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Dyeing, fastness and antimicrobial properties of woolen yarns dyed with gallnut (*Quercus infectoria* Oliv.) extract

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ABSTRACT

The present study was conducted to investigate the dyeing, fastness, and antimicrobial properties of woolen yarns using gallnut extract as a natural dye. Comparative results of color fastness (fastness to light, wash, and rub) and colorimetric properties (CIELab and color strength (K/S) values) of dyed woolen yarns were studied to quantify the effect of mordants. The antimicrobial activity of gallnut extract before and after application on woolen yarn was tested against common pathogens *Escherichia coli, Staphylococus aureus*, and *Candida albicans*. Gallnut extract proved very effective in inhibiting microbial growth, both in the solution phase as well as after application on wool. A reduction in antimicrobial activity was observed when mordanted samples were examined. The wash durability of antimicrobial activity was also evaluated after one, five, and ten washing cycles. The antimicrobial finish was found to be semi-durable.

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1. Introduction

Increasing environmental awareness has made people realise the importance of living in a world with a clean atmosphere. The major hindrance that comes en route to achieving this is posed by microorganisms, which are the causative sources of objectionable odour, stains, dermal infection, product deterioration, allergies and other related diseases. Textiles materials find immense applications in day-to-day life. Textiles, especially of natural origin, are susceptible to microbial attack, as these provide a large surface area and absorb moisture, which facilitates microbial growth. Hence, there has been growing demand to develop antimicrobial finishing for textile materials, which offer improved protection to users against microbes without destroying the desirable characteristics [1,2].

Nowadays, popularity of more natural lifestyle based on naturally sustainable goods is on the rise. The use of natural dyes for textile coloration has re-flourished due to their recently discovered deodorizing, antimicrobial [3], antifeedant [4] and UV protective [5] properties, in addition, to the sober and elegant shades on different

types of fabrics. Globally, considerable research work has already been done and is currently underway on textile coloration with natural dyes for assessment of dyeing, colorimetric and fastness properties [6–13]. A few researchers had also studied the antimicrobial properties of naturally dyed textile materials [14–18]. But, the available literature on the vast field of applications of natural dyes in textile coloration is very limited.

The oak gall is an abnormal growth on oak tree (*Quercus infectoria* Oliv.) provoked by the bite of female cynipid wasp (*Cynips Gallae-tinctoria*). Gall wasp punctures young twigs of oak tree and lays its eggs inside. The gall particles of *Q. infectoria* are gray-brown and globulous with a surface coating of stout, pointed spines, and they measure 6–10 mm in diameter. *Q. infectoria* is indigenous to Greece, Asia Minor, Syria, and Iran. The galls of *Q. infectoria* contain a mixture of gallotannin (Fig. 1a), gallic acid (Fig. 1b), ellagic acid (Fig. 1c), starch, and glucose as principal constituents (50–70%). The galls find extensive application in tanning, mordanting, dyeing, and manufacturing of ink. The main coloring component in gallnut extract is ellagic acid, which has an affinity for dyeing substrates due to the presence of –OH (auxochrome group) [19–21].

Q. infectoria is found to exhibit a variety of pharmacological properties such as astringent, anti-diabetic, anesthetic, antiviral, antifungal [21], antibacterial [22], larvicidal [23], anti-inflammation [24] and wound-healing [25] properties. The literature shows that

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Gallotannin

Fig. 1. Constituents of gallnut extract.

tannins, especially those of plant origin, have been found to possess antimicrobial activity [26]. The high tannin component present in oak galls might be responsible for its antimicrobial activity.

The purpose of this research is to study the dyeing, fastness, and antimicrobial properties of woolen yarns using gallnut extract as a natural dye. The fastness properties of dyed samples were obtained with respect to light, washing, and rubbing. CIELab and K/ S values were also recorded. The antimicrobial activity of gallnut extract before and after application on woolen yarn was tested against a gram-negative bacterium (Escherichia coli), gram-positive bacterium (Staphylococcus aureus), and common fungus (Candida albicans). The durability of antimicrobial activity towards washing was also examined.

2. Experimental

2.1. Materials

2.1.1. Wool yarn, dye and mordants

100% pure New Zealand Semi worsted woolen yarn (60 counts) was procured from MAMB Woolens Ltd. Bhadohi, S R Nagar Bhadohi (UP), India. Powdered gallnut dye was purchased from Sir Biotech India Ltd. Kanpur, India. Metallic salt mordants, stannous chloride (SnCl₂,2H₂O) and potash alum (K₂Al₂(SO₄)₄,24H₂O) were used for mordanting. Alum is comparatively safer mordant for use in dyeing of textile materials [27,28]. All chemicals used were of Laboratory grade.

2.1.2. Strains and media

For antimicrobial testing, two bacteria namely E. coli MTCC 443(Gram negative), S. aureus MTCC 902 (Gram positive) and yeast (C. albicans ATCC 10261) were selected due to their popularity and suitability of being selected as test organisms. Bacterial stock cultures were cultured in McConky agar (HiMedia, India) at 4 °C, whereas fungal stock culture was maintained on slants of nutrient agar (yeast extract 1%, peptone 2%, p-glucose 2% and agar 2.5%). To initiate growth for experimental purposes, one loop full of cells from an agar culture was inoculated into 25 mL of respective nutrient media and incubated at 30-37 °C for 24 h i.e., up to stationary phase (primary culture). Cells from primary culture (10⁸ cells mL⁻¹) were re-inoculated into 100 mL fresh YPD medium and grown for 8-10 h i.e., upto mid-log phase (10^6 cells mL⁻¹).

Ellagic acid

2.2. Methods

2.2.1. Mordanting and dveing

Woolen yarns were mordanted by pre-mordanting method using stannous chloride (1% o.w.f.) and potash alum (10% o.w.f.) as mordants. Before the application of mordants, woolen yarns were soaked in water and mordants were dissolved in water in separate baths, and liquor ratio (M:L) for mordanting was kept at 1:40. Water soaked woolen yarn samples were immersed in mordants solutions. Temperature of both mordant baths was raised till simmering point (91–93 °C) and left at that temperature for 1 h with constant stirring. Mordanted woolen yarn samples were rinsed with tap water to remove superfluous mordants (unused).

Dyeing experiments were performed using M:L (material to liquor) ratio of 1:40 in separate baths with manual agitation at acidic pH (pH 4) using 6% and 12% o.w.f. (on the weight of fabric/ yarn) dye concentrations. Woolen yarns were drenched to dyeing baths containing warm dye solution. Dye bath temperatures were raised to simmering point (91–93 $^{\circ}$ C) and maintained at that level for 1 h. Dyed samples were treated with 5 mL/L non-ionic detergent (Safewash Wipro), rinsed with tap water and dried in shade.

2.2.2. Determination of dye exhaustion

Dye uptake was determined by measuring the absorbance (at wavelength of maximum absorbance, $\lambda_{\rm max} \approx 450$ nm) of dye bath solution before and after dyeing. The % dye exhaustion was calculated by the given formula:

% Dye exhaustion =
$$[(A_0 - A_1)/A_0] \times 100$$
 (1)

Where, A_0 and A_1 are absorbance of dye before and after dyeing respectively.

2.2.3. Color measurement

The colorimetric properties of dyed woolen yarn samples were obtained with Gretag Macbeth Color-Eye 7000 A Spectrophotometer in terms of CIELab values (L^* , a^* , b^* , c^* , h^0) and color strength (K/S). The color strength (K/S) in visible region of the spectrum (400–700) was calculated based on Kubelka–Munk equation:

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

Where (K) is adsorption coefficient, (R) is reflectance of dyed sample and (S) is scattering coefficient.

Total color difference of dyed woolen yarn samples were obtained using following relationships:

Color Difference
$$(\Delta E) = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$
 (3)

where $\Delta L = L^*_{mordanted} - L^*_{unmordanted}$; $\Delta a = a^*_{mordanted} - a^*_{unmordanted}$; $\Delta b = b^*_{mordanted} - b^*_{unmordanted}$; 'L' describes lightness, 'a' measures redness (+ve) or greenness (-ve) and 'b' measures yellowness (+ve) or blueness (-ve).

2.2.4. Color fastness tests

The light fastness of dyed woolen yarn samples were conducted on Digi light Nx[™] having water cooled Mercury Blended Tungsten lamp, as per test method AATCC 16e-1993 (2004) similar to ISO 105-B02:1994 (Amd.2:2000) and ratings were given on 1–8 grey scale. The wash fastness of the dyed woolen yarn samples were measured in Digi wash SS[™] (Launder-o-meter) as per the ISO 105-C06:1994 (2010) specifications. Samples were also assessed for staining on white adjacent fabrics (wool and cotton). Dry and wet rub fastness of dyed woolen yarn samples were tested using a Digi crock[™] (Crockmeter) as per Indian standard IS 766:1988 (Reaffirmed 2004) based on ISO 105-X12:2001 by mounting the fabric on panel and giving ten strokes for both dry and wet rub fastness tests.

2.2.5. Antimicrobial activity of gallnut extract in solution

2.2.5.1. Minimum inhibitory concentration. The Minimum Inhibitory Concentration (MIC) was determined by *in vitro* susceptibility tests using standard methods described in the guidelines of document NCCLS/CLSI M11-A6 [29] for gram negative, document CLSI M100-S15 [30] for gram positive, and document NCCLS M27-A2 [31] for yeast. The effect of dye concentration (0.01–5% w/v) on antimicrobial activity was assessed.

2.2.5.2. Disc diffusion assay. Strains were inoculated into liquid YPD (Yeast extract, Peptone, Dextrose) medium and grown overnight at 35 °C. The cells were then pelleted and washed three times with distilled water. Approximately 10⁵ cells/mL were inoculated in molten agar media at 40 °C and poured into 100-mm-diameter petriplates. Filter discs were kept on solid agar and dye was spotted on discs. Test compound dissolved in double distilled water with

final concentrations of 1%, 5% and 10% (w/v), or control (distilled water) was pipetted onto 4-mm-diameter filter disc.

The diameter of zone of inhibition was measured in millimeters after 48 h, and compared with that of control.

Index of sensitivity was defined as:

\(\sum_{\text{Zone diameter (mm)/concentration (mg/mL)}} \) = \(\text{clearing (mm/mg)} \)

Values were shown in terms of Mean \pm standard error of all three respective categories.

2.2.5.3. Growth studies of microbes. Growth studies of tested microorganisms were done as described earlier [32] with slight modifications. Prior to testing, test microorganisms were subcultured at least twice and grown for 24 h at 35 °C on SDA plates. For growth studies, 10^6 cells (optical density $A_{600} = 0.1$) of test strains were grown aerobically in 50 mL media on automated shaker set at 35 °C with agitation of $200 \times \text{rpm}$. Q. infectoria dye with final concentrations of 6% and 12% w/v aqueous solution of dye along with negative and positive controls (1% w/v of ampicillin for both bacteria and 1% w/v of fluconazole for fungus) for each test isolate were also added to the cultures. Aliquots were removed at pre-determined time points (after every 2 h) for 24 h and growth was followed turbidometrically at 595 nm using LABOMED Spectrophotometer (USA). Optical density was recorded for each concentration against time.

2.2.6. Determination of antimicrobial activity of dyed yarn

Antimicrobial efficacy of dyed woolen yarn was carried out using absorbance method by recording the optical density of incubated culture medium at 595 nm. Enhancement in microbial growth is directly proportional to turbidity and optical density, which are directly related to the number of microbial cells in media [2,15,17,33].

Susceptibility test of microbial strains to the gallnut dyed woolen yarn and mordanted wool were done by introducing 1 inch² dyed yarn in 50 mL nutrient broth inoculated with a desired microbe and incubated overnight at 37 °C. A broth was inoculated similarly with distilled water as control.

The reduction of microbial growth by dyed yarn was expressed as follows:

$$R = B - A/A \times 100$$

Where R = % reduction in microbial population; B = absorbance (595 nm) of media inoculated with microbe and undyed yarn; A = absorbance (595 nm) of media inoculated with microbe and dyed yarn.

2.2.7. Determination of durability of antimicrobial finishing to washing

Antimicrobial activity of dyed woolen yarn was evaluated after several washing cycles and durability of antimicrobial finishing was calculated in terms of % retention of antimicrobial activity by using formula:

% Retention of antimicrobial activity
$$=\frac{R_n}{R_0} \times 100$$

where, $R_n = \%$ microbial reduction after n wash cycles and $R_0 = \%$ microbial reduction before washing.

2.3. Statistical analysis

Each experiment was performed twice in triplicate. Results obtained were expressed in terms of mean \pm standard error.

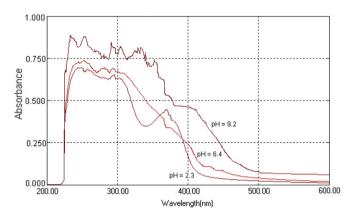


Fig. 2. UV-Visible spectra of aqueous solution of gallnut extract at different pH.

Statistical analyses were performed and P value \leq 0.05 was considered significant.

3. Results and discussion

The UV-Visible spectra of gallnut extract solution at different pH (Fig. 2) shows that the absorbance value is low at lower pH. The gallnut dye exhibited sensitivity towards pH. As pH increases, wavelength of maximum absorption shifts towards red end of spectrum (bathochromic shift). Higher absorbance values at higher pH indicate that the color of dye solution intensifies with increasing pH.

3.1. Dye exhaustion

The amounts of dye uptake by woolen yarn samples were expressed as % dye exhaustion and results are shown in Fig. 3. Higher exhaustion was observed at low dye concentration. Mordanting increased dye exhaustion to a significant extent. Tin mordant was more found to be helpful in increasing dye exhaustion. Maximum exhaustion was observed in case of tin mordanted samples followed by alum and unmordanted woolen yarn samples.

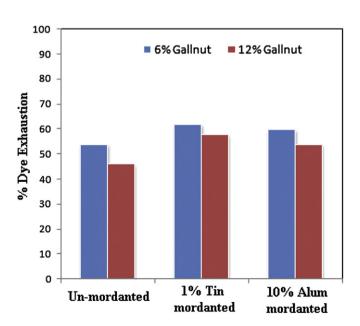


Fig. 3. Effect of mordants on dye exhaustion.

Table 1CIELab values of dved woolen varn samples.

Dye (Q. infectoria)	Mordant	L*	a*	b*	c*	hº	ΔΕ
6%	Unmordanted	77.57	2.1	20.88	20.98	84.25	_
	1% SnCl ₂	74.03	2.01	23.07	23.15	85.02	4.16
	10% Alum	77.38	0.94	24.49	24.5	87.8	3.79
12%	Unmordanted	73.05	2.99	21.26	21.46	81.99	_
	1% SnCl ₂	74.14	1.65	23.2	23.25	85.93	2.59
	10% Alum	75.43	2.24	25.05	25.14	84.89	4.53

The difference in exhaustion rate was due to the difference in interaction between fibre-mordant-dye.

3.2. Colorimetric properties

CIELab and CIELch values of woolen yarn samples dyed with gallnut extract are given in Table 1. Application of gallnut extract produced light yellow shades, having hue angle ranging between 80° and 90° for unmordanted as well as mordanted samples, with high lightness (L*) and low chroma (c^*) values indicating light and bright shades. Mordanting has little effect on colorimetric properties as marginal changes were observed in L*, a*, b*, c* and h⁰ values for mordanted samples in comparison to unmordanted ones. From a^*-b^* plot (Fig. 4), it can be seen that mordanted samples were found a little shifted towards yellow co-ordinate in red yellow zone of CIELab color space. Shift towards yellow co-ordinate was higher in case of alum mordanted samples. In general, all samples dyed with lower dye concentration were light, bright, and less saturated (higher L* and lower c* values) than samples dyed with higher dye concentration. The force responsible for dye transfer from dye bath to fibre is function of concentration gradient of dye in two phases (dye solution and fibre). Extent of dye transfer from solution to wool substrate enhanced with increase in dye bath concentration, and thus apparent depth of shades also increased. Fig. 5 is representation of color strength in terms of K/S values for all dyed woolen yarn samples. When alum and tin mordants were used color became more intense resulting in higher K/S values. Relatively high value of K/S for mordanted samples underlines the

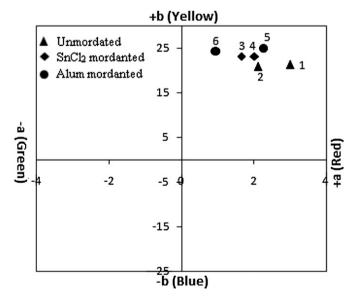


Fig. 4. a^*-b^* plot of dyed woolen yarns. (1) 12% gallnut, (2) 6% gallnut, (3) 1% $SnCl_2+12\%$ gallnut, (4) 1% $SnCl_2+6\%$ gallnut, (5) 10% alum + 12% gallnut, (6) 10% alum + 6% gallnut.

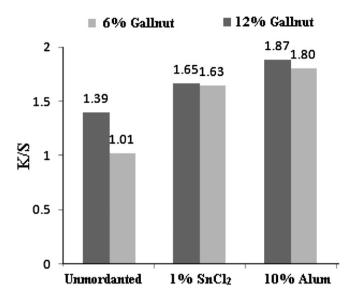


Fig. 5. Effect of mordants on color strength K/S graph of gallnut dyed woolen yarns.

fact, that metallic mordants have significantly increased dye exhaustion. Alum mordant has more prominent effect on color strength than tin mordant. Color difference values (ΔE) given in Table 1 show slight change in color for mordanted samples.

3.3. Fastness properties

Fastness properties of dyed woolen yarn samples are given in Table 2. All samples have shown good light and wash fastness. Tin and alum mordants have no effect on light and wash fastness values. Dry rub fastness was found to be relatively better than wet rub fastness. Rub fastness data indicate that mordanting have increased resistance of transfer of color to adjacent fabrics (cotton and wool).

3.4. Antimicrobial activity of gallnut extract in solution

Antimicrobial (antibacterial and antifungal) activities of gallnut dye when compared with standard antibacterial and antifungal drugs (Ampicillin and Fluconazole) proved significant and conforming to the requirements.

3.4.1. Minimum inhibitory concentration (MIC)

The MIC of dye was determined against two bacterial and one fungal species using micro-broth dilution method. The minimum inhibitory concentration (MIC) of dye against bacteria was observed to be 0.62% w/v, whereas that of fungi was observed to be as low as 0.3% w/v.

3.4.2. Disc diffusion assay

The results of disc diffusion assay are given as index of sensitivity in Table 3. All the tested microbes showed high degree of

Table 2 Fastness properties of dyed sample.

Dye (gallnut)	Mordant	Light fastness	Wash fastness		Rub fastness		
			c.c.	c.s.	c.w.	Dry	Wet
6%	Un-mordanted	5	5	5	5	4	3
12%		5	5	5	5	4	3-4
6%	1% SnCl ₂	5	5	5	5	5	4
12%		5	5	5	5	4-5	3 - 4
6%	10% Alum	5	5	5	5	5	4
12%		5	5	5	5	4-5	3-4

Table 3Sensitivity index of inhibition zone (mm) to the concentration (mg/mL) of the *Q. infectoria extract* in all tested isolates

Isolates	Q. infectoria dye
	Sensitivity index
E. coli	9.6 ± 0.01
S. aureus	13.64 ± 0.07
C. albicans	18.2 ± 0.03

sensitivity as evident from zone of clearance (Fig. 6). Highest index of sensitivity (18.20) was shown in case of fungal isolate (*C. albicans*). Bacterial isolates showed less sensitivity to gallnut extract. Dye was found more active against gram (+ve) bacterium, *S. aureus* (13.64) than gram (-ve) bacterium, *E. coli* (9.6).

3.4.3. Growth studies

Fig. 7 represents growth rates of *E. coli*, *S. aureus* and *C. albicans* in the presence of *Q. infectoria* extract at 6% and 12% (w/v) dye concentrations. Absorbance obtained for growth control (only organism) showed that test cultures reached stationary growth phase after 16 h showing a normal growth pattern. The curve depicts a lag phase in initial phase of growth, active log phase and stationary phase. All test microorganism isolates were found to be susceptible to the test dye. It is observed from Fig. 7 that at higher gallnut dye concentration more inhibitory effect is shown than corresponding commercial antimicrobials. Dye has shown inhibitory effect of more than 90% reduction in microbial growth against all tested microbes.

3.5. Antimicrobial activity of gallnut dyed woolen yarn

Since gallnut extract proved quite active against all tested microbes in solution phase, it was thought worthwhile to test bioactivity after application on wool substrate. Since most of natural dyes need mordants to increase affinity between dye and fibre, antimicrobial activity of mordanted woolen yarn dyed with different concentrations of dye was also tested. Commercial antimicrobials (ampicillin for bacteria and fluconazole for yeast) were also studied for comparison. Quantitative evaluation of antimicrobial activity on woolen yarns was done by spectroscopic assessment. The comparative results were summarized in Table 4. Results obtained were quite satisfactory since gallnut treated woolen yarn samples have shown very high activity against both bacterial as well as fungal strains.

The antibacterial activity of gallnut dyed samples against E. coli and S. aureus are presented in Fig. 8(a) and (b), which shows that bacterial reduction is better in case of both the bacteria. From the above figures it is clear that varns dved with gallnut alone without mordants exhibit higher activity than mordanted samples. Antibacterial activity of dyed samples increased with dye concentration. At higher concentration of dye (12% o.w.f), 82-87% reduction in E. coli population and 91–95% reduction in S. aureus population was observed; whereas at lower dye concentration (6% o.w.f), microbial reduction was found to be 69–78% in E. coli and 61–77% in S. aureus. The antifungal activity of gallnut dyed samples against C. albicans is presented in Fig. 8(c). C. albicans was found to be very sensitive to gallnut extract. At higher dye concentration (12% o.w.f), 87–96% fungal reduction was observed; while 74–84% fungal reduction was observed for samples dyed with 6% o.w.f dye concentration. It is worth to note that at higher dye concentration unmordanted dyed yarns showed almost equal fungal reduction as commercial antifungal agent used in this study (fluconazole). Mordants were found to have little inhibitory effect on growth of microbes as observed from Fig. 8. Alum mordant was found slightly

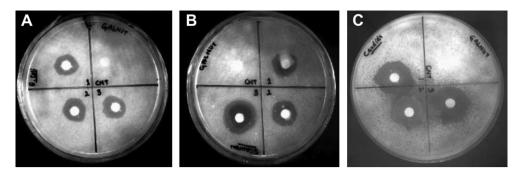


Fig. 6. Disc diffusion assay of E. coli (Panel-A), and S. aureus (Panel-B) C. albicans (Panel-C) treated with different concentrations of gallnut extract dye (1%, 5% and 10%).

more active against both bacterial as well as fungal isolates than tin mordant. The reduction % values exhibited by mordanted dyed samples were found to be lower than those reported in case of unmordanted samples. However, this decrease in antimicrobial activity is more apparent in alum mordanted samples than tin mordanted samples. This could be the consequence of variable complex forming abilities of different metal ions with active functional groups of dye.

3.6. Durability of antimicrobial finishing to washing

Durability of antimicrobial activity to washing is one of the major concerns of textile researchers and users, because textiles are subjected to frequent laundering. Antimicrobial activity imparted by gallnut extract was found semi-durable to washing against all the tested microbes; however, washing has almost negligible effect on color of dyed yarns. Durability of antimicrobial activity of

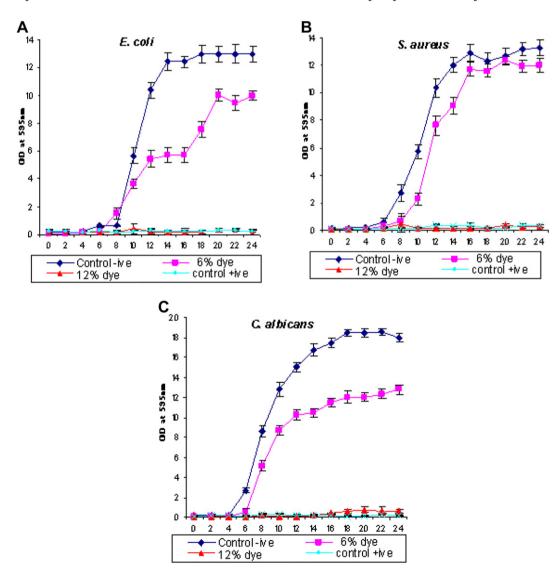


Fig. 7. The effect of various concentrations of the dye on the growth of (A) *E. coli*, (B) *S. aureus and* (C) *C. albicans*. The cells were grown with 0% dye (Control –ve), 1% w/v of ampicillin for bacteria and 1% w/v of fluconazole for yeasts (Control +ve), 6% dye and 12% dye.

Table 4 Antimicrobial activity of gallnut dyed wool yarn.

Microbe		% Microbial reduction							
	Blank	Ampicillin/Fluconazole	Untreated wool	6% gallnut			12% gallnut		
				Unmordanted	1% SnCl ₂	10% Alum	Unmordanted	1% SnCl ₂	10% Alum
E. coli	0	95.9	0.7	78.6	72.4	69.1	87.2	83.6	82.4
S. aureus	0	98.2	3.8	76.6	69.4	60.7	94.8	91.3	93.2
C. albicans	0	97.9	6.8	84.3	77.4	74.6	96.2	90.2	87.8

finished yarns was obtained after one, five and ten washing cycles and its data is presented in Table 5. Mordanting has a negative effect on antimicrobial reduction, but found very effective in increasing retention capability of bioactivity. The high fastness obtained for mordanted samples also support this finding. It is because of the fact that mordant acts as a link between dye and fibre and improves the anchorage of dye molecules to the fibre. Fig. 9 shows that washing durability of antimicrobial finishing of unmordanted samples was low. After five washings yarns dyed with 12% gallnut can retain 65–80% activity, and after 10 washings antimicrobial activity decreased to 45–55% from original activity. Fig. 9 showed that, mordanted samples have shown better washing

durability, after five washings tin mordanted samples can still retain 78-92% activity, but after 10 washings the activity retention drops to 60-70%. However, alum treated samples had shown moderate retention capability, ranging between 75 and 90% activity retention after 5 washings and 58-72% activity retention after ten washing cycles.

3.7. Cost analysis

The cost of natural dyeing of per kg of woolen yarn has been calculated on laboratory scale and listed in Table 6. Both tin as well as alum mordanting has almost equal effect on dyeing and

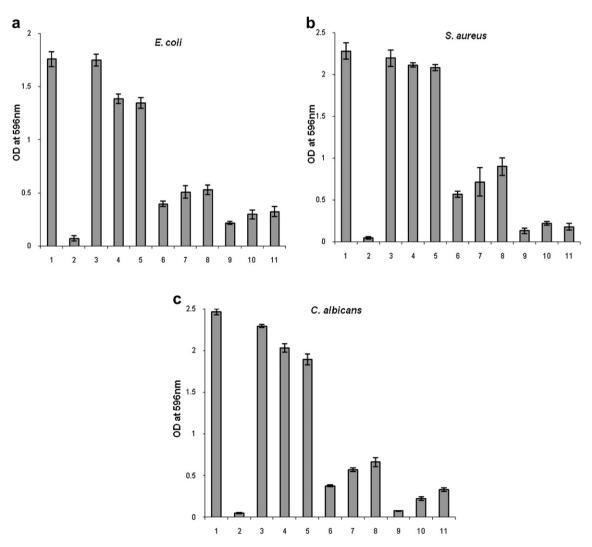
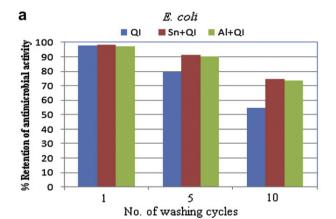
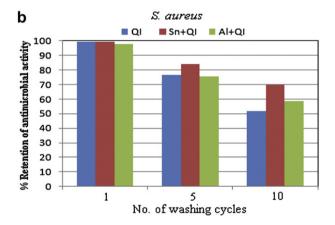


Fig. 8. Antimicrobial activity of the woolen yarn treated with gallnut extract. Bar 1 represents the control cells without any treatment; 2 represents the treatment of cells with their respective known available antimicrobial agent; 3 is untreated wool; 4 & 5 represents 1% Sn & 10% alum, 6, 7 & 8 represents wool yarn treated with 6% gallnut, 1% Sn + 6% gallnut & 10% alum + 6% gallnut respectively; 9, 10 & 11 represents wool yarn treated with 12% gallnut, 1% Sn + 12% gallnut & 10% alum + 12% gallnut, respectively.

Table 5Durability of antimicrobial finishing to washing.

Test microbe	Woolen yarn treated with	% Microbial reduction			
		After 'n' washing cycles		ycles	
		1	5	10	
E. coli	12% QI	85.3	69.8	47.9	
	1% SnCl ₂ + 12% QI	82.1	76.2	62.2	
	10% Alum + 12% QI	80.3	74.5	60.5	
S. aureus	12% QI	92.4	74.2	49.9	
	1% SnCl ₂ + 12% QI	90.6	76.7	63.9	
	10% Alum + 12% QI	91.4	70.4	54.5	
C. albicans	12% QI	95.8	64.9	46.9	
	1% SnCl ₂ + 12% QI	89.8	70.6	58.1	
	10% Alum + 12% QI	86.3	74.1	56.8	





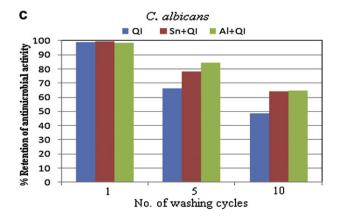


Fig. 9. % Retention of antimicrobial activity to washing.

Table 6Cost of gallnut natural dyeing (in Indian Rupees and US Dollar) per kg of woolen yarn.

Shade	Cost (Rupees) per kg of woolen yarn	Cost (U\$) per kg of woolen yarn
6% Gallnut (Unmordanted)	30-35	0.67-0.78
12% Gallnut (Unmordanted)	60-65	1.34-1.45
1% Stannous chloride + 6% Gallnut	45-50	1.00-1.11
1% Stannous chloride 12% Gallnut	80-85	1.78 - 1.89
10% alum + 6% Gallnut	35-40	0.78 - 0.89
10% alum + 12% Gallnut	65-70	1.45 - 1.56

antimicrobial properties of gallnut dyed woolen yarns, but cost of alum pre-mordanted shades proved far better than tin mordanted samples. Dyeing with gallnut extract was found bit costly but considering non-toxic nature of dyed material, natural feeling, and biodegradability, the cost offered in natural dyeing could be compromised and gallnut extract can be used in dyeing and bioactive finishing of textile materials.

4. Conclusion

The study successfully investigated the possibility of dyeing and antimicrobial finishing of wool yarn with gallnut extract. A common dyeing process imparts both color as well as antimicrobial property to dyed substrate.

Following conclusions were drawn on the basis of above study:

- Gallnut extract can be applied on woolen yarn with or without mordants to produce bright ivory to light brownish yellow color with good fastness properties against light, washing and rubbing.
- Gallnut extract exhibits high activity against *E. coli, S. aureus* and *C. albicans* in solution and retains its activity when applied on woolen yarn. Dye was found to be most active against *C. albicans* followed by *S. aureus* and *E. coli*.
- The antimicrobial activity of gallnut-dyed wool is semidurable. Mordanting with metal salt mordants has a negative effect on antimicrobial activity of dyed samples, however, durability of antimicrobial finishing improved considerably after mordanting.

Thus a non-toxic, eco-friendly, antimicrobial finishing with better durability has been developed for woolen yarns, which may prove an alternative to very expensive and sometimes toxic synthetic antimicrobial textile finishing agents presently available in market.

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References

- Cardamone JM. Proteolytic activity of Aspergillus flavus on wool. AATCC Rev; 2002:30-5.
- [2] Singh R, Jain A, Panwar S, Gupta D, Khare SK. Antimicrobial activity of some natural dyes. Dyes Pigm 2005;66:99–102.
- [3] Lee Y, Hwang E, Kim H. Colorimetric assay and antibacterial activity of cotton, silk and wool fabrics dyed with peony, pomegranate, clove, Coptis chinenis and gallnut extracts. Materials 2009;2:10–21.

- [4] Kato H, Hata T, Tsukada M. Potentialities of natural dyestuffs as antifeedants against varied carpet beetle, Anthrenus verbasci. [ARO 2004;38(4):241–51.
- [5] Grifoni D, Bacci L, Zipoli G, Carreras G, Baronti S, Sabatini F. Laboratory and outdoor assessment of UV protection offered by Flax and Hemp fabrics dyed with natural dyes. Photochem Photobiol 2009;85:313—20.
- [6] Gulrajani ML, Srivastava RC, Goel M. Color gamut of natural dyes on cotton yarns. Color Technol 2001;117:225–8.
- [7] Betchtold T, Turcanu A, Ganglberger E, Geissler S. Natural dyes in textile dyehouses – how to combine experiences of two centuries to meet the demands of the future? J Clean Prod 2003;11:499–509.
- [8] Khan MA, Khan M, Srivastava PK, Mohammad F. Extraction of natural dyes from myrobalan, gallnut, and pomegranate and their application on wool. Colourage; 2005:53–60.
- [9] Kamel MM, El-Shishtawy RM, Yussef BM, Mashaly H. Ultrasonic assisted dyeing III. Dyeing of wool with lac as a natural dye. Dyes Pigm 2005;65: 103-10.
- [10] Nagia FA, El-Mohamedy RSR. Dyeing of wool with natural anthraquinone dyes from Fusarium oxyporum. Dyes Pigm 2007;75:550—5.
- [11] Vankar PS, Shanker R, Mahanta D, Tiwari SC. Ecofriendly sonicator dyeing of cotton with Rubia cordifolia Linn. using biomordants. Dyes Pigm 2008;76: 207–12.
- [12] Samanta AK, Agrawal P. Application of natural dyes on textiles. Indian J Fibre Text Res 2009;34:384–99.
- [13] Zarkogianni M, Mikropoulu E, Varella E, Tsatsaroni E. Color and fastness of natural dyes: revival of traditional dyeing techniques. Color Technol 2010; 127:18–27.
- [14] Han S, Yang Y. Antimicrobial activity of wool fabric treated with curcumin. Dyes Pigm 2005;64:157–61.
- [15] Gupta D, Khare SK, Laha A. Antimicrobial properties of natural dyes against Gram-negative bacteria. Color Technol 2004;120:167-71.
- [16] Gupta D, Laha A. Antimicrobial activity of cotton fabric treated with Quercus infectoria extract. Indian | Fibre Text Res 2007;32:88–92.
- [17] Khan MI, Ahmad A, Khan SA, Yusuf M, Shahid M, Manzoor N, et al. Antimicrobial activity of catechu and its dyed substrate. J Clean Prod 2011;19: 1385—94
- [18] Yusuf M, Ahmad A, Shahid M, Khan MI, Khan SA, Manzoor N, et al. Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (*Lawsonia inermis*). J Clean Prod 2012; 27:42-50.

- [19] Wealth of India raw materials, Vol. VIII. CSIR; 1969. Ph-Re351-352.
- [20] Onal A, Sari A, Soylak M. Ellagic acid from gallnut (*Quercus infectoria*): extraction and determination of its dyeing conditions for natural fibres. J Sci Ind Res 2005:64:491–5.
- [21] Soon LK, Hasni E, Law KS, Waliullah SS, Farid CG, Syed Mohsin SSJ. Ultrastructural findings and elemental analysis of *Quercus infectoria Oliv*. Ann Microsc 2007;7:32–7.
- [22] Basri DF, Fan SH. The potential of aqueous and acetone extracts of galls of Quercus infectoria as antibacterial agents. Indian | Pharmacol 2005;37:26–9.
- [23] Redwane A, Lazrek HB, Bouallam S, Markouk M, Amarouch H, Jana M. Larvicidal activity of extracts from *Quercus Lusitania* var. *infectoria* galls (Oliv.). | Ethnopharmacol 2002;79:261–3.
- [24] Kaur G, Hamid H, Ali A, Alam MS, Athar M. Antiinflammatory evaluation of alcoholic extract of galls of *Quercus infectoria*. J Ethnopharmacol 2004;90: 285–92.
- [25] Umachigi SP, Jayaveera KN, Kumar CKA, Kumar GS, Swamy BMW, Kumar DVK. Studies on wound healing properties of Quercus infectoria. Trop J Pharm Res 2008;7(1):913–9.
- [26] Min BR, Pinchak WE, Merket R, Walker S, Tomita G, Anderson RC. Comparative antimicrobial activity of tannin extracts from perennial plants on mastitis pathogens. Sci Res Essays 2008;3(2):66–73.
- [27] Buchhanan R. Mordant safety in dyes from nature: plants & gardens. Brooklyn, New York: Brooklyn Botanic Garden Record; 1990. 89–90.
- [28] Subramanian S, Phalgumani GR. Eco-friendly Textiles: Important Issues for Exports in Seminar on Eco-friendly Textiles: Challenges to the Textile Industry. Textile Committee, Ministry of Textiles, Govt. of India; 1995. 1–10.
- [29] CLSI/NCCLS, Methods for Antimicrobial Susceptibility Testing of Anaerobic Bacteria; Approved Standard, 6th ed. M11–A6; 2004.
- [30] CLSI. Performance Standards for Antimicrobial Susceptibility Testing; Approved Standard M100—S15. Wayne, PA: Clinical and Laboratory Standards Institute; 2005.
- [31] NCCLS. Reference Method for Broth Dilution Antifungal Susceptibility Testing of Yeasts; Approved Standard M27—A2. Wayne, PA: National Committee on Clinical Laboratory Standards; 2002.
- [32] Khan A, Ahmad A, Manzoor N, Khan LA. Antifungal activities of Ocimum sanctum essential oil and its lead molecules. Nat Prod Commun 2010;5(2): 345–9
- [33] Calis A, Celik GY, Katircioglu H. Antimicrobial effect of natural dyes on some pathogenic bacteria. Afr J Biotechnol 2009;8(2):291–3.