticle Treatments for Cotton:** Nanoparticles have unique property of higher surface to area ratio hence provide more surface energy to react with the substrate. Therefore, nanoparticle treatment can be an alternative to metallic mordants to enhance the dye uptake of natural dye on the fabric (Nazari, 2019 and Gupta *et al.*, 2021) [2, 1]. The cotton fabric was treated with different metallic nanoparticles using exhaust method. To optimize the treatment process, different ranges of concentrations and conditions were taken on the basis of available literature. The six different variables i.e. nanoparticle treatment stage, nanoparticle concentration, treatment pH, treatment time, treatment temperature and M:L Ratio with different ranges of variables were optimized. The optimization of different treatment parameters was done on the basis of percent dye absorption and wash fastness of treated dyed samples.

**i. Optimization of treatment stage:** For optimization of nanoparticle treatment stage, selected nanoparticles were applied to cotton and wool fabrics at pre, simultaneous and post treatment stages of fabric dyeing.

**a. Pre treatment**: In pre treatment stage, prior to dyeing the scoured cotton were treated separately with 1 percent concentration of each nanoparticle (owf) in Infrared beaker dyeing machine. During nanoparticle treatment other variables i.e. treatment temperature: 80 °C, treatment time: 30 minutes, pH 6 and M:L ratio 1:30 were kept constant. After nano treatment, the samples were allowed to cool at room temperature in treatment solution, squeezed and immediately dyed in the Infrared beaker dyeing machine with both the selected dyes with optimum dyeing conditions as mentioned in Table 1. After dyeing, the treated dyed samples were allowed to cool in dye solution at room temperature and then rinsed with hot water. Afterwards, soaping of the samples was done with 2 g/l nonionic detergent at 60°C maintaining M:L ratio 1:20 for 15-20 minutes. The samples were then washed thoroughly with cold water, squeezed and dried at ambient temperature.

**b. Simultaneous treatment:** In the simultaneous stage of nanoparticle treatment, 1 percent concentration (owf) of each selected nanoparticle was added to bath containing natural dye. The samples of cotton fabric were treated and dyed simultaneously with each dye in the Infrared beaker dyeing machine. During simultaneous treatment stage, other variables of nanoparticle treatment and dyeing were kept constant as mentioned in section 3.5.1.i.a. Subsequently, the treated dyed samples were washed with hot water followed by soaping with 2 g/l nonionic detergent at 60°C having MLR 1:20 for 15-20 minutes. The samples were then washed thoroughly with cold water, squeezed and dried in shade.

**c. Post treatment:** The cotton fabric samples were dyed separately with both the selected natural dyes using optimum dyeing conditions. After dyeing, the samples were taken out, allowed to cool down to room temperature and squeezed. Thereafter, cotton fabric dyed with both the dyes were treated individually with 1 percent concentration of each selected nanoparticle (owf) in the Infrared beaker dyeing machine. After the nanoparticle treatment, the fabric samples were washed with hot water, soaped, rinsed thoroughly in cold water, squeezed and dried at ambient temperature.

The nanoparticle treatment stage was optimized for cotton and wool fabrics on the basis of maximum percent dye absorption, colour strength and wash fastness of the treated dyed samples with both the selected dyes.To determine the percent dye absorption in cotton and wool fabrics, values of dye bath were measured by taking the absorbance of the dye liquor before and after dyeing on Photocalorimetre instrument and optical density (OD) were recorded from 600-700 nm wavelength. The percent dye absorption of the dyed samples was

calculated using the following formula:

$$\text{Percent dye absorption} = \frac{\text{OD before dyeing} - \text{OD after dyeing}}{\text{OD before dyeing}} \text{x} 100$$

**ii. Optimization of nanoparticle concentration:** To determine the optimum concentration of nanoparticles for cotton and wool fabrics, four different concentrations i.e. 0.25, 0.50, 0.75 and 1.0 percent (owf) of each nanoparticle were taken and fabric samples were dyed with both the selected natural dyes in the Infrared beaker dyeing machine. The concentration of each selected nanoparticle that demonstrated maximum percent dye absorption, colour strength and enhanced wash fastness grades with both the natural dyes for cotton was selected as optimum concentration of respective nanoparticle.

**iii. Optimization of treatment pH:** The treatment bath were prepared using optimum concentration of each selected nanoparticle and set at different pH values i.e. 6.0, 6.5, 7.0 and 7.5 for cotton fabric. Dyeing of samples was carried out with natural. The pH value that displayed maximum percent dye absorption, colour strength and elevated wash fastness grades was selected as optimum treatment pH for cotton.

**iv. Optimization of treatment temperature:** For determination of optimum treatment temperature, the selected nanoparticles were applied on cotton and wool fabric samples using optimum concentration and optimum pH values at four different temperatures i.e. 60, 70, 80 and 90ºC and simultaneously dyed with both the selected dyes. The temperature reflecting maximum dye absorption, colour strength and wash fastness grades on the cotton and wool fabrics was selected as optimum treatment temperature for both the fabrics.

**v. Optimization of treatment time:** For optimization of treatment time, nanoparticle treatments were given to samples of both the fabrics for four different durations i.e. 15, 30, 45 and 60 minutes with optimum concentration, optimum treatment pH for optimum treatment time, whereas other variables were kept constant and dyeing of cotton fabric samples was done using selected natural dyes. The time that demonstrated maximum dye absorption, colour strength and wash fastness grades on the cotton and wool fabrics was selected as optimum treatment time.

**vi. Optimization of material to liquor ratio:** To determine the optimum material to liquor ratio (M:LR) for all the nanoparticle treatments, four different ratios of treatment solutions i.e. 1:10, 1:20, 1:30 and 1:40 were taken with optimized conditions (nanoparticle concentration, pH value, treatment temperature and treatment time) and dyeing of was carried out using both the selected natural dyes. The material to liquor ratio presenting maximum dye uptake, colour strength and wash fastness was selected as optimum material to liquor ratio for nanoparticle treatment of cotton.

**Application of Nanoparticles and Natural Dyes on Cotton and Wool Fabrics**

The nanoparticle treatment and dyeing of scoured cotton and wool fabrics were carried out through exhaust method in Infrared beaker dyeing machine. The cotton fabric samples were treated with each selected nanoparticle separately in the bath containing optimum nanoparticle concentration with optimum material to liquor ratio at optimum pH, optimum temperature for optimum duration of time and simultaneously dyed with both the natural dyes.

**Result and Discussion**

To achieve the desired results number of experiments were carried out to optimize the nanoparticle treatment stage, nanoparticle concentration, treatment pH, treatment time, treatment temperature and M:L Ratio of treatment bath. On the basis of improvement in dye absorption, colour strength (K/S) and wash fastness (CC) grades of treated dyed cotton fabric samples, optimization of process variables for all the three nanoparticles and dyeing with the natural dyes was done.

**i. Optimization of nanoparticle treatment stage:** For determining the optimum treatment stage for all the three selected nanoparticles, the scoured cotton fabric samples were treated with copper oxide (CuO), titanium dioxide ($TiO_2$) and zinc oxide (ZnO) nanoparticles at pre, simultaneous and post treatment stages and dyed with eucalyptus bark and madder root dyes. For the selection of optimum treatment stage, effect of nanoparticle treatment on percent dye absorption, colour strength (K/S) and wash fastness (CC) of treated dyed cotton fabric samples was analyzed and related data are presented in Table 1.

**Table 1:** Effect of nanoparticle treatment stage on dye absorption and colour properties of dyed cotton fabric

| Nanoparticles | Treatment Stages | Nanoparticle treated dyed samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | Eucalyptus bark | | | Madder root | | |
| | | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) |
| Copper oxide | Pre | 22.34 | 12.23 | 4/5 | 21.54 | 13.78 | 4 |
| | Simultaneous | 25.54 | 14.28 | 4/5 | 25.14 | 15.49 | 4/5 |
| | Post | 19.32 | 11.79 | 4 | 24.33 | 11.56 | 4 |
| Titanium Dioxide | Pre | 20.69 | 13.70 | 4 | 21.65 | 13.38 | 4 |
| | Simultaneous | 25.72 | 14.23 | 4 | 25.98 | 15.67 | 4 |
| | Post | 23.89 | 11.67 | 4 | 21.15 | 12.88 | 4 |
| Zinc oxide | Pre | 18.21 | 12.30 | 4/5 | 24.73 | 14.45 | 4/5 |
| | Simultaneous | 26.45 | 14.45 | 4/5 | 25.94 | 15.60 | 4/5 |
| | Post | 23.45 | 11.51 | 4 | 22.60 | 12.28 | 4 |

CC: Colour change

It is apparent from the table that when cotton fabric was dyed with eucalyptus bark dye in the presence of copper oxide nanoparticles, maximum dye absorption (25.54%) was noticed at simultaneous treatment stage with the highest

colour strength (14.28) and very good (4/5) wash fastness rating. The application of copper oxide nanoparticles at pre and post treatment stage exhibited 23.34 and 19.32 percent dye absorption having 12.23 and 11.79 colour strength with very good (4/5) and good (4) wash fastness ratings respectively. Similarly, treatment with titanium dioxide and dyeing of cotton fabric with eucalyptus bark dye reflected maximum dye absorption (25.72%) at simultaneous treatment stage followed by post (23.89%) and pretreatment stage (20.69%) exhibiting 14.23, 11.67 and 13.70 colour strength values respectively with good (4) wash fastness grades at each stage of nano treatment. Data regarding zinc oxide nanoparticle treatment and dyeing with eucalyptus bark dye unveil that the dye absorption was maximum (26.45%) at simultaneous treatment stage followed by post (23.45%) and pre (18.21%) treatment stage having colour strength values 14.45, 11.51, 12.30 and with very good (4/5), very good (4/5) and good (4) wash fastness ratings respectively.

The data in the table further reveal that when cotton fabric was treated with copper oxide nanoparticles and dyed with madder root dye, the highest dye exhaustion (25.14%) was attained at simultaneous treatment stage with maximum colour strength (15.49) and very good (4/5) wash fastness rating. At pre and post nano treatment stage of copper oxide, 21.54 and 24.33 percent dye absorption with 13.78 and 11.56 colour strength values having good (4 each) wash fastness ratings were attained when cotton fabric was dyed with madder root dye at both the treatment stages. In case of titanium dioxide nanoparticle treatment and dyeing of cotton fabric with madder root dye, simultaneous treatment stage displayed maximum dye absorption (25.98%) followed by pre (21.65%) and post treatment stage (21.15%) demonstrating 15.67, 13.38 and 12.88 colour strength values respectively and good (4 each) wash fastness grades of all the three dyed fabric samples. Data concerning zinc oxide nanoparticle treatment and dyeing with madder root dye reveal that the dye absorption of dyed cotton fabric samples was maximum (25.94%) at simultaneous stage followed by pre (24.73%) and post (22.60%) treatment stages exhibiting 15.60, 14.45 and 12.28 colour strength values with very good (4/5), very good (4/5) and good (4) wash fastness ratings respectively.

**ii. Optimization of nanoparticle concentration:** Optimization of nanoparticle concentration was done on the basis of maximum percent dye absorption, colour strength (K/S) and wash fastness (CC) grades of treated dyed cotton fabric samples. The results regarding optimization of nanoparticle concentration are given in Table 2.

It is clear from data presented in the table that when cotton fabric was dyed with eucalyptus bark dye using 0.25 percent concentration of copper oxide nanoparticles, the dye absorption was 20.43 percent with 11.23 colour strength and good (4) wash fastness rating. When concentration of copper oxide nanoparticles in the dye solution was increased from 0.50 to 0.75 percent, the percent dye absorption and colour strength values increased from 21.44 to 25.32 percent and from 14.20 to 14.69 with good (4) to very good (4/5) wash fastness grades. With further increase in concentration of copper oxide nanoparticles to 1 percent, the dye absorption (22.27%) and colour strength (13.34) were found to be decreased with good (4) wash fastness rating. Similarly when cotton fabric was dyed with eucalyptus bark dye in the presence of 0.25 percent titanium dioxide nanoparticles, the percent dye absorption was 20.69 with 10.45 colour strength and good (4) wash fastness grades. The increment in concentration of titanium dioxide nanoparticles from 0.5 to 1.0 percent, the dye absorption and colour properties of treated dyed samples also showed an increasing trend i.e. increase in dye absorption from 21.72 to 25.19 percent, colour strength from 11.69 to 14.45 and wash fastness grades from good (4) to very good (4/5). In case of zinc oxide nanoparticle treatment of cotton fabric and dyeing with eucalyptus bark dye, at 0.25 percent concentration the dye absorption was 18.21 percent having 11.12 colour strength with good (4) wash fastness rating. When the concentration of the zinc oxide nanoparticles in the dye solution was increased from 0.5 to 1.0 percent, the dye absorption and colour properties of treated dyed samples also increased i.e. dye absorption from 22.45 to 26.67 percent, colour strength from 12.20 to 15.23 with good (4) to very good (4/5) wash fastness grades.

**Table 2:** Effect of nanoparticle concentration on dye absorption and colour properties of dyed cotton fabric

| Nanoparticles | Concentrations (%) | Nanoparticle treated dyed samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | Eucalyptus bark | | | Madder root | | |
| | | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) |
| Copper oxide | 0.25 | 20.43 | 11.23 | 4 | 21.54 | 12.22 | 4 |
| | 0.50 | 21.44 | 14.20 | 4 | 23.34 | 14.47 | 4 |
| | 0.75 | 25.32 | 14.69 | 4/5 | 25.98 | 15.34 | 4/5 |
| | 1.00 | 22.27 | 13.34 | 4 | 23.47 | 13.38 | 4 |
| Titanium dioxide | 0.25 | 20.69 | 10.45 | 4 | 24.15 | 12.67 | 4 |
| | 0.50 | 21.72 | 11.69 | 4 | 24. 33 | 12.88 | 4 |
| | 0.75 | 23.89 | 12.25 | 4 | 25.15 | 13.45 | 4/5 |
| | 1.00 | 25.19 | 14.45 | 4/5 | 26.81 | 15.68 | 4/5 |
| Zinc oxide | 0.25 | 18.21 | 11.12 | 4 | 22.67 | 11.28 | 4 |
| | 0.50 | 22.45 | 12.20 | 4 | 24.83 | 12.34 | 4 |
| | 0.75 | 24.43 | 14.27 | 4/5 | 25.74 | 14.40 | 4 |
| | 1.00 | 26.67 | 15.23 | 4/5 | 28. 46 | 15.77 | 4/5 |

CC: Colour change

The data incorporated in the table unveil that when cotton fabric was dyed using madder root dye with addition of 0.25 percent concentration of copper oxide nanoparticles, the dye absorption was 21.54 percent with 12.22 colour strength and good (4) wash fastness rating. As the concentration of copper oxide nanoparticles was increased from 0.50 to 0.75 percent, the dye absorption and colour strength increased from 23.34 to 25.98 percent and from 14.47 to 15.34 with good (4) to

very good (4/5) wash fastness grades. With further increase in concentration of copper oxide nanoparticles to 1 percent, the dye absorption (23.47%) and colour strength (13.38) were noticed to be decreased with good (4) wash fastness rating. In case of dyeing of cotton fabric with madder root dye in the presence of 0.25 percent titanium dioxide nanoparticles, the dye absorption was 24.15 percent with 12.67 colour strength exhibiting good (4) wash fastness grades. The increase in concentration of nanoparticles from 0.5 to 1.0 percent, evinced an increment in dye absorption from 24.33 to 26.81 percent, colour strength from 12.88 to 15.68 and wash fastness grades from good (4) to very good (4/5). The treatment of cotton fabric simultaneously with zinc oxide nano particles and madder root dye at 0.25 percent concentration, 22.67 percent dye absorption with 11.28 colour strength and good (4) wash fastness rating was recorded. By treating the scoured cotton fabric with 0.5, 0.75 and 1.0 concentration of the zinc oxide nanoparticles and dyeing simultaneously with madder root dye, the dye absorption and colour strength of treated dyed samples also found to be increased having 24.83, 25.74 and 28.46 percent dye absorption with 12.34, 14.40 and 15.77 colour strength values, good (4), good (4) and very good (4/5) wash fastness grades respectively.

**iii. Optimization of nanoparticle treatment pH:** Optimization of nanoparticle treatment pH was done on the basis of maximum percent dye absorption, colour strength and wash fastness of treated dyed samples. The results regarding optimization of pH for nanoparticle treatment are arranged in Table 3.

**Table 3:** Effect of nanoparticle treatment pH on dye absorption and colour properties of dyed cotton fabric

| Nanoparticles | Treatment pH | Nanoparticle treated dyed samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | Eucalyptus bark | | | Madder root | | |
| | | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) |
| Copper oxide | 6.0 | 25.63 | 14.54 | 4/5 | 27.58 | 15.22 | 4/5 |
| | 6.5 | 24.44 | 13.23 | 4/5 | 25.14 | 14.17 | 4/5 |
| | 7.0 | 23.32 | 12.46 | 4 | 25.90 | 12.34 | 4 |
| | 7.5 | 22.28 | 12.21 | 4 | 23.49 | 12.14 | 4 |
| Titanium dioxide | 6.0 | 26.66 | 14.45 | 4/5 | 28. 65 | 14.60 | 4/5 |
| | 6.5 | 24.72 | 13.45 | 4 | 26. 34 | 12.88 | 4 |
| | 7.0 | 23.87 | 12.35 | 4 | 24.12 | 13.45 | 4 |
| | 7.5 | 22.18 | 11.12 | 4 | 23.81 | 12.68 | 4 |
| Zinc oxide | 6.0 | 26.29 | 14.34 | 4/5 | 28.37 | 14.58 | 4/5 |
| | 6.5 | 25.55 | 12.34 | 4/5 | 25.88 | 12.39 | 4/5 |
| | 7.0 | 24.42 | 12.20 | 4 | 26.71 | 12.46 | 4 |
| | 7.5 | 22.61 | 12.12 | 4 | 24.46 | 11.78 | 4 |

CC: Colour change

It is clearly evident from the table that when pH of treatment solution containing copper oxide nanoparticles and eucalyptus bark dye was maintained at 6.0 for dyeing of cotton fabric exhibited the maximum dye absorption (25.63%) and colour strength (14.54) with very good (4/5) wash fastness rating. When the pH of copper oxide nanoparticle treatment solution was increased from 6.5 to 7.5, the dye absorption was noticed to be decreased from 24.44 to 22.28 percent, colour strength values from 13.23 to 12.21 and wash fastness grades from very good (4/5) to good (4). In case of nano titanium dioxide treatment and dyeing of cotton fabric with eucalyptus bark dye at pH 6.0, the highest dye absorption (26.66%), colour strength (14.45) and very good (4/5) wash fastness rating were achieved. Whereas, with the increment in pH from 6.5 to 7.5 of titanium dioxide treatment solution having eucalyptus bark dye, a decreasing trail in the percent dye absorption and colour properties of the dyed cotton samples was observed. The dye absorption decreased from 24.72 to 22.18 percent, colour strength from 13.45 to 11.12 and wash fastness rating from 4/5 to 4. When zinc oxide nanoparticle treatment was given to scoured cotton fabric by maintaining the 6.0 pH of treatment bath and dyed simultaneously with eucalyptus bark dye, the maximum dye absorption i.e. 26.29 percent and colour strength 14.34 with very good (4/5) wash fastness rating was attained. As the pH of zinc oxide nanoparticle treatment was raised from 6.5 to 7.5 for dyeing of cotton fabric samples with eucalyptus bark dye, the dye absorption, colour strength and wash fastness grades were observed to be decreased from 25.55 to 22.61 percent, colour strength values from 12.34 to 12.12 and wash fastness from 4/5 to 4 respectively.

The data presented in the table further reveal that for dyeing of scoured cotton fabric with madder root dye, when pH of copper oxide nanoparticle treatment solution was maintained at 6.0, the maximum dye absorption (27.58%) with 15.22 colour strength and very good (4/5) wash fastness rating was acquired. With progressive increase in the pH of copper oxide nanoparticle treatment solution from 6.5 to 7.5, the percent dye absorption, colour strength and wash fastness grades were observed to be decreased from 25.14 to 23.49 and from 14.17 to 12.14 and 4/5 to 4 respectively for simultaneous dyeing of cotton fabric with eucalyptus bark dye. In case of titanium dioxide nano treatment and dyeing of cotton fabric with madder root dye at pH 6.0, maximum dye absorption (28.65%), colour strength (14.60) with very good (4/5) wash fastness rating was recorded. Whereas, with the progressive increment in the pH of titanium dioxide treatment solution from 6.5 to 7.5 and dyeing of cotton fabric samples simultaneously with madder root dye, a decreasing trend was seen in the dye absorption from 26.34 to 23.81 percent, in colour strength values from 12.88 to 12.68 with same wash fastness ratings i.e. good (4). Further, when pH of treatment solution was maintained at 6.0 for treatment of cotton fabric with nano zinc oxide, maximum dye absorption (28.37%) with the highest colour strength (14.58) and very good (4/5) wash fastness rating were attained. With the increment in pH

of zinc oxide nanoparticle treatment solution from 6.5 to 7.5 and dyeing of cotton fabric with madder root dye, the percent dye absorption, colour strength and wash fastness grades were noticed to be decreased from 25.88 to 24.46, 12.39 to 11.78 and 4/5 to 4 respectively.

Thus it is inferred that when cotton fabric was treated with all the three selected nanoparticles and simultaneously dyed with both the selected natural dyes viz. eucalyptus bark and madder root at pH 6.0, exhibited the maximum dye absorption and improved colour properties i.e. colour strength and wash fastness grades. As a result, treatment pH 6.0 was selected as optimum treatment pH for all the nanoparticle treatments and simultaneous dyeing of cotton fabric with both the selected natural dyes.

**iv. Optimization of nanoparticle treatment temperature:**

To optimize the temperature for nanoparticle treatment, the scoured cotton fabric samples were separately treated with all the three selected nanoparticles and simultaneously dyed with eucalyptus bark and madder root dyes at four different temperatures i.e. 50, 60, 70 and 80°C using optimum concentration of each nanoparticle at 6.0 pH, while other variables of nano treatment were kept constant. The data regarding optimization of nanoparticle treatment temperature are demonstrated in Table 4.

The data in the table reveal that at 50 $^0$C treatment temperature, the dye absorption, colour strength and wash fastness rating of copper oxide nanoparticle treated and eucalyptus bark dyed cotton sample were 20.89 percent, 11.28 and good (4) respectively. When temperature of copper oxide nanoparticle treatment was raised from 60 to 80 $^0$C, the progressive increase in dye absorption from 22.47 to 25.34 percent, colour strength values from 12.20 to 14.47 and wash fastness grade from good (4) to very good (4/5) was observed. It can be derived from the data that when titanium dioxide nanoparticle and eucalyptus bark dye were applied to cotton fabric at temperature range from 50 to 80 $^0$C, the dye absorption increased from 20.66 to 25.39 percent with increment in colour strength from 10.65 to 14.12 depicting good (4) to very good (4/5) fastness ratings. In case of zinc oxide nanoparticle treatment, with gradual increment in temperature from 50 to 80 $^0$C, enhanced dye absorption from 19.21 to 26.20 percent and colour strength from 10.31 to 14.20 having good (4) to very good (4/5) fastness ratings were achieved.

**Table 4:** Effect of nanoparticle treatment temperature on dye absorption and colour properties of dyed cotton fabric

| Nanoparticles | Treatment temperatures (°C) | Nanoparticle treated dyed samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | Eucalyptus bark | | | Madder root | | |
| | | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) |
| Copper oxide | 50 | 20.89 | 11.28 | 4 | 20.54 | 11.84 | 4 |
| | 60 | 22.47 | 12.20 | 4 | 21.14 | 13.70 | 4 |
| | 70 | 24.30 | 12.46 | 4/5 | 22.41 | 15.34 | 4/5 |
| | 80 | 25.34 | 14.47 | 4/5 | 26.67 | 15.70 | 4/5 |
| Titanium dioxide | 50 | 20.66 | 10.65 | 4 | 24. 65 | 11.67 | 4 |
| | 60 | 21.55 | 13.24 | 4 | 23. 32 | 13.26 | 4 |
| | 70 | 23.59 | 14.35 | 4 | 24.10 | 12.68 | 4 |
| | 80 | 25.39 | 14.12 | 4/5 | 26.33 | 14.89 | 4 |
| Zinc oxide | 50 | 19.21 | 10.31 | 4 | 21.17 | 11.58 | 4 |
| | 60 | 21.48 | 12.24 | 4 | 24.83 | 12.89 | 4 |
| | 70 | 25.49 | 12.64 | 4 | 23.71 | 13.43 | 4/5 |
| | 80 | 26.20 | 14.20 | 4/5 | 27.44 | 15.76 | 4/5 |

CC: Colour change

It can be observed from the data in Table 5 that when nanoparticle treatment and simultaneously dyeing of scoured cotton fabric was carried out with madder root dye at higher temperature i.e. 80 $^0$C, the percent dye absorption, colour strength and wash fastness ratings of treated dyed cotton fabric samples were observed to be improved. In case of nano copper oxide treatment and dyeing of cotton fabric at 50 $^0$C, the dye absorption was noted as 20.54 percent having 11.84 colour strength and good (4) wash fastness grades. With further increment in temperature from 60 to 80 $^0$C, the percent dye absorption and colour properties also found to be elevated i.e. 21.14, 22.41 and 26.67 percent dye absorption, 13.70, 15.34 and 15.70 colour strength and good (4), very good (4/5) and very good (4/5) wash fastness grades at 60, 70 and 80 $^0$C temperature respectively. The data in the table regarding optimization of temperature for treatment of nano titanium dioxide and simultaneous dyeing of cotton fabric with madder root dye depict that at 50 $^0$C the dye absorption was 24.65 percent having 11.67 colour strength with good (4) wash fastness grades. The progressive increase in treatment temperature also improved the dye absorption and colour properties of treated dyed samples. The percent dye absorption of 23.32, 24.10 and 26.33 with 13.26, 12.68 and 14.89 colour strength values and good (4 each) wash fastness ratings were attained when scoured cotton samples were treated with titanium dioxide nanoparticles and dyed simultaneously with madder root dye at 60, 70 and 80 $^0$C respectively. The table elucidates that when zinc oxide nanoparticle treatment and simultaneous dyeing with madder dye was carried out at 50 $^0$C, the dye absorption was 21.17 percent, having 11.58 colour strength and good (4) wash fastness rating. When temperature of nano treatment and dye bath was raised from 60 to 80 $^0$C temperature, the dye absorption increased from 24.83 to 27.44 percent, colour strength from 12.89 to 15.76 and wash fastness ratings from good (4) to very good (4/5).

It can be inferred from the data that maximum percent dye absorption, highest colour strength (K/S) values and wash fastness ratings (CC) were achieved at 80 $^0$C treatment and dyeing temperature for all the three nanoparticles and both the dyes. Therefore, 80 $^0$C temperature was found to be optimum temperature for imparting nanoparticle treatment and dyeing

of cotton fabric with eucalyptus bark and madder root dyes.

**v. Optimization of nanoparticle treatment time:** To optimize the nanoparticle treatment time on the basis of percent dye absorption, colour strength (K/S) and wash fastness (CC) grades of treated dyed cotton samples, nanoparticle treatment was imparted with all the three nanoparticles and simultaneously dyed with eucalyptus bark and madder root dyes for four different time durations i.e. 15, 30, 45 and 60 minutes with optimum concentrations of each nanoparticle and keeping 6.0 pH at $80^0$ C temperature. The value for percent dye absorption, colour strength and wash fastness for different time durations are given in Table 5.

It is apparent from the table that after 15 minutes of copper oxide nanoparticles treatment and dyeing of cotton samples with eucalyptus bark dye, 20.83 percent dye absorption with 11.15 colour strength and good (4) wash fastness grades were recorded. It can be observed from the data that an increase in percent dye absorption and colour strength of copper oxide nanoparticles treated and eucalyptus bark dyed cotton samples was noticed with further progression in treatment and dyeing from 30 to 45 minutes, the percent dye absorption in treated dyed samples increased from 22.24 to 25.32 percent, colour strength values from 13.16 to 14.78 having good (4) and very good (4/5) fastness rating. The further increase in treatment time to 60 minutes led to decline in dye absorption (22.27%), colour strength (13.22) and wash fastness (4) grades. In case of titanium dioxide nanoparticles, when treatment time was increased from 15 to 45 minutes, the percent dye absorption values were observed to be increased from 18.67 to 25.29 percent, colour strength values from 11.12 to 14.35 with good (4) to very good (4/5) fastness ratings for eucalyptus bark dyed cotton samples. When titanium dioxide nanoparticle treatment and dyeing was performed for 60 minutes reduction in dye absorption (23.49%), colour strength (14.10) and wash fastness (4) grades was noted. It is further derived from the table that when zinc oxide nanoparticle treatment time was raised from 15 to 45 minutes, elevation in dye absorption from 19.22 to 26.67 percent colour strength from 10.91 to 14.56 and wash fastness rating from good (4) to very good (4/5) was observed in nanotreated eucalyptus dyed cotton samples. With further increase in treatment time to 60 minutes, the percent dye absorption (24.43%), colour strength (12.34) and washing fastness grades (4) were noticed to be reduced.

**Table 5:** Effect of nanoparticle treatment time on dye absorption and colour properties of dyed cotton fabric

| Nanoparticles | Treatment time (minutes) | Nanoparticle treated dyed samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | Eucalyptus bark | | | Madder root | | |
| | | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) |
| Copper oxide | 15 | 20.83 | 11.15 | 4 | 21.54 | 11.56 | 4 |
| | 30 | 22.24 | 13.16 | 4 | 23.14 | 13.78 | 4 |
| | 45 | 25.32 | 14.78 | 4/5 | 25.98 | 15.46 | 4/5 |
| | 60 | 22.27 | 13.22 | 4 | 23.47 | 12.89 | 4/5 |
| Titanium dioxide | 15 | 18.67 | 11.12 | 4 | 21.65 | 11.77 | 4 |
| | 30 | 21.42 | 12.84 | 4/5 | 24.33 | 13.49 | 4 |
| | 45 | 25.29 | 14.35 | 4/5 | 26.81 | 14.95 | 4/5 |
| | 60 | 23.49 | 14.10 | 4 | 24.15 | 12.49 | 4 |
| Zinc oxide | 15 | 19.22 | 10.91 | 4 | 22.67 | 11.40 | 4 |
| | 30 | 23.49 | 12.64 | 4 | 24.83 | 13.56 | 4/5 |
| | 45 | 26.67 | 14.56 | 4/5 | 28.86 | 15.87 | 4/5 |
| | 60 | 24.43 | 12.34 | 4 | 25.74 | 12.45 | 4 |

CC: Colour change

Further, it is observed from the table that for 15 minutes treatment of cotton fabric with copper oxide nanoparticles and dyeing with madder root dye, 21.54 percent dye absorption with 11.56 colour strength and good (4) wash fastness were observed. When nanoparticle treatment time was increased from 30 to 45 minutes, dye absorption of treated dyed samples also increased from 23.14 to 25.98 percent, colour strength values from 13.78 to 15.46 having good (4) and very good (4/5) fastness ratings. The further progression in treatment time to 60 minutes led to reduction in dye absorption (23.47%), colour strength (12.89) with very good (4/5) wash fastness grades. In case of titanium dioxide nanoparticle treatment, when duration of treatment was rised from 15 to 45 minutes dye absorption in madder root dyed cotton samples escalated from 21.65 to 26.81 percent, colour strength from 11.77 to 14.95 and fastness ratings from good (4) to very good (4/5). The 60 minutes treatment time exhibited decline in dye absorption (24.15%), 12.49 colour strength and wash fastness grades (4). It is further apparent from the table that when duration of zinc oxide nanoparticle treatment and dyeing of cotton fabric with madder root dye was raised from 15 to 45 minutes, the percent dye absorption of treated dyed samples increased from 22.67 to 28.86 and colour strength values from 11.40 to 15.87 and wash fastness ratings from good (4) to very good (4/5). With further elevation in treatment and dyeing time to 60 minutes, lower dye absorption (25.74%), colour strength (12.45) and good (4) wash fastness grades were noticed in madder root dyed cotton samples.

Hence, it is inferred that when treatment duration of all the nanoparticle and dyeing of cotton fabric with both the dyes was increased from 15 to 45 minutes, percent dye absorption, colour strength values and wash fastness grades were found to be increased but with 60 minutes treatment time, the colour properties noticed to be decreased for all the three nanoparticles and both the dyes. Hence, 45 minutes duration was selected as optimum treatment time for treatment of all the three nanoparticles and simultaneous dyeing of cotton fabric with eucalyptus bark and madder root dyes.

**vi. Optimization of material to liquor ratio of treatment bath:** To determine the optimum material to liquor ratio

(MLR) for treatment of cotton fabric with all the three selected nanoparticles separately and simultaneously dyeing with eucalyptus bark and madder root dyes, four different ratios of treatment solutions i.e. 1:10, 1:20, 1:30 and 1:40 were taken with optimized conditions viz. 0.75 percent concentration of copper oxide, 1 percent of titanium oxide and zinc oxide nanoparticles, 6.0 pH, 80 $^0$C temperature and 45 minutes treatment time. The material to liquor ratio that presented maximum dye uptake, colour strength and wash fastness was selected as optimum material to liquor ratio for treatment of cotton fabric with each selected nanoparticle and dyeing with both the selected natural dyes. The data pertaining to different M:L ratio used for nanoparticle treatment and dyeing with both the natural dyes are presented in Table 6.

**Table 6:** Effect of M:L Ratio of treatment bath on dye absorption and colour properties of dyed cotton fabric

| Nanoparticles | M:L Ratio | Nanoparticle treated dyed samples | | | | | |
|---|---|---|---|---|---|---|---|
| | | Eucalyptus bark | | | Madder root | | |
| | | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) | Dye absorption (%) | Colour strength (K/S) | Wash fastness grades (CC) |
| Copper oxide | 1:10 | 21.43 | 11.25 | 4 | 21.54 | 11.67 | 4 |
| | 1:20 | 21.44 | 13.67 | 4 | 22.14 | 13.93 | 4 |
| | 1:30 | 25.92 | 14.80 | 4/5 | 26.98 | 15.65 | 4/5 |
| | 1:40 | 21.27 | 13.56 | 4 | 23.87 | 13.77 | 4 |
| Titanium dioxide | 1:10 | 20.99 | 11.67 | 4 | 24.65 | 12.00 | 4 |
| | 1:20 | 21.72 | 12.87 | 4 | 24.33 | 13.77 | 4/5 |
| | 1:30 | 25.88 | 14.56 | 4/5 | 26.15 | 15.15 | 4/5 |
| | 1:40 | 24.19 | 12.10 | 4 | 25.21 | 13.66 | 4 |
| Zinc oxide | 1:10 | 18.21 | 11.23 | 4 | 22.69 | 11.76 | 4 |
| | 1:20 | 22.55 | 12.88 | 4/5 | 23.13 | 13.89 | 4 |
| | 1:30 | 26.40 | 14.90 | 4/5 | 28.74 | 16.23 | 4/5 |
| | 1:40 | 20.97 | 12.44 | 4 | 21.47 | 13.40 | 4 |

CC: Colour change

It is anticipated from the table that when copper oxide nanoparticle treatment was imparted to cotton fabric and simultaneously dyed with eucalyptus bark dye keeping 1:10 material to liquor ratio, 21.43 percent dye absorption, 11.25 colour strength and good (4) wash fastness were witnessed. When material to liquor ratio was increased from 1:20 to 1:30, nano copper oxide treated and eucalyptus bark dyed cotton fabric samples showed an increment in dye absorption from 21.44 to 25.92 percent, colour strength from 13.67 to 14.80 and wash fastness ratings from 4 to 4/5. With an escalation in ML ratio to 1:40, the dye absorption (21.27%), colour strength 13.56 and wash fastness ratings (4) were found to be decreased for nano copper oxide treated and eucalyptus bark dyed cotton fabric. The data regarding titanium dioxide nanoparticle treatment on cotton fabric and dyeing with eucalyptus bark dye reveal that at 1:10 material to liquor ratio, the dye absorption was 20.99 percent and colour strength was 11.67 with good (4) wash fastness rating. When material to liquor ratio was increased from 1:20 to 1:30, the dye absorption (25.88%), colour strength (14.56) and wash fastness grades (4/5) were found to be maximum for nano titanium dioxide treated and eucalyptus bark dyed cotton fabric sample. With further rise in material to liquor ratio to 1:40, the dye absorption (24.19%), colour strength (12.10) and wash fastness (4) were found to be reduced in nano titanium dioxide treated and eucalyptus bark dyed cotton fabric. The data related to zinc oxide nanoparticle treatment on cotton fabric and simultaneous dyeing with eucalyptus bark dye unveil that at 1:10 ML ratio, 18.21 percent dye absorption and 11.23 colour strength with (4) good wash fastness grade were obtained. With gradual increment in material to liquor ratio from 1:20 to 1:30, increase in the dye absorption from 22.55 to 26.40 percent, colour strength from 12.88 to 14.90 with very good (4/5 each) wash fastness was attained for zinc oxide nanoparticle treatment and dyeing with eucalyptus bark dye. Whereas, at 1:40 ML ratio, the dye absorption was 20.97 percent, colour strength was 12.44 with good (4) wash fastness rating in case of nano zinc oxide treated and eucalyptus bark dyed cotton fabric.

The table further reveal that when cotton fabric was treated with copper oxide nanoparticles and dyed simultaneously with madder root dye at 1:10 material to liquor ratio, 21.54 percent dye absorption and 11.67 colour strength with (4) good wash fastness grade were attained. With a rise in material to liquor ratio from 1:20 to 1:30, copper oxide nanoparticle treated and madder root dyed cotton fabric samples exhibited the enhancement in dye absorption from 22.14 to 26.98 percent, colour strength from 13.93 to 15.65 and wash fastness rating from good (4) to very good (4/5). When ML ratio was raised to 1:40, the reduction in dye absorption (23.87%), colour strength (13.77) and wash fastness rating (4) were noticed for nano copper oxide treated and madder root dyed cotton fabric. In case of titanium dioxide nanoparticle treatment on cotton fabric and simultaneous dyeing with madder root dye by maintaining the ML ratio of treatment bath at 1:10, the dye absorption was 24.65 percent with colour strength 12.00 having good (4) wash fastness rating. By raising the ML ratio from 1:20 to 1:30, the dye absorption (26.15%), colour strength (15.15) and wash fastness grades (4/5) were observed to be maximum for nano titanium dioxide treated and madder root dyed cotton fabric. With an increase in ML ratio to 1:40, the dye absorption (25.21%), colour strength (13.66) and wash fastness (4) were found to be reduced for nano titanium dioxide treated and madder root dyed cotton samples. The data about zinc oxide nanoparticle treatment on cotton fabric and dyeing with madder root dye reveal that at 1:10 material to liquor ratio, the percent dye absorption was 22.69 with 11.76 colour strength and good (4) wash fastness grade. With gradual increase in ML ratio from 1:20 to 1:30, the dye absorption increased from 23.13 to 28.74 percent, colour strength from 13.89 to 16.23 and wash fastness from good (4)

to very good (4/5) for nano zinc oxide treated and madder root dyed samples. Whereas, at 1:40 ML ratio, reduction in dye absorption (21.47%), colour strength (13.40) and wash fastness rating (4) was recorded for nano zinc oxide treated and madder root dyed cotton fabric.

It is apparent from the table that when cotton fabric was treated with all the three nanoparticles and simultaneously dyed with both the selected natural dyes at 1:30 ML ratio, the percent dye absorption, colour strength and wash fastness grades were found to be maximum. Therefore, 1:30 ML ratio was selected as optimum ML ratio for treatment of cotton fabric with nanoparticles and dyeing simultaneously with eucalyptus bark and madder root dyes.

**Application of nanoparticles and natural dyes on cotton fabric using optimized variables**

The scoured cotton fabric was treated separately with all the three selected nanoparticles i.e. copper oxide, titanium dioxide and zinc oxide and dyed simultaneously with eucalyptus bark and madder root dyes using exhaust method with the optimized process variables as presented in Table 7.

**Table 7:** Optimized variables of nanoparticle treatment for dyeing of cotton fabric with natural dyes

| Optimized variables of nano treatment | | Optimized conditions/values |
|---|---|---|
| Nanoparticle treatment stage | | Simultaneous |
| Nanoparticle concentration (%) | Copper oxide | 0.75 |
| | Titanium dioxide | 1.0 |
| | Zinc oxide | 1.0 |
| Treatment pH | | 6.0 |
| Treatment temperature ($^0$C) | | 80 |
| Treatment time (minutes) | | 45 |
| Material to liquor ratio | | 1:30 |

The nanoparticle treatment and simultaneous dyeing of cotton fabric samples with eucalyptus bark and madder root dyes was carried out in the treatment solution containing 0.75 percent concentration of copper oxide, 1 percent concentrations of each titanium oxide and zinc oxide, keeping 1:30 material to liquor ratio at pH 6, at 80 $^0$C temperature for 45 minutes by exhaust method 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 2 g/l non-ionic detergent using ML ratio 1:30 at 60 $^0$C temperature for 15-20 minutes. Afterward, the samples were washed thoroughly in cold water, squeezed and dried at ambient temperature. The shdaes obtained on nanotreated and natural dyed cotton fabrics are presented in Plate 1.


**Plate 1:** Shades Obtained with Natural Dyes on Nanotreated Cotton Fabrics

## Conclusion

The use of nanoparticles as mordants is a new approach to replace the conventional heavy metal based mordants used in large quantity for dyeing of textiles with natural dyes. Also, for successful commercial use of natural dyes, appropriate and systematic procedures need to be standardized to achieve better colour yield with very good colour fastness properties and minimal pollution load on environment. The present study was carried out to enhance the dyeability of cotton and wool fabrics with natural dyes using metal based nanoparticles as surface modifiers. The scoured cotton fabric samples were immersed separately in the treatment solution

containing 0.75 percent concentration of copper oxide, 1 percent concentration each of titanium dioxide and zinc oxide keeping 1:30 ML ratio at pH 6. The nanoparticle treatments were given at 80 $^{0}$C for 45 minutes with simultaneous dyeing of cotton fabric separately with eucalyptus bark and madder root dyes by exhaust method using IR beaker dyeing machine. It is thus concluded that nanoparticle treatments can be imparted successfully with nanosized copper oxide, titanium dioxide and zinc oxide to improve the dyeability and colour fastness properties of cotton with natural. By incorporation of nanoparticles in dyeing, a range of brown to yellowish brown can be obtained with eucalyptus bark dye and maroon to brownish maroon with madder root dye on cotton fabric.

**References**

1. Gupta V, Jose S, Kadam V, Shakyawar DB. Sol gel synthesis and application of silica and titania nano particles for the dyeing and UV protection of cotton fabric with madder. Journal of Natural Fibers 2021.
2. Nazari A. Superior self-cleaning and antimicrobial properties on cotton fabrics using nano titanium dioxide along with green walnut shell dye. Fibers and Polymers 2019;20(12):2503-2509.
3. Nimkar U. Sustainable chemistry: A solution to the textile industry in a developing world. Current Opinion in Green and Sustainable Chemistry 2018;9(4):13-17.
4. Samant L, Jose S, Rose NM, Shakyawar DB. Antimicrobial and UV protection properties of cotton fabric using enzymatic pretreatment and dyeing with *Acacia catechu*. Journal of Natural Fibers 2020;45(5):1-11.
5. Sawada K, Tokino S, Ueda M, Wang X. Bioscouring of cotton with pectinase enzyme. Journal of the Society of Dyers and Colourists 2003;114(4):333-336.
6. Singh HB, Bharti AK. Handbook of Natural Dyes and Pigments. Woodhead Publishing Pvt. Limited, New Delhi 2014, 6-12.
7. Verma M. Effect of biopolymer treatment on dyeing efficiency of cotton fabric. Doctoral Thesis, CCS Haryana Agricultural University, Hisar 2017.
8. Vigneswaran C, Ananthasubramanian M, Anbumani N, Kandhavadivu P. Eco-friendly approach to improve pectinolytic reaction and process optimization of bioscouring of organic cotton textiles. Journal of Engineered Fibers and Fabrics 2013;8(2):121-133.