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Effect of biopolymer treatments on dyeing efficiency of cotton fabric with marigold petals

Mona Verma, Saroj SJ Singh and Neelam M Rose

Abstract
To achieve the objectives of the study, different biopolymer along with natural dye (marigold petals). It was found that chitosan treated samples exhibited highest percent dye absorption (50.25%), colour strength (10.51) and wash fastness grades was found same (4) for all biopolymer treated dyed fabric. Among these biopolymers the chitosan showed the highest dye absorption, colour strength and wash fastness rating with natural dye. Thus we can efficiently use the chitosan as a mordant to replace the synthetic harmful mordant with biopolymer in environmental friendly manner, to reduce pollution load on environment and save resources.

Keywords: Biopolymer, chitosan, natural dye, fabric, marigold petals

Introduction
India is rich in natural wealth and there is ample scope to explore and revive application of natural dye on textiles. There is need to know the chemistry of dyes and interaction among mordant, dyes and fibres to get maximum yield of colourants and reproducible shades, to have commercial availability of extracted natural dyes in powder form to develop newer shades and to improve dye ability with natural dye. Cotton textile dyeing was done since the medieval period using cheap natural dyes. Nature has gifted us more than 500 dye-yielding plant species. Natural dyes have better bio degradability and generally have higher compatibility with the environment. They are nontoxic, non-allergic to skin, non-carcinogenic, easily available and renewable. Certain problems with the use of natural dyes in textile dyeing are color yield, complexibility of dying process, reproducibility results, limited shades, blending problems and inadequate fastness properties. But these problems can be overcome by using chemicals called as mordants. Mordants are metal salts which produce an affinity between the fabric and the dye (Satyanarayana and Chandra, 2013; Samanta and Agarwal, 2009) [18, 17]. Synthetic or metallic salts which are commonly used in dyeing of cotton fabric with natural dyes for better fixation of colour create problems because of its carcinogenic and harmful characteristics and take long time to degrade through environment cycles leading to water pollution. So, there is an urgent need to search natural, safe and biodegradable mordants to make natural dyeing process completely environmental friendly. These days environmental protection has become a challenge for the textile industry because it utilizes a lot of chemicals for colouration of textile materials. These chemicals are harmful for both human as well as environment (Singh and Srivastava, 2015) [19]. Cationization is one of the most important modifications for cotton to improve affinity toward anionic substances such as dyes in conventional textile processing and metal ions or unfixed dyes in effluent treatment. Cationic modification agents consist of two functional characteristics such as multiple functional groups that could react with cotton under alkaline conditions and cationic amino groups that could reduce the negatively charged barrier between fiber and dye. Modification is possible with the help of biopolymers, an environmentally benign route. It is well-known that biopolymers are capable of forming ionic interactions with cotton cellulose by rendering positive charge and provide other functional properties to fibre. Biopolymers can replace the salts such as alum, ferrous sulphate, sodium sulphate, sodium carbonate and sodium chloride which have been widely used for dyeing of cotton with natural and synthetic dyes to improve the fastness properties and absorption of dye. The dyeing of cotton with natural dyes using biocompatible and biodegradable modification agents such as chitosan and cyclodextrin will be the cost effective environmental friendly approach in the field of dyeing industry and emphasized that the modification of the fabric is one of the best routes to improve the affinity between dye and fabric (Sahan and Demir 2014; Sundrarajan *et al.*, 2012) [16, 20]. Chitosan is a versatile polycationic biopolymer derived from alkaline deacetylation of chitin. Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, non-toxic,

biodegradability as well as film formation properties (Venter *et al*.2006) [21]. Chitosan possesses hydroxyl and amino functional groups which can easily be fabricated with desired functional properties (Pokhrel *et al*. 2015; Dutta *et al*. 2004) [13, 5]. It was reported that chitosan can be used in production of man-made fibers and textile wet processing. Its potential can be utilized in dyeing to improve the dye-ability, in finishing as antimicrobial agent and in printing as natural thickener in printing paste (Gupta and Haile, 2007) [8].

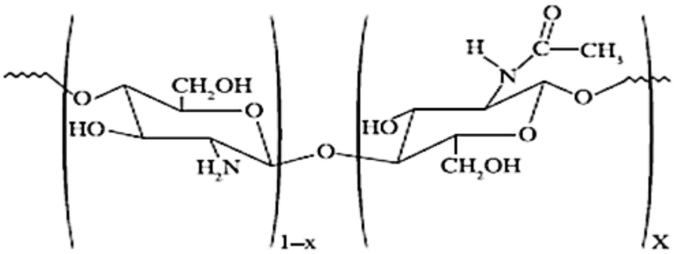


Fig 1: Structure of chitosan

Materials

1. **Preparation of Dye Material:** The fresh flowers were collected, washed to remove debris and shade dried. After being completely dried, the material was crushed into small pieces, pulverized into coarse powder and stored in a air tight containers free from environmental climatic changes, till usage.

Table 1: Plants material used for dyeing of cotton fabric for selection of dye

S. No.	Local name of the plant	Botanical name of plant	Family	Part used as dye
1.	Marigold	*Calendula officinalis*	Calendula Eye	Petals

2. **Preparation of Cotton Fabric:** To ensure complete wetting and uniform absorbency of the extracts during the padding, it must undergo preparatory processes. Desizing and scouring treatments were given to the woven cotton fabric to remove foreign materials before imparting finish.

i) **Enzymatic Desizing:** The cotton fabric was given desizing treatment using 2ml/l Americos Amylase 543 at 60^0C temperature for 60 minutes with 1:20 material to liquor ratio by maintaining 7 pH. The treatment liquor was drained out and given one hot rinsed and cold wash and dried (Vigneshwaran *et al.*, 2013) [22].

ii) **Enzymatic Scouring:** Desized cotton fabric was scoured in a bath containing 1.5% (owf) Palkoscour APCL enzyme, at 60 ^{0}C for 60 minutes at material to liquor ratio 1:15 maintained at 7.0 pH. The fabric was rinsed in hot and cold water and dried (Rajendran *et al.*, 2011) [14].

iii) **Biopolymers:** Three biopolymers i.e. beta- cyclodextrins chitosan and sericin were taken and applied on cotton fabric separately and dyed with marigold petal dye. Comparison was made among the three biopolymer on the basis of colour strength (k/s) value and wash fastness in terms of colour change (CC) of dyes.

Methods

1. **Selection of Extraction Method for Natural Dye:** Three different mediums of extraction were used and one medium of extraction was chosen on the basis of presence of phytochemicals in dye extract, simplicity of process and cost. The extraction of selected dye was done using Lokesh and Kumara-Swamy, 2013 [12] methods:

Aqueous Extraction: Aqueous extract was prepared by soaking 10 g of dye powder in 100 ml distilled water, in a stainless steel vessel overnight to loosen the cell structure. The mixture was boiled at 80-85°C for 1 hour to get the dye solution, allowed to stand till it reached to room temperature and filtered to remove non dye plant remnants.

Ethanolic Extraction: Dye powder was soaked in 100% ethanol and heated in a beaker, in water bath at 45-50°C for 1 hour to get the dye solution, allowed to cool at room temperature and then filtered to remove non dye plant remnants**.**

Methanolic Extraction: 5 g of dye powder was soaked in 100 ml methanol at 45-50°C for 1 hour to get the dye solution and allowed to cool till it reached to room temperature. The solution filtered to remove non dye plant remnants and was sieved through fine mesh nylon cloth**.**
The extracts were sieved through fine nylon mesh and filtrate was collected for phytochemical analysis.

2. Phytochemical Analysis of the Dye Extract: The phytochemical analysis of the dye extract was done using standard procedure given by Edeogal *et al.* (2005) [6] and Selvi *et al.* (2011). The following analysis was done:

Alkaloids: Plant extracts were boiled with 1% aqueous HCl in water bath and filtered. The filtrate was treated with 2g iodine in 6g of KI (Potassium Iodide) in 100 ml distilled water. Formation of brown or reddish brown precipitate indicated presence of alkaloids.

Phenol: Phenols were tested by adding 2 ml of ferric chloride solution to 2 ml of plant extract. Appearance of bluish green colour solution indicated the presence of phenols.

Tannins: Few drops of 1% lead acetate were added to 5 ml of plant extract and appearance of yellow precipitate indicated the presence of tannins.

Saponins: 5ml of extract was boiled in 10 ml distilled water in a test tube and was shaken vigorously for about 30 seconds. The test tube was allowed to settle for half an hour, formation of froth indicated the presence of saponins.

Steroids: 1 ml dye extract was dissolved in 10 ml chloroform and equal volume of concentrated sulphuric acid was added from the walls of the test tube. Appearance of red colour in the upper layer with yellow with green fluorescence indicated the presence of steroids.

Cardiac Glycosides: 1 ml of dye extract was added in glacial acetic acid with few drops of ferric chloride followed by adding concentrated sulphuric acid from the walls of the test tube. Appearance of the reddish brown at the junction of two layers and the bluish green colour in the upper layer indicated the presence of cardiac glycosides.

Anthraquinones: 5 ml of dye extract was boiled with 10 ml of sulphuric acid and filtered while hot. The filtrate was shaken with 5 ml of chloroform. The chloroform layer was pipette out into another test tube and 1 ml of dilute ammonia was added. The resulting solution was observed for colour changes. The change in colour indicated the presence of anthraquinones.

Flavonoids: A few drops of dilute sodium hydroxide were added to 1 ml of extract. An intense yellow colour was observed which became colourless on addition of few drops of dilute acid. This indicated the presence of flavonoids.

Terpenoids: 1 ml of extract was dissolved in 1ml of chloroform and 1ml of acetic anhydride was added following the addition of 2 ml of concentrated sulphuric acid. Formation of reddish colour indicated the presence of terepenoids.

Reducing Sugar: Five to ten drops of Fehling solution were added in 1 ml of dye extract. Mixture was then subjected to boiling for 15 minutes, appearance of brick red precipitate indicated the presence of reducing sugar.

3. Application of biopolymer

Beta-Cyclodextrin: The surface modification of cotton fabric was carried out with beta cyclodextrin (0.75 g/l) and cross-linking agent (citric acid 0.25 g/l) at 80 ^{0}C for 60 minutes using 1:30 M:L Ratio. The treated samples were washed and dried.

Chitosan Application: Scoured cotton fabric was soaked in 1% chitosan solution (dissolved in 1% acetic acid (v/v) containing 6% citric acid and 6% sodium hypophosphite and squeezed in padding mangle for uniform fixing and dried at 80^{0}C for 10 minutes followed by fixing at 100^{0}C for 5 minutes (Sundrarajan *et al.*, 2012) [20]. *Sericin application:* Cotton sample was dipped in 0.50 percent sericin solution (owf) with 4% concentration of citric acid and 1% sodium hypophosphite using 1:30 material to liquor ratio at pH 8.0. The fabric was treated for 45 minute at 50^{0}C temperature. The fabric was passed between padding rollers, dried at 70^{0}C for 4 minutes and cured at 150^{0}C for 2 minutes (Bhandari, 2014) [4].

4. Dyeing Method: Dyeing of mordanted cotton samples was done with 5% dye owf using 1:30 M: L Ratio at 70 ^{0}C for one hour. The samples were washed with hot water followed by cold water and dried in shade (Annapoorani and Sundarraj, 2014 and Saravanan *et al.*, 2013) [1].

5. Percent dye Absorssption: Percent dye absorption was calculated using the following formula

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

6. Colour Measurement: The colours of dyed samples were measured numerically through computerized colour matching machine. The reference spectra of dyed samples were observed by using spectrophotometer SS5100A, K/S value and CIE LAB co-ordinates L*, a* and b* were noted down directly from the computer screen. This spectrophotometer uses CIE LAB (1976) colour space, D65 illuminate matching and appraisal and 420 nm wavelength to measure the actual colour and change in colour. The kubelka munk theory was used to predict the colour value.

$K/S = (1-R)^2/2R$

7. Assessment of Fastness to Washing of Dyed Fabrics: Wash fastness test was carried out as per recommendation of IS: 3361-1979 method (BIS, 1979). The nine- step scale consisting of half fastness rating was used. A piece of original dyed sample and the test specimen was placed side by side in the same plane. The light was incident upon the surfaces at approximate angle of 45^0 and the direction of viewing approximately perpendicular to the plane of surface. The visual differences were compared between the original and tested material with the difference represented by the Grey Scale.

Results

Preliminary Properties of Selected Fabric

The selected cotton fabric was enzymatically desized and scoured, resultant fabric was assessed for fabric count, weight and thickness. The data on preliminary properties in Table1 indicate that the fabric count of unscoured cotton fabric used for the study was 44 x 40 ends and picks per inch, weighing 140.4 g/m^2 with thickness 0.284 mm whereas the fabric count of desized and scoured fabric was 46 x 41 and 47x 43 ends and picks per inch, weighing 136.4 and 135.0 g/m^2 with thickness 0.276 and 0.232mm respectively.

Table 2: Preliminary properties of the cotton fabric

Samples	Preliminary properties			
	Fabric Count (ends and picks/ inch)		Weight (g/m^2)	Thickness (mm)
	Warp /Ends	Weft /Picks		
Unscoured	44	40	140.4	0.284
Desized	46	41	136.4	0.276
Scoured	47	43	135.0	0.232

Effect of enzymatic desizing and scouring on the whiteness and brightness index: The effect of enzymatic desizing and scouring treatment on the whiteness and brightness index of cotton fabric is presented through Figure 1. It was observed that after enzymatic desizing of cotton fabric, whiteness index increased from 81.27 to 83.19, brightness index from 70.11 to 70.80 whereas yellowness index decreased from -10.87 to -12.03. It was also noticed from the figure that after enzymatic scouring, the whiteness index increased from 81.27 to 85.40, brightness index from 70.11 to 72.63 and yellowness index decreased from -10.87 to -12.31. Vigneswaran *et al.* 2013 reported that the higher concentration of cellulase enzyme treated fabric showed higher brightness index due to surface smoothness of the organic cotton fabric. It was also noticed that pectinase and cellulase enzymes plays important role in brightness index of the bioscoured organic cotton fabrics.

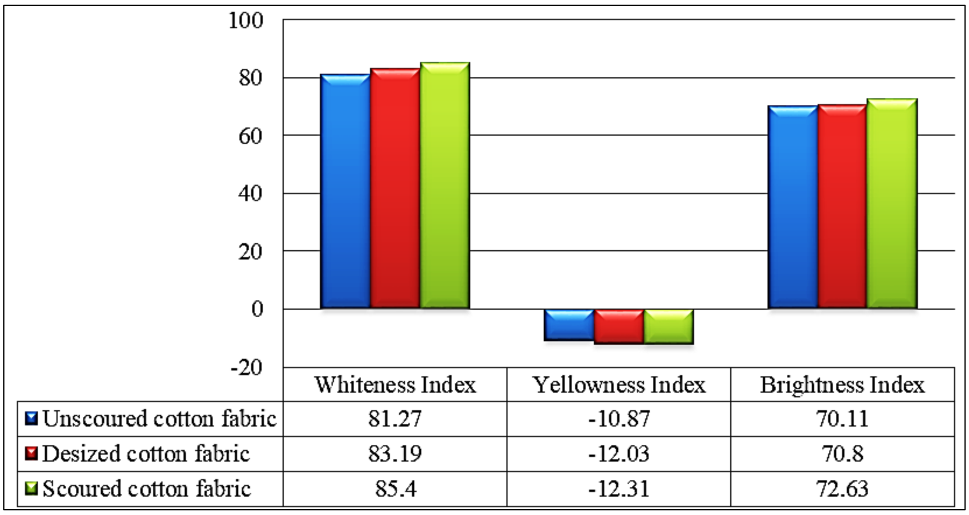


Fig 1: Effect of enzymatic preparatory processes on the whiteness and brightness of cotton fabric

Table 3: Phytochemical analysis of natural dye (Marigold Petals)

S. No.	Natural dyes	Extraction mediums	Phytochemicals									
			Phenol	Alkaloids	Steroids	Cardiac-glycosides	Terenoids	Tannins	Flavonoids	Anthraquinone	Saponins	Reducing Sugar
1.	Marigold petals	Aqueous	-	+	-	-	+		+	-	+	-
		Ethanol	-	+	+	+		+	-	-	+	-
		Methanol	-	-	+	-	+	+	-	-		+

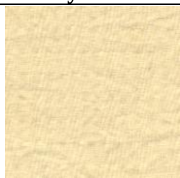
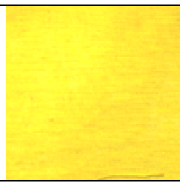
In the table 2 depicts the presence of phytochemicals in different mediums of extraction. In aqueous medium there was presence of alkaloids, terenoids, flavonoids and saponins. While the ethanol medium showed the presence of alkaloids, steroids, cardiac glycosides, tannins and saponins. In methanol extraction medium, steroids, terenoids, tannins and reducing sugar were present. It is clear from the table that the ethanol medium of extraction showed the more number of phytochemical presence as compared to methanol and aqueous extraction medium. But the aqueous medium of extraction was used to the due to the presence of colouring substance responsible for producing colour on textile material. Guinot *et al.*, 2008 [7] extracted flavonoids from marigold flowers and reported its dyeing potential.

Table 3: Selection of biopolymer and natural dye on the basis of colour properties

S. No.	Natural dyes	Alum treated fabric (control)			Biopolymers treated fabrics								
					Beta cyclodextrin			Chitosan			Sericin		
		% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades
1.	Marigold petals	50.25	9.68	4	49.22	8.84	3/4	50.25	10.51	4	49.74	8.87	4

It is clear from the Table 3 that amongst all three biopolymer treated samples dyed with marigold petal dye, chitosan treated samples exhibited highest percent dye absorption (50.25%), colour strength (10.51) and wash fastness grades was found same (4) for all biopolymer treated dyed fabric. Among these biopolymers the chitosan showed the highest dye absorption, colour strength and wash fastness rating with natural dye. This might be due to that the amino groups of chitosan were cationic in nature reacted more with dye anions. Kavitha *et al.* (2007) [10] stated that chitosan can be considered as multifunctional textile finishing agent because of its dyeing improvement function. Bashar and Khan (2013) [3] also found that the cotton fibres form cross-linking with chitosan facilitating positive dye sites on the fibre surface due to the formation of cationic sites for dye anions.

Table 4: Alum and biopolymer treated natural dyed (marigold petals) fabric.

S. No.	Plant Name	Treated and dyed fabrics fabrics			
		Alum	Beta-cyclodextrin	Chitosan	Sericin
1.	**Marigold** Botanical Name: *Calendula officinalis* Family: Calendulaeae				

Conclusion
Textile dyeing and printing industry is one of the most polluting sectors from an ecological point of view. There is need to approach new strategies, methods, material for dyeing treatment of cotton fabric with natural dyes using environment benign route. Chitosan treated marigold petals dyed fabrics enhanced colour properties without using any harsh chemicals and is capable enough to replace the use of salts in dyeing with natural dye.

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