Shubham Joshi[1], Vinay Midha[1], Subbiyan Rajendran[2]
[1] Dr B. R. Ambedkar National Institute of Technology, Department of Textile Technology, Jalandhar,144011, India
[2] The University of Bolton, Institute for Material Research and Innovation, Bolton, BL3 5AB, United Kingdom

Investigation of Durable Bio-polymeric Antimicrobial Finishes to Chemically Modified Textile Fabrics Using Solvent Induction System

Raziskava trajnih biopolimernih protimikrobnih apretur za kemijsko plemenitenje tekstilij z uporabo indukcijskega sistema s topilom

Original scientific article/*Izvirni znanstveni članek*
Received/*Prispelo* 8-2020 • Accepted/*Sprejeto* 10-2020

Corresponding author/*Korespondenčni avtor:*
Mr. Shubham Joshi
E-mail: shubhambmjoshi@gmail.com
Telephone: +917814086011
ORCID: 0000-0003-0292-5317

Abstract
New technologies and materials required for developing antibacterial textiles have become a subject of interest to the researchers in recent years. This study focuses on the investigation of the biopolymeric antibacterial agents, such as neem, aloe vera, tulsi and grapeseed oil, in the trichloroacetic acid-methylene chloride (TCAMC) solvent used for the pretreatment of polyethylene terephthalate (PET) polyester fabrics. Different PET structures, such as 100% polyester, polyester/viscose, polyester/cotton and 100% texturised, are treated with four different concentrations (5%, 10%, 15% and 20%) of biopolymeric antibacterial finishes. The antibacterial activity of the treated samples is tested against both the *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) bacteria. Taguchi mixed orthogonal array Design L16 (4^3 2^2) is chosen for an experimental plan to determine the optimum conditions. Among all the fabric samples, the 100% polyester fabric treated with 20% grapeseed oil registers the highest antibacterial activity of 86%, and 73% against *S. aureus* and *E. coli* respectively. However, the antibacterial effect is reduced to 37%, and 34% respectively after 10 machine launderings.
Keywords: solvent induced polymerisation, polyester and polyester blends, natural extracts, antibacterial activity, trichloroacetic acid-methylene chloride

Izvleček
Nove tehnologije in sredstva za razvoj protibakterijskih tekstilij so v zadnjih letih v središču zanimanja raziskovalcev. Ta študija se osredinja na raziskave biopolimernih protibakterijskih sredstev, kot so indijska melija, aloe vera, sveta bazilika in olje grozdnih pešk, na poliestrskih tkaninah, predhodno obdelanih s topilom trikloroocetne kisline in metilenklorida (TCAMC). Tkanine iz 100-odstotnega poliestra, poliestra/viskoze, poliestra/bombaža in iz 100-odstotnega teksturiranega poliestra so bile obdelane z biopolimernimi protibakterijskimi sredstvi štirih različnih koncentracij (5 %, 10 %, 15 % in 20 %). Protibakterijsko delovanje obdelanih vzorcev je bilo preizkušano proti bakterijama Staphylococcus aureus (Grampozitivna bakterija) in Escherichia coli (Gramnegativna bakterija). Eksperimentalni načrt za določitev optimalnih pogojev je bil izdelan z uporabo Taguchijevega mešanega pravokotnega niza L16 (4^3 2^2). Med vsemi vzorci je imela

tkanina iz 100-odstotnega poliestra, obdelana z 20-odstotnim oljem iz grozdnih pešk, najvišjo, 86-odstotno protibakterijsko aktivnost proti S. aureus in 73-odstotno aktivnost proti E. coli. Protibakterijski učinek po desetih laboratorijskih pranjih se je zmanjšal na 37 oziroma 34 odstotkov.
Ključne besede: polimerizacija v raztopini, poliester, mešanice s poliestrom, naravni ekstrakt, protibakterijska aktivnost, trikloroocetna kislina-metilenklorid

1 Introduction

It is well established that textiles are used by pathogenic microorganisms to promote and spread diseases. The microorganisms also produce a range of unwanted effects, including unpleasant odour, stains, allergies, and affect the colour and tensile properties of the fabric [1–2]. Most of the textiles currently used in hospitals and hotels are prone to cross-infection or transmission of diseases caused by micro-organisms, particularly by pathogenic bacteria and fungi [2]. In view of this, prevention of microbial growth has become increasingly crucial and it demands the development of fabrics that possess a desired antimicrobial effect. Antimicrobial finishes also improve the performance and durability of textile products. With the aim to develop antimicrobial textile materials, considerable research has been carried out by making use of organic and inorganic compounds, such as Triclosan, which inhibits the growth of microorganisms using an electrochemical mode of action to penetrate and disrupt their cell walls, quaternary ammonium compounds, biguanides, amines and glucoprotamines that bind microorganisms to their cell membrane and disrupt the structure resulting in the breakdown of the cell. Organic compounds, such as metallic complex compounds based on metals like cadmium, silver, copper and mercury, cause inhibition of the active enzyme centres (inhibition of metabolism) [3–5].
However, many of the commercial antimicrobial agents, such as inorganic salts, organometallics, iodine and iodophors, phenolic compounds, ammonium salt-based compounds, heterocyclic and anionic groups, nitro compounds, urea and related compounds, formaldehyde derivatives and amines, currently available in the market are synthetic and not environment-friendly. Furthermore, a vast majority of these antimicrobial agents are of leaching type, and thus their gradual release from textiles into surroundings results in a decrease of their concentration and gradually falls under the limit of effectiveness, i.e. minimum inhibitory concentration (MIC). The release of these agents also acts as poison to a wide spectrum of bacteria and fungi [6–12].
Natural bioactive agents with antimicrobial properties have become progressively essential for producing non-toxic and environment-friendly textile products. These antimicrobial compounds, which are mostly extracted from plants (aloe vera, tea tree and eucalyptus oil (EO), neem, grapefruit seed, tulsi leaf extracts, etc.), include phenolics and polyphenols (simple phenols, phenolic acids, quinones, flavonoids, flavones, flavonols, tannins and coumarins), terpenoids, essential oils, alkaloids, lectins, polypeptides and polyacetylenes. These components possess not only antimicrobial but also antioxidant properties. Neem *(Azadirachta indica),* one of the richest sources of biologically active compounds, has attracted worldwide attention in recent years owing to its wide range of medicinal properties. [13–17]. It possesses active antimicrobial compounds, such as azadirachtin, salannin and meliantriol, which are also effective in controlling the insect growth and are used as an antifeedant. Researchers have studied the antibacterial activity of various components of the neem tree, such as oil, bark, seed extract, on the 100% cotton fabric and polyester/cotton blend fabric. Some researchers studied the antibacterial properties of neem oil in combination with other herbal oils, such as clove, tulsi and karanga on cotton textiles [11]. In another study, Joshi et al. extracted an antimicrobial agent from the seeds of a neem tree for imparting antibacterial activity to polyester/cotton blend fabric and produced a semi-durable antibacterial finish [16, 18]. The accommodation of a high amount of antimicrobial neem ingredients in the polyester structure resulted in higher antimicrobial activity without significant decrease in crystallinity and tensile properties of polyester fabric. It is concluded from previous studies that neem is effective against bacteria on cotton fabrics and it showed more microbial resistance than aloe vera. The fabric finished with neem is durable even after 15 washes [2]. Aloe vera is another well know bioactive compound used for cosmeto-finishes, antibacterial finishes and skin care agents. [19–21]. It has been reported that the increased concentration of aloe vera gel increases the antibacterial activity against both Gram-positive and

Gram-negative bacteria. It is reported that aloe vera is effectively inhibiting the microbial growth on treated cotton fabrics. Fabrics finished with a combination of aloe vera and neem are also found to be durable. [22]. Tulsi (also known as holy basil) is known for its antimicrobial, insecticidal antiprotozoal, diaphoretic and expectorant properties. The main constituents of tulsi (*Osmium basilicum*) are eugenol (70%), methyl eugenol (20%), carvacrol (3%), etc. In their research, Sathinaranan et al. applied tulsi leaf (*Ocimum sanctum*) extracts on cotton fabrics by direct application, i.e. microencapsulation, resin cross-linking methods and their combinations. It is stated that fabrics treated with tulsi extract exhibit excellent antimicrobial activity, and the major component responsible for the antimicrobial properties is eugenol. The fabrics treated with the direct method showed poor durability of the finish compared to microencapsulation and resin cross-linking methods [23]. Grapeseed oil is technically known as Vitis vinifera and is used for thousands of years for its medicinal and nutritious properties, such as anti-inflammatory, cardio protective, antimicrobial, antifungal and anti-cancer. The main components responsible for these effects are tocopherol, linolenic acid, resveratrol, quercetin, procyanidins, carotenoids and phytosterols [24]. Several studies reported the antimicrobial activity of grapeseed oil, which is effective against both the spectrum of Gram-negative and Gram-positive bacteria [25–26]. The chemical structures of most of the above mentioned natural bioactive agents are complex and contain mixtures of multiple compounds. Selective isolation and extraction of these bioactive agents are difficult and will increase the quantity of the agent required to obtain a minimum inhibition concentration.

Most of the natural antimicrobial agents are insoluble in water and also adversely affect the physical and other desirable properties of textiles. In order to imbue the bioactive substance, various techniques have been suggested by researchers. Bioactive agents also lose their bioactivity when they react with textile materials. Hence, intensive research was carried out in order to explore and exploit the best utilisation of environment-friendly antimicrobial agents [10–11]. However, it is difficult to achieve the enhanced and durable antimicrobial property of polyester due to semi-crystalline and highly compact structure and the absence of active polar groups in the polyester structure, which facilitates crosslinking of antimicrobial agents, in addition to exhibiting low surface energy [16–18]. Various functional finishes can easily be imparted to polyester/cotton fabric taking advantage of cotton amorphous structure. Earlier study on polyester/cotton blend using neem antibacterial agent with different crosslinking agents proved that the finished fabric retained the desired antimicrobial activity against Gram-positive bacteria for the maximum of five machine washes, while thereafter the effect is decreased on subsequent washes. [16]. Previous studies suggested many approaches to impart antibacterial activity to the polyester and polyester blended textiles, including coating, spraying, microencapsulation, grafting and insertion of dope additives into the fibre structure [27–30]. An alternative approach to enhance the antibacterial effect of polyester is to open up the compact structure of polyester by making use of suitable interacting solvents, which facilitates the easy entry of antimicrobial agents into the compact polyester structure [31–32]. This paper deals with the antibacterial effect of neem, aloe vera, tulsi, grapeseed oil on polyester and its blends with cotton and viscose, which have been previously treated with the TCAMC solvent system.

2 Materials and methods

Polyester (PES), polyester/viscose (PES/CV), polyester/cotton (PES/CO) and texturised polyester (texturised PES) fabric samples of 165 g/m^2 using Oxford weave (derivative of plain weave) are used. The characteristics of the materials are presented in Table 1.

The pretreatment of the samples is carried out using various concentration of trichloroacetic acid-methylene chloride (TCAMC) solvent system. Trichloroacetic acid, methylene chloride and acetone were obtained from Sigma-Aldrich Chemical Co. Ltd. It is known that TCAMC interacts with the polyester structure and dissolves out completely at 25% in 5 minutes at room temperature (~30 °C) [31]. It is reported elsewhere that the structural modification of polyester takes place and the compact polymer structure is opened up at a lower concentration of TCAMC treatment without significantly affecting its strength [20]. The effect of different TCAMC concentration on polyester structure has been optimised [32]. The treatment is carried out in a closed trough at ~ 30 °C for 3 minutes. The treated samples are then rinsed with methylene chloride followed by acetone to remove any adhering reagent. Afterwards, the samples are wrung and dried in an open atmospheric

Table 1: Fabric characteristics

Sample no.	Fabric	Mass per unit area (g/m²)	Weave	Yarn density (warp × weft)	Linear density (warp × weft)	Tensile strength (warp × weft) (N)	Elongation (warp × weft) (%)	Thickness (mm)
1	100% PES	165	2/2 oxford weave	$64^{a)} \times 44^{b)}$	$2/30^{c)} \times 2/30^{c)}$	1600 ×1400	25 × 20	0.85
2	PES/ CV (65/35)	165	2/2 oxford weave	$64^{a)} \times 44^{b)}$	$2/30^{c)} \times 2/30^{c)}$	1600 ×1400	25 × 20	0.85
3	PES/ CO (65/35)	165	2/2 oxford weave	$64^{a)} \times 44^{b)}$	$2/30^{c)} \times 2/30^{c)}$	1600 ×1400	25 × 20	1.1
4	100% PES texturised	165	2/2 oxford weave	$144^{a)} \times 110^{b)}$	$150^{d)} \times 150^{d)}$	1400× 1200	40 × 35	0.8

$^{a)}$ ends/cm; $^{b)}$ picks/cm; $^{c)}$ Ne; $^{d)}$ den

Table 2: Experimental design (Taguchi L-16 (4^3 2^1) Mixed orthogonal array)

Fabric	Levels		
	Antibacterial agents	Concentration (%)	M:L ratio
PES	Neem	5	01:20
PES/CV	Aloe vera	10	01:25
PES/CO	Tulsi	15	-
Texturised PES	Grapeseed oil	20	-

condition before applying the above mentioned biopolymeric finishes.

Commercially available neem, aloe vera, tulsi and grapeseed oil were chosen for this study. Table 2 shows the experimental design used in the study. Taguchi mixed orthogonal array Design L16 (4^3 2^2) was chosen for the experimental plan and the larger the better response (antimicrobial efficiency) was selected to determine the optimum conditions.

The TCAMC treated samples were immersed in the solution at 5%, 10%, 15%, 20% concentration of neem, aloe vera, tulsi, grapeseed oil with ethanol at room temperature, resulting in active substances which are subsequently dissolved in ethanol. The treatment is carried out with the help of acetic acid at 80 °C for 20 minutes at different liquor ratio of (1:20 and 1:25). The add-on% is calculated using equation 1.

$$\text{Add-on\%} = (A - B) \times 100/B \quad (1)$$

where A represents a dry weight of biopolymer finished sample and B represents a dry weight of TCAMC treated sample.

The ASTM standard D5035 and Tinus Olsen universal tensile tester are used to test the fabric tensile strength and elongation. Fabric tear strength is tested using tongue tear tester according to the D 2261 standard. The colour values of the finished fabrics are measured using Spectra Scan 5100+ spectrophotometer (RayScan) instrument.

The antibacterial activity of untreated and treated control samples is tested qualitatively by parallel streak method (AATCC-147) and quantitatively by colony count method (AATCC 100) using *S. aureus* (Gram-positive) and *E. Coli* (Gram-negative) bacteria. In the parallel streak method, bacterial suspension in the form of streaks is placed on the plate with the help of a sterilised wire loop. Three streaks are made on the upper side of solid agar plate 1 cm apart from each other; the fabric swatches (5.08 cm × 2.54 cm or 2” × 1”) of untreated and treated samples placed on the agar plates are incubated for 24 hours at 37 ± 0.5 °C. After 24 hours of incubation, the swatches are examined for any potential bacterial growth underneath and around the specimen [33].

In the colony count method, the swatches are placed separately in a previously sterilised flask containing Luria broth solution and subjected to 37 ± 0.5 °C for 24 hours in a laboratory shaker for 200 rpm. After 24 hours of incubation, the bacterial suspension is diluted serially (for example 10^2, 10^4, 10^6 times) using sterilised water. 10 μL of diluted bacterial suspension is spread on the plate and incubated again at 37 ± 0.5 °C. After 24 hours of incubation, the agar plates are removed from the incubator to count the bacterial growth inside the plates. The percent reduction in number of colonies in the treated samples as compared to the untreated samples gives the antibacterial activity of the treated samples (equation 2) [34].

$$\text{Antibacterial activity or \% reduction} = (A - B)/B \times 100 \quad (2)$$

where A represents the bacteria colony (CFU/ml) of untreated fabric and B represents the bacterial colony of the treated fabric.

The treated fabrics are then washed in launder-o-meter according to the AATCC Test Method 61-1996 (2A) using Lissapol N, a non-ionic detergent (1% on the weight of fabric) at 40 °C for 60 minutes to check the wash fastness and staining of the treated fabric samples. It is also mentioned that 1 AATCC machine wash is equal to 5 home laundry cycles [35].

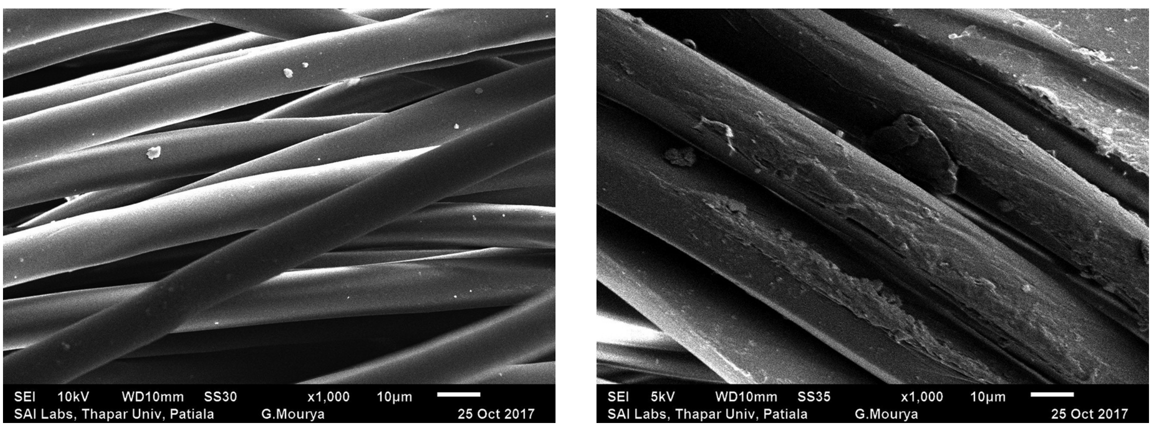
3 Results and discussion

3.1 Effect of biopolymer finish on add-on%

To determine the dry add-on% of the TCAMC-treated finished fabric samples, the samples are kept at 20 °C and 65% RH for 24 hours and the weight variation calculated according to equation 1. Table 3 shows that polyester fabric has weight reduction after the TCAMC treatment. After applying various finishes, the gain in weight is observed from 1.06% to 2.39%. Similar gain in weight is observed in polyester/viscose, polyester/cotton and texturised TCAMC-treated fabric samples. The scanning electron microscopy (SEM) topography of the TCAMC-treated polyester fibre is shown in Figure 1. It is evident from Figure 1 that the TCAMC induces swelling of polyester fibre and creates several voids and micro cracks.

3.2 Effect of biopolymer finish on tensile and tear properties

In this study, the tensile and tear strength of biopolymer finished polyester and polyester blend fabrics, which have been previously treated with 1% TCAMC for 3 minutes, are tested and evaluated. Table 4 shows the strength loss% of all types of treated fabric samples. All four types of fabrics suffered a reduction in tensile strength ranging from 4.75 to 11.79%. The major loss in strength is due to the interaction of TCAMC reagent. Further the TCAMC-pretreated samples have been treated with biopolymeric finishes. The treatment is carried out using the exhaustion method which is carried out at high temperature. It is obvious from Table 4 that 100% texturised fabric registered a highest strength loss of 11.79%. Perhaps it offered more surface area compared to the surface area of normal polyester and its blends for the TCAMC to interact with the structure. It is evident from Figure 1 that the TCAMC reagent interacted with polyester and disturbed its compact structure, and thus suffered strength loss. In the case of functional textiles, a percentage loss of about 15%



Before TCAMC treatment After TCAMC treatment

Figure 1: Effect of TCAMC concentration (1%) on polyester

Table 3: Add-on% of different antimicrobial agents on various fabrics

Fabric	Activity	Weight (g)			
		Neem treated	Aloe vera treated	Tulsi treated	Grapeseed oil treated
PES	Before TCAMC treatment	7.76	7.78	7.77	7.73
	After TCAMC treatment	7.62	7.67	7.58	7.52
	Weight loss (%)	**1.8**	**1.41**	**2.45**	**2.72**
	Finished	7.71	7.76	7.66	7.63
	Add -on (%)	**1.18**	**1.17**	**1.06**	**1.46**
PES/CV	Before TCAMC treatment	7.85	7.75	7.72	7.7
	After TCAMC treatment	7.59	7.51	7.26	7.54
	Weight loss (%)	**3.31**	**3.1**	**5.96**	**2.08**
	Finished	7.68	7.57	7.35	7.67
	Add -on (%)	**1.19**	**0.8**	**1.24**	**1.72**
PES/CO	Before TCAMC treatment	5.51	5.4	5.94	5.58
	After TCAMC treatment	5.34	5.22	5.75	5.33
	Weight loss (%)	**3.09**	**3.33**	**3.2**	**4.48**
	Finished	5.4	5.27	5.87	5.41
	Add -on (%)	**1.12**	**0.96**	**2.09**	**1.5**
Texturised PES	Before TCAMC treatment	5.23	5.33	5.51	5.69
	After TCAMC treatment	5.07	5.13	5.22	5.43
	Weight loss (%)	**3.06**	**3.75**	**5.26**	**4.57**
	Finished	5.13	5.39	5.28	5.56
	Add -on (%)	**1.18**	**1.13**	**1.15**	**2.39**

is acceptable, while a higher percentage may cause the deterioration of textile structure. The TCAMC and biopolymer finish treatment also influence the tearing strength of fabrics. It is observed from Table 4 that the reduction in tear strength varies from 5.44% to 11.10%, of which 100% texturised polyester showed a maximum reduction of 11.10%.

3.3 Effect of biopolymer treatment on antibacterial activity

Antibacterial activity of untreated polyester and TCAMC (1%) treated polyester imbued with neem, aloe vera, tulsi and grapeseed oil are evaluated qualitatively by parallel streak method as stipulated in AATCC 147. Both Gram-positive *S. aureus* and Gram-negative *E. coli* bacteria are used for antibacterial assessment. Figure 2 shows the results of antibacterial activity of untreated and neem-imbued TCAMC-treated fabric samples. It is obvious from Figures 2(a) and 2(f)) that a heavy growth of both *S. aureus*, and *E. Coli* bacteria respectively, is seen in the case of untreated polyester, while moderate to high bacterial resistance is observed in TCAMC-treated fabrics Figure 2(b–e) and 2(g–j). It supports the observation published elsewhere that the TCAMC reagent increases the segmental mobility of the polyester polymer and as a result structural rearrangement takes place thereby creating more voids and micro cracks to facilitate the entry of antibacterial agents inside the polymer structure [31]. Similar results are observed in Figures 3–5 for aloe vera, tulsi and grapeseed oil-imbued TCAMC-treated fabric samples.

Table 4: Tensile and tear strength of biopolymer finished fabrics (warp way)

Fabric	Treatment	Tensile strength		Tear strength	
		Mean (N)	Loss (%)	Mean (N)	Loss (%)
100% PES	Control	1600	-	150	-
	Neem	1470	8.13	139	6.96
	Aloe vera	1485	7.19	140	6.93
	Tulsi	1474	7.88	135	9.84
	Grapeseed oil	1510	5.63	142	5.49
PES/CV	Control	1600	-	125	-
	Neem	1495	6.56	116	6.8
	Aloe vera	1502	6.13	114	8.8
	Tulsi	1494	6.63	113	9.15
	Grapeseed oil	1524	4.75	118	5.44
PES/CO	Control	1600	-	125	-
	Neem	1465	8.44	115	7.84
	Aloe vera	1468	8.25	114	8.96
	Tulsi	1460	8.75	115	8.16
	Grapeseed oil	1520	5.00	114	8.8
100% texturised PES	Control	1400	-	100	-
	Neem	1235	11.79	89	10.5
	Aloe vera	1265	9.64	90	9.5
	Tulsi	1250	10.71	89	11.1
	Grapeseed oil	1295	7.5	92	7.6

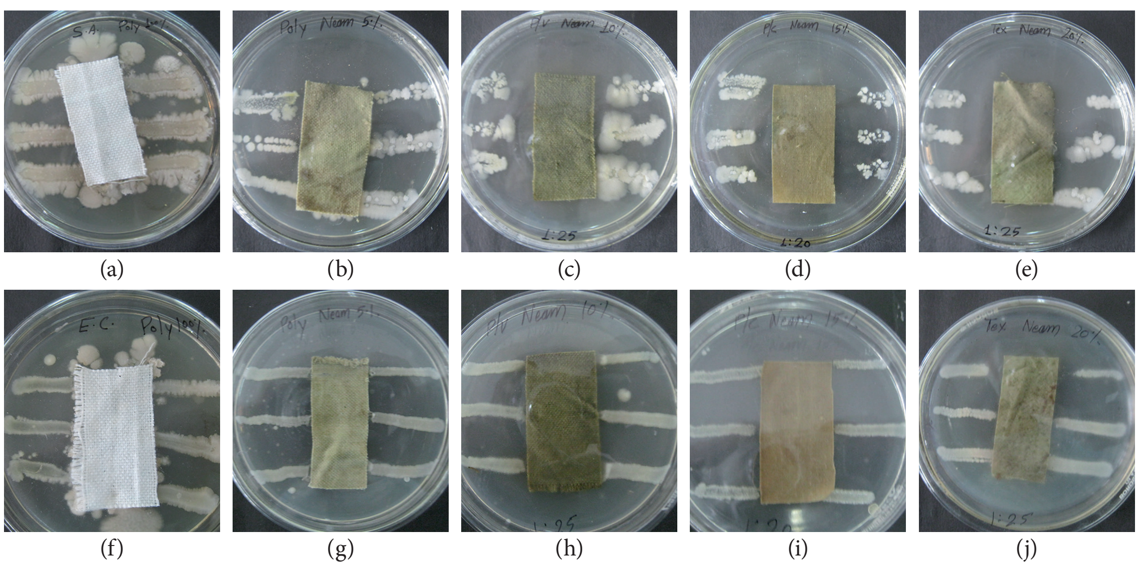


Figure 2: Antibacterial activity of untreated and neem-imbued TCAMC-treated fabrics: Against S. aureus (a–e): (a) untreated 100% PES; (b) TCAMC-treated 100% PES; (c) TCAMC-treated PES/CV; (d) TCAMC-treated PES/CO; and (e) TCAMC-treated texturised PES. Against E. coli (f–j): (f) untreated 100% PES; (g) TCAMC-treated 100% PES; (h) TCAMC-treated PES/CV; (i) TCAMC-treated PES/CO; and (j) TCAMC-treated texturised PES

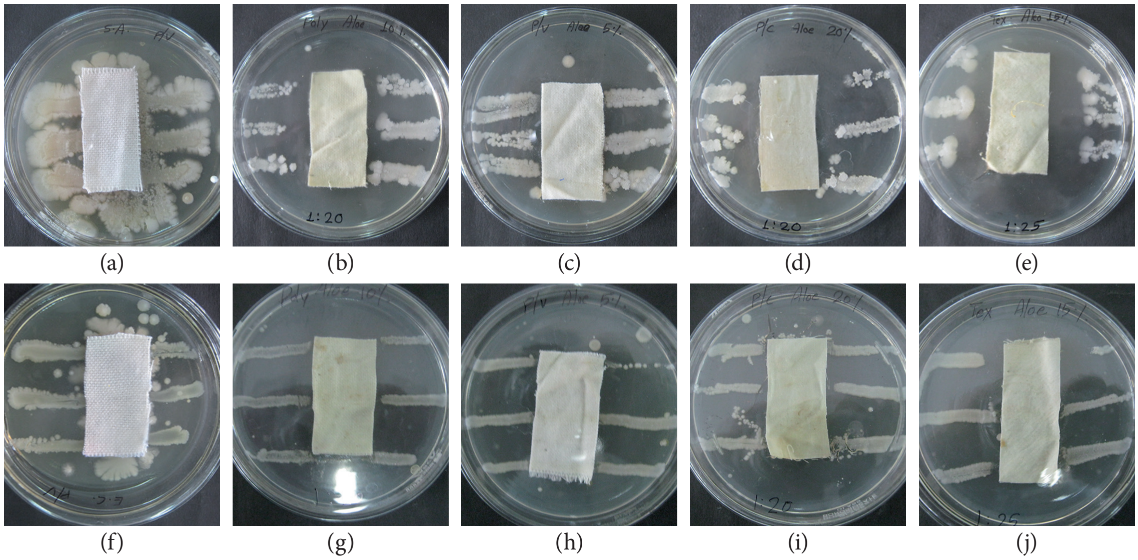


Figure 3: Antibacterial activity on untreated and aloe vera-imbued TCAMC-treated fabrics: Against S. aureus (a–e): (a) untreated 100% PES; (b) TCAMC-treated 100% PES; (c) TCAMC-treated PES/CV; (d) TCAMC-treated PES/CO; and (e) TCAMC-treated texturised PES. Against E. coli (f–j): (f) untreated 100% PES; (g) TCAMC-treated 100% PES; (h) TCAMC-treated PES/CV; (i) TCAMC-treated PES/CO; and (j) TCAMC-treated texturised PES

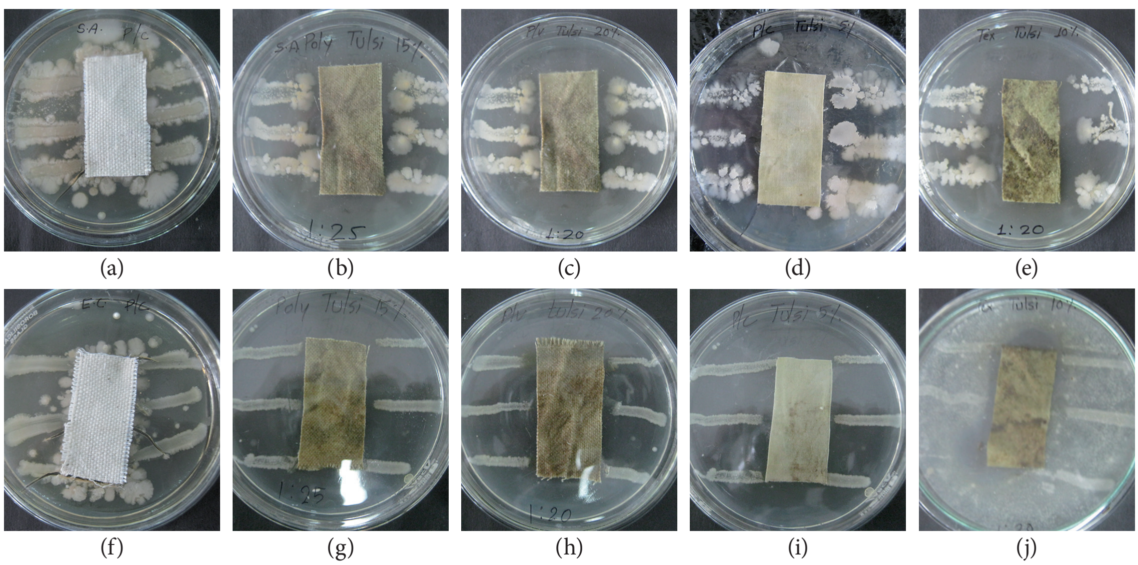


Figure 4: Antibacterial activity on untreated and tulsi-imbued TCAMC-treated fabrics: Against S. aureus (a–e): (a) untreated 100% PES; (b) TCAMC-treated 100% PES; (c) TCAMC-treated PES/CV; (d) TCAMC-treated PES/CO; and (e) TCAMC-treated texturised PES. Against E. coli (f–j): (f) untreated 100% PES; (g) TCAMC-treated 100% PES; (h) TCAMC-treated PES/CV; (i) TCAMC-treated PES/CO; and (j) TCAMC-treated texturised PES

The antibacterial activity of untreated and TCAMC-treated (with neem, aloe vera, tulsi and grapeseed oil finish) polyester fabrics is assessed quantitatively against both the Gram-positive and Gram-negative bacteria, and the results are presented in Table 5. It is evident from Table 5 that grapeseed oil-imbued TCAMC-treated 100% polyester shows an 86% and 73% antibacterial activity against both the Gram-positive and Gram-negative bacteria. A similar trend in arresting the growth of bacteria is also evidenced

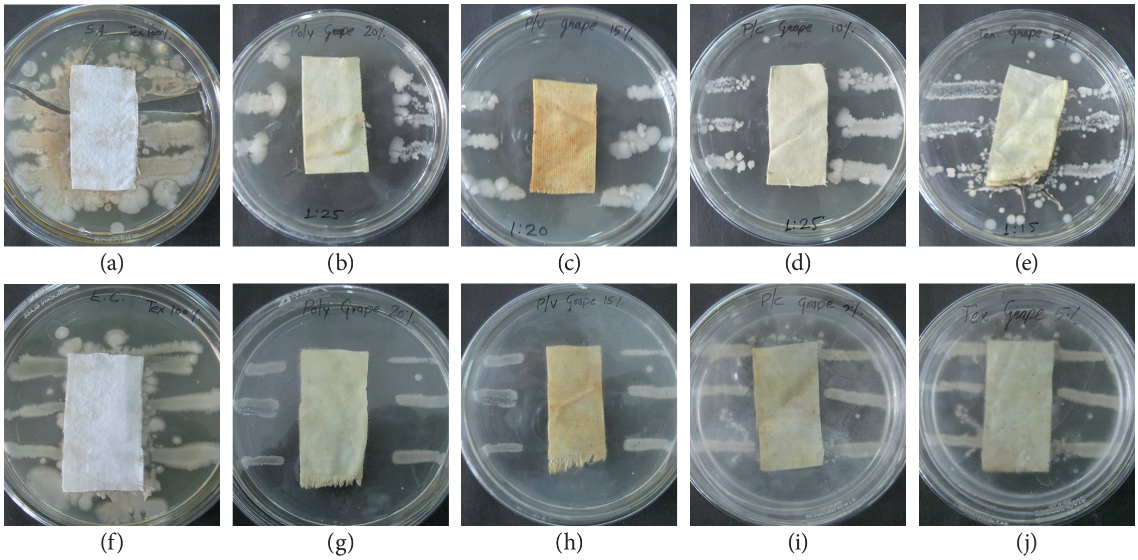


Figure 5: Antibacterial activity on untreated and grapeseed oil-imbued TCAMC-treated fabrics: Against S. aureus (a–e): (a) untreated 100% PES; (b) TCAMC-treated 100% PES; (c) TCAMC-treated PES/CV; (d) TCAMC-treated PES/CO; and (e) TCAMC-treated texturised PES. Against E. coli (f–j): (f) untreated 100% PES; (g) TCAMC-treated 100% PES; (h) TCAMC-treated PES/CV; (i) TCAMC-treated PES/CO; and (j) TCAMC-treated texturised PES

in other biopolymer-imbued TCAMC-treated fabrics. It should be noted that the TCAMC pretreatment contributed a significant role in enhancing the antibacterial activity of neem, aloe vera, tulsi and grapeseed oil treated polyester. TCAMC modifies the structure of polyester and creates more voids and microcracks in the structure to entrap the antimicrobial agents [16, 22]. It is observed that with the increase in concentration of finishes, the antibacterial activity also increases as evidenced in Figures 2–5, which show bacterial free regions. It is also obvious form Figures 2–5 that the inhibition zone is influenced by the type of finish and its concentration, which is further reaffirmed by quantitative test results.

3.4 Effect of laundering on the antibacterial activity

It is observed that laundering affects the effectiveness of antibacterial finishes and the degree of antibacterial activity is reduced with increase in wash cycles (Table 5). Table 5 shows that all treated fabric samples show modest activity against both *S. aureus* and

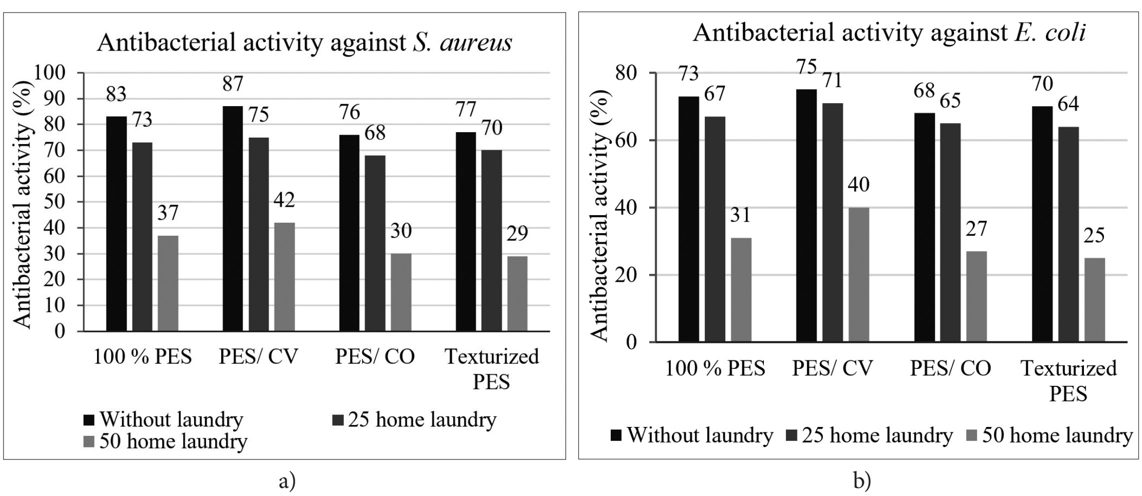


Figure 6: Antimicrobial activity of grapeseed oil-imbued TCAMC-treated fabrics against: a) *S. aureus* and b) *E. coli* after several machine washes

Table 5: Antibacterial activity of treated fabrics after various use-wash cycles (according to Taguchi design)

Fabric	Finish type	Finish concentration (%)	Liquor ratio	Without laundering				
				S. aureus (Gram-positive)		*E. coli* (Gram-negative)		
				CFU[a]	AA	CFU[a]	AA	
Untreated	-	-	-	78	-	110	-	
100% PES	Neem extract	5	1:20	45	**42**	65	**41**	
100% PES	Aloe vera gel	10	1:20	42	**46**	60	**45**	
100% PES	Tulsi extract	15	1:25	37	**53**	45	**59**	
100% PES	Grapeseed oil	20	1:25	11	**86**	30	**73**	
PES/CV	Neem extract	10	1:25	46	**41**	67	**39**	
PES/CV	Aloe vera gel	5	1:25	48	**38**	69	**37**	
PES/CV	Tulsi extract	20	1:20	36	**54**	53	**52**	
PES/CV	Grapeseed oil	15	1:20	10	**87**	25	**77**	
PES/CO	Neem extract	15	1:20	45	**42**	66	**40**	
PES/CO	Aloe vera gel	20	1:20	44	**44**	63	**43**	
PES/CO	Tulsi extract	5	1:25	34	**56**	41	**63**	
PES/CO	Grapeseed oil	10	1:25	12	**85**	22	**80**	
Texturised PES	Neem extract	20	1:25	35	**55**	45	**53**	
Texturised PES	Aloe vera gel	15	1:25	31	**60**	46	**58**	
Texturised PES	Tulsi extract	10	1:20	45	**42**	66	**40**	
Texturised PES	Grapeseed oil	5	1:20	42	**46**	62	**44**	

[a] ml ×10^8; [b] antibacterial activity (%)

E. coli even after 10 AATCC machine washes. The grape seed oil treated 100% PES and PES/CV show 34% and 32 % antibacterial activity after 10 machine washes (50 home laundry cycles) against *S. aureus* and *E. coli* bacteria. This is due to the finish concentration as lower concentration also decreases the effect of antibacterial activity. Figure 6 shows the effect of laundering on antibacterial activity for all kind of polyester fabrics treated with grapeseed oil-imbued TCAMC with 20% grapeseed oil at a liquor ratio of 1:25 . It is evident that after 5 and 10 machine laundry cycles the finish is leeched out and the antibacterial activity reduced accordingly.

3.5 Effect of biopolymer finish on colour properties

Table 6 shows the effect of biopolymeric finishes on the colour properties of all treated samples. It was observed that all fabric samples treated with neem, tulsi and grapeseed oil show a significant change in colour properties. Table 6 shows that the relative colour strength is highly influenced by the finish type and finish concentration. Relative strength increased with higher finish concentration under all conditions. It was observed that the neem and tulsi treated fabric samples show higher colour strength values. The relative colour strength had the highest value 10994 in case of PES/CV neem. It was also observed that the increase in finish concentration from 5% to 20% leads to higher colour strength values in all cases. From Table 6, the difference in lightness (DL*) has been observed negative, which also confirms the darker shade appearance as compared to the control sample in all cases. The changes in hue values are represented by DH* and its tendency towards a specific colour (such as red, yellow or blue) can be explained by the Da* and Db* values in Table 6.

3.6 Analysis and evaluation of experimental results

Analysis of the effect of each control factor fabric type, finish type, concentration and liquor ratio on the antibacterial activity of both *S. aureus* and *E. coli* with signal-to-noise (S/N) response are shown in Table 7. Normally, there are three kinds of quality characteristics in the analysis of the S/N ratio, i.e. lower -the -better, higher-the-better, and nominal-the-best. The S/N ratio is calculated based on

5-× machine washes				10-× machine washes			
S. aureus (Gram-positive)		*E. coli* (Gram-negative)		*S. aureus* (Gram-positive)		*E. coli* (Gram-negative)	
CFU[a)]	AA	CFU[a)]	AA	CFU[a)]	AA	CFU[a)]	AA
78	-	110	-	78	-	110	-
48	**38**	68	**38**	68	**13**	98	**11**
62	**21**	88	**20**	75	**4**	107	**3**
39	**50**	58	**47**	64	**18**	94	**15**
18	**77**	35	**68**	49	**37**	73	**34**
51	**35**	73	**34**	67	**14**	96	**13**
60	**23**	86	**22**	69	**12**	105	**5**
38	**51**	57	**48**	61	**22**	90	**18**
15	**81**	26	**76**	51	**35**	75	**32**
49	**37**	72	**35**	61	**22**	82	**25**
58	**26**	87	**21**	72	**8**	99	**10**
52	**33**	76	**31**	65	**17**	94	**15**
24	**69**	46	**58**	60	**23**	91	**17**
46	**41**	72	**35**	58	**26**	84	**24**
55	**29**	81	**26**	71	**9**	102	**7**
47	**40**	68	**38**	63	**19**	92	**16**
46	**41**	72	**35**	62	**21**	90	**18**

Table 6: Colour strength values and colour coordinates of treated fabric samples

Fabric	Treatment	Conc. (%)	DL*	Da*	Db*	Dc*	dE*	DH*	Strength (%)
100% PES	Standard	-	-	-	-	-	-	-	100
	Neem	5	−37.66	1.6	13.77	13.84	40.13	−0.77	5254
	Aloe vera	10	−10.32	0.9	15.23	15.25	18.42	−0.36	704.75
	Tulsi	15	−31.25	2.05	19.07	19.16	36.67	−0.87	5062.1
	Grapeseed oil	20	−15.54	6.69	31.24	31.85	35.52	−2.49	2221.9
PES/CV	Standard	-	-	-	-	-	-	-	100
	Neem	10	−46.79	0.91	14.51	14.53	49	−0.38	10994
	Aloe vera	5	−6.07	1.93	10.39	10.51	12.18	−1.08	400.06
	Tulsi	20	−47.26	4.66	14.98	15.51	49.8	−2.35	9897.9
	Grapeseed oil	15	−36.89	14.94	23.25	26.89	46.09	6.38	5415.9
PES/CO	Standard	-	-	-	-	-	-	-	100
	Neem	15	−28.58	3.69	16.86	17.17	33.39	−1.76	3136.9
	Aloe vera	20	−17.7	3.38	25.71	25.9	31.39	−1.31	2247.5
	Tulsi	5	−18.14	1.71	17	17.07	24.92	−0.75	1922.9
	Grapeseed oil	10	−16.5	6.88	34.15	34.75	38.54	−2.54	3211.4
100% texturised PES	Standard	-	-	-	-	-	-	-	100
	Neem	20	−39.23	1.67	16.45	16.52	42.57	−0.74	6266.7
	Aloe vera	15	−18.52	3.62	25.11	25.33	31.41	−1.43	1974.9
	Tulsi	10	−30.64	0.32	15.16	15.16	34.19	−0.06	3513.3
	Grapeseed oil	5	−11.75	0.8	22.46	22.48	25.37	−0.22	1427

the S/N analysis. This analysis focuses on finding the best combination among each process parameter for better antibacterial activity. Therefore, higher the better is the quality technique used as shown in Equation 3 given below:

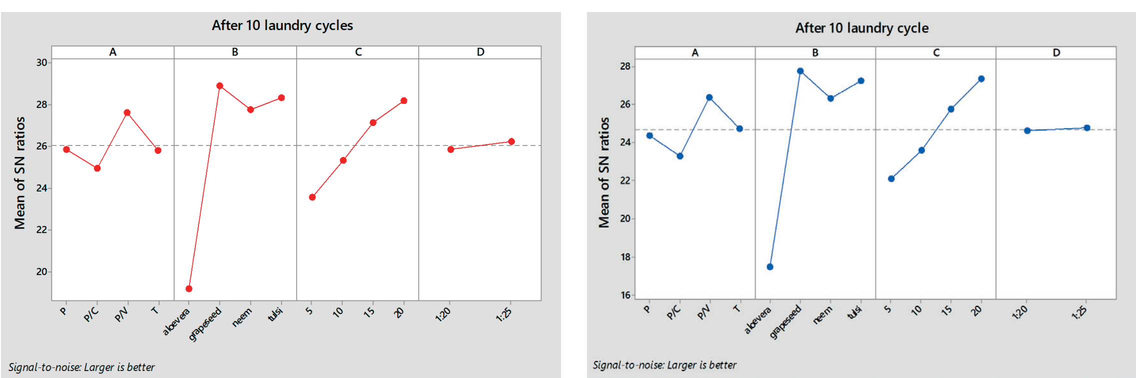
$$\eta = \frac{S}{Ns} = -10 \times log_{10}(sum(\frac{\frac{1}{Y^2}}{n}) \quad (3)$$

Here, *Y* represents the observed data in the experiment and *n* represents the number of observations in the experiment [35–36]. The response tables of S/N for *S. aureus* and *E. coli* are shown in Table 7. This table is made using the Taguchi technique and shows the optimal levels of control factors for the optimal process to enhance antibacterial activity. The level values of control factors for *S. aureus* and *E. coli* given in Table 7 are shown in Figure 7. Optimal process parameters of the control factors for minimising the antibacterial activity of *S. aureus* and *E. coli* can be easily determined from these graphs. The best level for each control factor is found according to the highest S/N ratio in the levels of that control factor. According to this, the levels and S/N ratios for the factors giving the best activity against *S. aureus* value are specified as factor A (Level 3, S/N = 26.68), factor B (Level 2, S/N = 28.92), factor C (Level 4, S/N = 28.19) and factor D (Level 2, S/N = 25.79). For *E. coli,* values are specified as factor A (Level 3, S/N = 26.39), factor B (Level 2, S/N = 27.75), factor C (Level 4, S/N = 27.36) and factor D (Level 2, S/N = 24.77). In other words, the optimum activity can be achieved for both *S. aureus* and *E. coli* using polyester/viscose fabric with grapeseed oil finish at a 20% concentration at a Liquor ratio of 1:25 respectively.

Table 8 shows the ANOVA analysis to study the effect of process parameters after 10 laundry cycles against both *S. aureus* and *E. coli*. The analysis is carried out at 5% significance and at 95% confidence level. The significance of control factors in ANOVA is determined by comparing the F values of each control factor. According to Table 8, the percentage contribution of the fabric, finish, concentration and liquor ratio on the *S. aureus* antibacterial activity is 2.80%, 66.73%, 30.06%, and 0.41 respectively. Thus, the important factors affecting the antibacterial activity are finish type (66.73%) and concertation (30.06%). Similarly, for *E. coli* the effect of laundering on fabric, finish, concentration and liquor ratio against the

Table 7: Response table for Signal to noise ratio for S. aureus and E. coli

	S/N ratio for *S. aureus*				S/N ratio for *E. coli*			
Level	A	B	C	D	A	B	C	D
1	22.89	16.55	23.89	24.38	24.37	17.48	22.09	24.62
2	24.95	**28.92**	21.10	**25.79**	23.29	**27.75**	23.58	**24.77**
3	**26.68**	26.50	27.15		**26.39**	26.32	25.74	
4	25.81	28.37	**28.19**		24.73	27.22	**27.36**	
Delta	3.78	12.37	7.08	1.40	3.10	10.27	5.27	0.15



(a) (b)

Figure 7: Effect of 10 machine laundry cycles on antibacterial activity: a) against S. aureus, b) against E. coli

Table 8: ANOVA analysis after 10 laundry cycle

Bacteria	Variance source	Degree of freedom (DF)	Sum of squares (SS)	Mean square (MS)	F ratio	Contribution (%)
S. aureus	Fabric	3	136.69	45.56	0.14	2.80
	Finish	3	3280.69	1093.56	3.33	66.73
	Concentration	3	1475.19	491.73	1.50	30.06
E. coli	Fabric	3	60.19	20.063	0.11	1.37
	Finish	3	2953.19	984.40	5.60	69.91
	Concentration	3	1203.69	401.23	2.28	28.46

antibacterial property is shown in Table 8. The percentage contribution of the fabric, finish, concentration and liquor ratio on the *E. coli* antibacterial activity is 1.37%, 69.91%, 28.46%, and 0.26% respectively. Thus, the important factor affecting the antibacterial activity is finish type that has a maximum contribution of 66.73% and 69.91% in both cases. The trends are presented using design generated graphs in Figure 7. It is observed that the grapeseed oil finish shows better antibacterial activity against both *S. aureus* and *E. coli* compared to others finishes after 10 laundry cycles. It has been observed that as the concentration increases the durability of finishes increases. It is also observed from the study that the increase in the liquor ratio from 1:20 to 1:25 increases the antibacterial activity. It is due to the increase in the mobility of the molecule in the solution, which helps in more uniform finishing. Among different types of fabrics, polyester/cotton and polyester/viscose blends show more affinity to adhere to the molecules into the polymer structure as compared to polyester and texturised polyester.

4 Conclusion

Different polyester structures are treated with already optimised concentration of TCAMC solvent. The pretreatment modifies the polyester structure and creates more voids and cracks in the compact structure. In this study, the Taguchi method is used to determine optimal process parameters in the antibacterial assessment of the bio polymeric finished pretreated polyester structure. The Taguchi analysis shows that the polyester/viscose fabric with 20% grapeseed finish at a liquor ratio of 1: 25 is the optimum condition for antibacterial activity against both *S. aureus* and *E. coli*. According to the results of statistical analysis, it is found that the finish type is the most significant parameter with contributions of 66.73% and 69.91%, respectively for *S. aureus* and *E. coli*. Grapeseed oil finish is observed to be the best antimicrobial finish; which shows 21–37% antibacterial activity even after 10 machine laundry cycles against *S. aureus* and 18–34% antibacterial activity after 10 machine laundry cycles against *E. coli*. Also, the neem, tulsi and aloe vera finish show a modest amount of antibacterial activity of about 14–26%, 13–22%, and 5–10% respectively for *S. aureus* after 10 machine laundry cycles. Similarly, the neem, tulsi and aloe vera treated samples show 11–24%, 12–18%, and 4–8% antibacterial activity after 10 machine laundry cycles against *E. coli* respectively.

References

1. ROBINSON, Tim, McMULLAN, Geoff, MARCHANT, Roger, NIGAM, Poonam. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 2001, **77**(3), 247–255, doi:10.1016/S0960-8524(00)00080-8.
2. MURUGESH BABU, K, RAVINDRA, K.B. Bioactive antimicrobial agents for finishing of textiles for health care products. *The Journal of The Textile Institute*, 2015, **106**(7), 706–717, doi: 10.1080/00405000.2014.936670.
3. PURWAR, R., SRIVASTAVA, C.M. Antimicrobial cellulose and cellulose derivative materials. In *Cellulose and cellulose derivatives : synthesis, modification and applications*. Edited by Md. Ibrahim H. Mondal. New York : Nova Science Publishers, 2015, 455–472, https://novapublishers.com/shop/cellulose-and-cellulose-derivatives-synthesis-modification-and-applications/

4. PATEL, B.H., DESAI, K.U. Corporate uniform fabrics with antimicrobial edge: preparation and evaluation methodology. *International Dyer*, 2014, **42**(2), 33–38, https://www.researchgate.net/publication/278764455.
5. GUGLIUZZA, A., DRIOLI, E. A review on membrane engineering for innovation in wearable fabrics and protective textiles. *Journal of Membrane Science,* 2013, **446**, 350–375, doi:10.1016/j.memsci.2013.07.014.
6. De CARVALHO, C.C. Biofilms : recent developments on an old battle. *Recent Patents on Biotechnology*, 2007, **1**(1), 49–57, doi: 10.2174/187220807779813965.
7. KIM, Y.H., NAM, C.W., CHOI, J.W., JANG, J.H. Durable antimicrobial treatment of cotton fabrics using N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride and polycarboxylic acids. *Journal of Applied Polymer Science,* 2003, **88**(6), 1567–157, doi: 10.1002/app.11845.
8. EL-TAHLAWY, K.F., EL-BENDARY, M.A., ELHENDAWY, A.G., HUDSON, S.M. The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan. *Carbohydrate Polymers*, 2005, **60**(4), 421–430, doi:10.1016/j.carbpol.2005.02.019.
9. BAGHERZADEH, R., MONTAZER, M., LATIFI, M., SHEIKHZADEH, M., SATTARI, M. Evaluation of comfort properties of polyester knitted spacer fabrics finished with water repellent and antimicrobial agents. *Fibers and Polymers,* 2007, **8**(4), 386–392, doi:10.1007/BF02875827.
10. DASTJERDI, R., MOJTAHEDI, M.R., SHOSHTARI, A.M., KHOSROSHAHI, A. Investigating the production and properties of Ag/TiO_2/PP antibacterial nanocomposite filament yarns. *The Journal of The Textile Institute*, 2010, **101**(3), 204–213, doi:10.1080/00405000802346388.
11. JOSHI, M., ALI, S.W., PURWAR, R., RAJENDRAN, S. Ecofriendly antimicrobial finishing of textiles using bioactive agents based on natural products. *Indian Journal of Fibre & Textile Research*, 2009, **34**(3), 295–304, http://nopr.niscair.res.in/handle/123456789/6083.
12. PURWAR, R., JOSHI, M. Recent developments in antimicrobial finishing of textiles - a review. *AATCC Review*, 2004, **4**(3), 22–26.1
13. COWAN, M.M. Plant products as antimicrobial agents. *Clinical Microbiology Reviews*, 1999, **12**(4), 564–582, doi:10.1128/CMR.12.4.564.
14. QIN, S., XING, K., JIANG, J.H., XU, L.H., LI, W.J. Biodiversity, bioactive natural products and biotechnological potential of plant-associated endophytic actinobacteria. *Applied Microbiology and Biotechnology,* 2011, **89**(3), 457–473, doi:10.1007/s00253-010-2923-6.
15. SUBAPRIYA, R., NAGINI, S. Medicinal properties of neem leaves : a review. *Current Medicinal Chemistry,* 2005, **5**(2), 149–156, doi:10.2174/1568011053174828.
16. JOSHI, M., ALI, S.W., RAJENDRAN, S. Antibacterial finishing of polyester/cotton blend fabrics using neem (*Azadirachta indica*) : a natural bioactive agent. *Journal of Applied Polymer Science,* 2007, **106**(2), 793–800, doi:10.1002/app.26323.
17. RAJENDRAN, R., RADHAI, R., BALAKUMAR, C., AHAMED, H.A., VIGNESWARAN, C., VAIDEKI, K. Synthesis and characterization of neem chitosan nanocomposites for development of antimicrobial cotton textiles. *Journal of Engineered Fibers and Fabrics,* 2012, **7**(1), 136–141, doi: 10.1177/155892501200700116.
18. ALI, W., SULTANA, P., JOSHI, M., RAJENDRAN, S. A solvent induced crystallisation method to imbue bioactive ingredients of neem oil into the compact structure of poly (ethylene terephthalate) polyester. *Materials Science and Engineering : C,* 2016, **64**, 399–406, doi:10.1016/j.msec.2016.04.002.
19. FIELDER, J.O., CARMONA, O.G., CARMONA, C.G., LIS, M.J., PLATH, A.M.S., SAMULEWSKI, R.B., BEZERRA, F.M. Application of Aloe vera microcapsules in cotton nonwovens to obtain biofunctional textile. *Journal of The Textile Institute*, 2020, **111**(1), 68–74, doi:10.1080/00405000.2019.1625607.
20. ALI, S.W., PURWAR, R., JOSHI, M., RAJENDRAN, S. Antibacterial properties of *Aloe vera* gel-finished cotton fabric. *Cellulose*, 2014, **21**(3), 2063–2072, doi: 10.1007/s10570-014-0175-9.
21. SATHIANARAYANAN, M.P., BHAT, N.V., KOKATE, S.S., WALUNJ, V.E. Antibacterial finish for cotton fabric from herbal products. *Indian Journal of Fibre & Textile Research*, 2010, **35**(1), 50–58, http://nopr.niscair.res.in/handle/123456789/7662.
22. RAJENDRAN, S., MISHRA, S.P. Chemical, structural and thermal changes in PET caused by solvent induced polymer crystallisation. *Polymers*

*& Polymer Composites,*2007, **15**(2), 103–110, doi: 10.1177/096739110701500203.

23. SIMONČIČ, B., TOMŠIČ, B. Structures of novel antimicrobial agents for textiles-a review. *Textile Research Journal,* 2010, **80**(16), 1721–1737, doi: 10.1177/0040517510363193.
24. SOTO, M.L., FALQUÉ, E., DOMÍNGUEZ, H. Relevance of natural phenolics from grape and derivative products in the formulation of cosmetics. *Cosmetics*, 2015, **2**(3), 259–276, doi: 10.3390/cosmetics2030259.
25. BAYDAR, N.G., ÖZKAN, G., SAĞDIÇ, O. Total phenolic contents and antibacterial activities of grape (*Vitis vinifera L.*) extracts. *Food Control*, 2004, **15**(5), 335–339, doi: 10.1016/S0956-7135(03)00083-5.
26. AL-HABIB, A., AL-SALEH, E., SAFER, A.M., AFZAL, M. Bactericidal effect of grape seed extract on methicillin-resistant *Staphylococcus aureus* (MRSA). *The Journal of Toxicological Sciences*, 2010, **35**(3), 357–364, doi: 10.2131/jts.35.357.
27. MONTAZER, M., AFJEH, M.G. Simultaneous x-linking and antimicrobial finishing of cotton fabric. *Journal of Applied Polymer Science,* 2007, **103**(1), 178–185, doi: 10.1002/app.25059.
28. RAJENDRAN, R., BALAKUMAR, C., SIVAKUMAR, R., AMRUTA, T., DEVAKI, N. Extraction and application of natural silk protein sericin from *Bombyx mori* as antimicrobial finish for cotton fabrics. *The Journal of The Textile Institute*, 2012, **103**(4), 458–462, doi: 10.1080/00405000.2011.586151.
29. DASTJERDI, R., MONTAZER, M., SHAHSAVAN, S. A new method to stabilize nanoparticles on textile surfaces. *Colloids Surfaces A : Physicochemical and Engineering Aspects*, 2009, **345**(1–3), 202–210, doi: 10.1016/j.colsurfa.2009.05.007.
30. RAJENDRAN, S., RAMASAMY, S.S., MISHRA, S.P. Tensile behavior of polyester yarns modified by trichloroacetic acid–methylene chloride treatment. *Journal of Applied Polymer Science,* 1996, **59**(1), 99–108, doi: 10.1002/(SICI)1097-4628(19960103)59:1<99::AID-APP15>3.0.CO;2-3.
31. SIVAKUMARAN, S., RAJENDRAN, S. A quick, room temperature method for polyester-cellulosic blend analysis. *Textile Research Journal,* 1986, **56**(3), 213–214, doi: 10.1177/004051758605600310.
32. 32 ALI, S.W., RAJENDRAN, S., JOSHI, M. Synthesis and characterization of chitosan and silver loaded chitosan nanoparticles for bioactive polyester. *Carbohydrate Polymers*, 2011, **83**(2), 438–446, doi: 10.1016/j.carbpol.2010.08.004.
33. AATCC Test Method 147–1993. Antibacterial activity assessment of textile materials : parallel streak method. Research Triangle Park : AATCC, 1993, 261-262.
34. AATCC Test Method 100–2004. Antibacterial activity assessment of textile materials : percentage reduction method. Research Triangle Park : AATCC, 2004, 149–150.
35. KIVAK, T. Optimization of surface roughness and flank wear using the Taguchi method in milling of Hadfield steel with PVD and CVD coated inserts. *Measurement,* 2014, **50**, 19–28, doi: 10.1016/j.measurement.2013.12.017.
36. ENGIN, A.B., ÖZDEMIR, Ö., TURAN, M., TURAN, A.Z. Color removal from textile dyebath effluents in a zeolite fixed bed reactor : determination of optimum process conditions using Taguchi method. *Journal of Hazardous Materials,* 2008, **159**(2–3), 348–353, doi: 10.1016/j.jhazmat.2008.02.065.