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Study on the Hydrophobicity and Antibacterial Activity of Silica Sol-Chitosan-HDTMS Treated Cotton Fabric Dipped in an Aquas Media

Hidrofobnost in protibakterijska aktivnost bombažne tkanine, obdelane s silicijevim solom, hitozanom in HDTMS iz vodnega medija

Original scientific article/*Izvirni znanstveni članek*
Received/*Prispelo* 11-2022 • Accepted/*Sprejeto* 1-2023

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Abstract

A hydrophobic surface with an antibacterial property has numerous uses, including self-cleaning, anti-sticking, anti-contamination, sports apparel, and wound healing/implant materials. The durability of the coating in an aquas media (pH 7.4) is a vital requirement for use in technical textile sectors, particularly in medical applications. In this study, we used silica sol, chitosan and hexadecyltrimethoxysilane (HDTMS) to create exceptionally hydrophobic surfaces with antibacterial properties on cotton fabrics. First, cotton fabric was treated with silica sol, which was produced by the hydrolysis and condensation of tetraethoxysilane (TEOS) in an alkaline environment. After that, chitosan was applied on the silica sol-treated fabric to add an antibacterial characteristic. The silica sol-chitosan-treated fabric was then given a hydrolysed HDTMS treatment to give a highly hydrophobic property. The hydrophobicity was assessed by measuring the water contact angle, while the AATCC-147 test protocol was used to assess the antibacterial property. The developed fabric exhibited a strong hydrophobic property. The fabric samples were immersed in an aquas media for 30 days to assess the coating durability by observing changes in hydrophobicity and anti-bacterial activity in terms of the zone of inhibition (ZOI). After 30 days of immersion in the aquas media, it was observed that the contact angle decreased from 151.7° to 129.5°, and the ZOI increased from 1 mm to 5 mm, which indicates an increase in anti-bacterial activity in relation to time of immersion. The wicking characteristics of coated and uncoated fabrics were also measured to determine how coating affects the wicking behaviour of fabric. EDS was performed to observe the coating stability for coated-dipped fabric samples after 30 days. SEM analysis was performed to examine the surface morphology, while FTIR was used to determine the surface functional groups after coating and changes after dipping in the aquas media. The developed hydrophobic cotton fabrics with anti-bacterial properties may help in the fabrication of natural biomaterials and other technical textile products.

Keywords: cotton, hydrophobic, antibacterial, silica sol, chitosan

Izvleček

Hidrofobna površina s protibakterijskimi lastnostmi ima številne uporabne lastnosti, vključno s samočistilnimi, proti sprijemanju in zamazanju, ki so pomembne za športna oblačila in materiale za celjenje ran ter vsadke. Obstojnost obdelave v vodi (pH 7,4) je bistvena zahteva za tehnične tekstilije, med njimi zlasti za medicinske tekstilije. Za izdelavo izjemno hidrofobne površine s protibakterijskimi lastnostmi na bombažni tkanini je bil v tej raziskavi uporabljen silicijev sôl, hitozan in heksadeciltrimetoksisilan (HDTMS). Najprej je bila bombažna tkanina obdelana s silicijevim sôlom, ki nastane s hidrolizo in kondenzacijo tetraetoksisilana (TEOS) v alkalnem okolju. Na tako obdelano tkanino je bil v naslednjem koraku za dosego protibakterijskih lastnosti nanesen hitozan. Sledila je naknadna obdelava s hidroliziranim HDTMS za dosego visoke hidrofobnosti. Hidrofobnost je bila ocenjena z merjenjem stičnega kota vode, protibakterijske lastnosti pa so bile določene z merjenjem cone inhibicije (ZOI). Obdelana tkanina je izkazala visoko hidrofobnost. Za oceno obstojnosti obdelave sta bili hidrofobnost in cona inhibicije (ZOI) določeni tudi na vzorcih, ki so bili za 30 dni potopljeni v vodni medij. Po 30 dneh potopa vzorcev v vodni medij se je stični kot vode zmanjšal s 151,7° na 129,5°, ZOI pa se je povečal z 1 mm, na 5 mm, kar kaže na povečanje protibakterijske aktivnosti s časom potopitve. Izmerjena je bila tudi vpojnost obdelanih in neobdelanih tkanin. S pomočjo analize EDS je bila proučena stabilnost obdelave na vzorcih tkanin. Analiza SEM je bila izvedena za proučevanje morfologije površine, FTIR pa je bil uporabljen za določitev funkcionalnih skupin na površini obdelanih vzorcev in kemijskih sprememb površine po namakanju v vodnem mediju. Razvoj hidrofobne bombažne tkanine s protibakterijskimi lastnostmi je lahko v pomoč pri izdelavi naravnih biomaterialov in drugih izdelkov iz tehničnih tekstilij.

Ključne besede: bombaž, vodoodbojnost, protimikrobnost, silika, hitozan

1 Introduction

Today, fabric made of natural fibres, such as cotton with hydrophobic and anti-bacterial properties, has many applications in different technical textile fields, in particular medical, industrial, military use, etc. The number of uses of hydrophobic surfaces in the technical field is increasing due to their self-cleaning, anti-sticking and anti-contamination properties [1, 3]. Natural textile materials, such as cotton, represent an excellent media for bacteria. Natural cotton fibres provide nutrients, oxygen and moisture to bacteria for their growth and multiplication [4–8]. Moreover, fabrics made of natural fibre yarn contain micropores inside the three-dimensional structure of the yarn. These micropores increase the chance of bacteria colony formation because bacteria can easily hide and proliferate inside the micropores [9–12]. The unfavourable tissue reaction of cotton biomaterial is higher than that in synthetic fibres, which declines after about a week [13]. This unfavourable tissue reaction is caused by the high hydrophilicity of cotton fibres because, after being implanted inside the body, their hydrophilic surfaces bind plasma proteins, such as coagulation factor XII, HMWK and prekallikrein [14, 15]. However, this issue can be avoided by generating surfaces that are extremely hydrophobic and have a contact angle of more than 120° [15–17]. Therefore, cotton fabrics require a hydrophobic coating with antibacterial properties for its use in medical, industrial, military and other similar purposes.

The hydrophobicity or hydrophilicity of a surface determines how liquids will interact with it. A hydrophobic surface can be achieved by changing the surface topology (roughness), by reducing reaction surface energy or through both [1, 18, 19]. The degree of wettability of a material can be determined by evaluating the water contact angle (WCA) between the solid and liquid phases. Based on the angle of contact between water droplets and the surface, a substance is categorized as either superhydrophobic (WCA > 150°), hydrophobic (90° < WCA < 150°) or hydrophilic (WCA < 90°) [1, 20]. Various methods are available for the fabrication of superhydrophobic surfaces on cotton, such as sol-gel, layer-by-layer deposition, plasma etching, chemical vapour deposition and nanoparticle deposition [18, 21–23]. Apart from other techniques, the sol-gel method, through the use of silica nanoparticles, has drawn the attention of researchers due to its biocompatibility, eco-friendliness and non-toxicity properties, and non-fluorinated nature with good experimental reproducibility [24, 25]. Zare et al. reported that silicone is extremely biocompatible when it interacts with host tissues because silicone is hydrophobic and has a low surface tension. It has good hemocompatibility and lowers the risk of encrustation when it comes into contact with body fluids [26].

Antibacterial properties on natural fibres can be developed by using natural, organic and inorganic antibiotics. Well-known natural antibiotics are chitosan and chitosan derivatives, while popular organic antibiotics are quaternary ammonium salts, guanidine, zwitterionic betaine compounds, peptide, etc. Similarly, inorganic antibiotics include Zn nanoparticles, Ti nanoparticles, Ag nanoparticles, etc. [27]. The most abundant polysaccharide found in nature is chitosan. Chitosan is a deacetylated derivative of the polysaccharide chitin, which is mostly found in crustacean exoskeletons and has received a lot of interest because of its versatility, non-toxicity, biodegradability and antibacterial characteristics [28–30].

Therefore, in this research, a hydrophobic surface with an antibacterial property was developed on scoured cotton woven fabric by using silica sol, HDTMS and chitosan. The silica sol was formed with the help of the sol-gel technique through hydrolysis and the condensation of tetraethoxysilane (TEOS) in alkaline conditions. First, the scoured fabric was treated with silica sol. The silica-sol treated cotton fabric was then coated with a chitosan solution to achieve an antibacterial property. After that, the chitosan-treated fabrics were coated with hydrolysed hexadecyltrimethoxysilane (HDTMS) to develop a highly hydrophobic surface through a reduction in surface energy.

Coating durability in an aquas media (pH 7.4) is important for application in medical use because post operative wounds generally take four to six weeks to heal [31]. For this reason, textile materials that are used for wound healing/implant materials will be in contact with physiological body fluid for a longer period (at least 30 days), during which time the average pH of physiological body fluid remains at 7.4 [32]. There is limited work on the exposure of silica sol, chitosan and HDTMS coated fabric in an aquas media (pH 7.4) for 30 days and its impacts on hydrophobicity and antibacterial activity.

The aim of this study was thus to develop a non-toxic, biodegradable hydrophobic fabric with anti-bacterial properties by using silica sol, chitosan and HDTMS, and to then study changes in the antibacterial activity and hydrophobicity of the surface when it is dipped in an aquas media (pH 7.4).

2 Experimental

2.1 Materials

The study was conducted using cotton woven fabric that was obtained from a local industry. The details of the fabric are presented in Table 1.

Table 1: Fabric details

Property	Value
Linear density of cotton warp (tex)	20.2
Linear density of cotton weft (tex)	30.1
Weave structure	plain
Fabric areal density (g/m^2)	110
Fabric density (EPCM × PPCM) (EPI × PPI)	26×17 (66 × 43)

The chemicals used for this study were TEOS (tetraethoxysilane), ethanol, NH_4OH, HDTMS (hexadecyltrimethoxysilane), chitosan (deacetylation degree of chitosan was ≥ 75.00%) and acetic acid. All the chemicals were purchased from Sigma-Aldrich. The cotton fabric was first de-sized using an acid de-sizing method to remove sized material and then scoured using sodium hydroxide (NaOH) to remove oily substances.

2.2 Methods

2.2.1 Synthesis of silica sol using sol-gel method

The alkaline hydrolysis and condensation of tetraethoxysilane (TEOS) in ammonium hydroxide (NH_4OH) and ethanol solution was used to make silica sol. A total of 5 ml of ammonium hydroxide (NH_4OH) solution was slowly added, with continuous stirring, into 100 ml of ethanol at 60 °C. The stirring was continued for 30 minutes. Subsequently, 6ml of tetraethoxysilane (TEOS) was slowly added into the solution, drop by drop, and stirring was carried out for 90 minutes to produce the silica solution.

2.2.2 Chitosan solution preparation

Chitosan solution was prepared by dissolving 2g of chitosan into 1000 ml of 2% acetic acid solution. The solution was then stirred for 2 hours.

2.2.3 Hexadecyltrimethoxysilane (HDTMS) hydration

Hexadecyltrimethoxysilane (HDTMS) (0.75 % V/V) was slowly added (drop by drop) into ethanol to

make the solution. The pH of the solution was maintained at 5.0 by applying acetic acid. Thereafter, the solution was stirred for 60 minutes to make an alkylsilanol solution.

2.2.4 Treatment of fabric

The scoured cotton woven fabric samples were dipped for 20 minutes in a silica sol solution. The samples were then padded using a laboratory padder with a wet pickup of 70% to 80% and dried for three minutes at 80 °C [33]. After that, the cotton fabrics were padded with a 2% chitosan solution. The padded fabrics were then dried at 80 °C for five minutes and cured at 140 °C for three minutes [34]. Subsequently, the cured samples were again dipped into HDTMS alkylsilanol solution for one hour and followed by drying at room temperature. Finally, the samples were cured at 120 °C for one hour [33]. The result was coated hydrophobic fabrics.

The durability of fabric coating was studied by immersing the fabrics in an aquas media (pH 7.4) for three days, 10 days and 30 days respectively. Changes in the contact angle and anti-bacterial property of the different dipped fabrics were then measured. The different fabric samples, before and after coating, are presented in Table 2. Moreover, the aquas media (pH 7.4) was prepared using distilled water and sodium carbonate. Sodium carbonate was added to distilled water to maintain the pH of media at 7.4.

Table 2: The different fabric samples before and after coating

Seq. no.	Sample code	Fabric
1	C1	Untreated cotton fabric
2	C2	Coated fabric (silica sol + chitosan (0.2%) + 0.75% (V/V) HDTMS)
3	C3	Dipped in aquas media for 3 days
4	C4	Dipped in aquas media for 10 days
5	C5	Dipped in aquas media for 30 days

2.3 Characterization technique used

Developed fabrics were characterized using the following techniques:

– **contact angle measurement**

The contact angles of different types of fabrics were measured to determine the surface wettability of the untreated, treated and dipped fabric. The contact angle as measured by using a Drop Shape Analyzer, Kruss, Germany.

– **determination of wicking properties**

A published method [35] was used to assess the wicking effect of coated and uncoated fabric. Fabric measuring 200 mm × 25 mm was cut for the purpose of evaluating wicking ability. A clamp was then equipped with a stainless-steel scale. After that, a glass reservoir was added to the frame's base. The fabric was also carefully controlled to avoid bending around its axis. The rise of liquid through the yarn of fabric was observed. The test was terminated when there was no indication that any liquid had been absorbed.

– **characterization of anti-bacterial property**

The antibacterial efficiency of coated fabric was evaluated using the AATCC-147 test protocol with *E. coli* bacteria [6]. A culture media was prepared using agar-agar (2%) and Luria broth (2%) in distilled water. The petri dish, tip, forceps, L rod and media were then sterilized in an autoclave for 15 minutes at 120 °C and a pressure of 1.05 kg/cm^2. The cultured media poured into petri dishes, and the petri dish, L rod, forceps, 1 ml tip box, pipette and fabric were again sterilized using UV sterilization for 15 minutes. A total of 100 µl of bacteria were dispersed in an agar media using an L rod after UV sterilization. The fabric was then placed in the centre of the petri dishes. The petri dishes were covered with paraffin paper. After this, the petri dishes were incubated for 24 hours at 37 °C. The zone of inhibition was determined to test antibacterial activity.

– **scanning electron microscopy (SEM) analysis**

The surface of the untreated and treated fabric was examined using a ZEISS Sigma 500 VP scanning electron microscope (Germany). Since cotton fibre is nonconductive, the fabric was coated with a thin film of gold before SEM measurements.

– **fourier infrared spectroscopy (FTIR) analysis**

Changes in the functional groups of untreated, treated and dipped fabric were observed using a BUKER ALPHA II FTIR spectrometer (Germany). The results were taken in a wavelength of 600 nm to 4000 nm.

– **energy dispersive X-ray spectroscopy (EDS) analysis**

EDS analyses of the uncoated, coated and dipped samples were performed to observe coating stability using an EDS, AMETEK ELECT PLUS device.

– **measurement of tensile strength**

The tensile behaviour of the yarns unravelled from coated fabric and from coated fabric dipped for 30 days were assessed using a Tinius Olsen Universal Testing Machine (UTM).The standard test norm ASTM D2256/D2256M 21 was applied to determine the tensile strength of the unravelled yarn.

– **measurement of tear strength**

The tearing strength of the uncoated and coated fabric was evaluated using the tongue (single rip) procedure (Constant Rate of Extension Tensile Testing Machine) according to standard test norm ASTM D2261.

– **measurement of stiffness**

The stiffness of the uncoated and coated fabric was measured according to the ASTM D1388-18 standard protocol.

3 Result and discussion

The procedure for forming a hydrophobic surface with antibacterial abilities on scoured cotton woven fabric is presented in section 2.2, while the potential chemical reactions are shown in Figure 1. Figure 1a illustrates how silica sol binds to cotton fabric through a condensation reaction between the hydroxyl groups of cotton and silica sol. Similar observations have also been document-

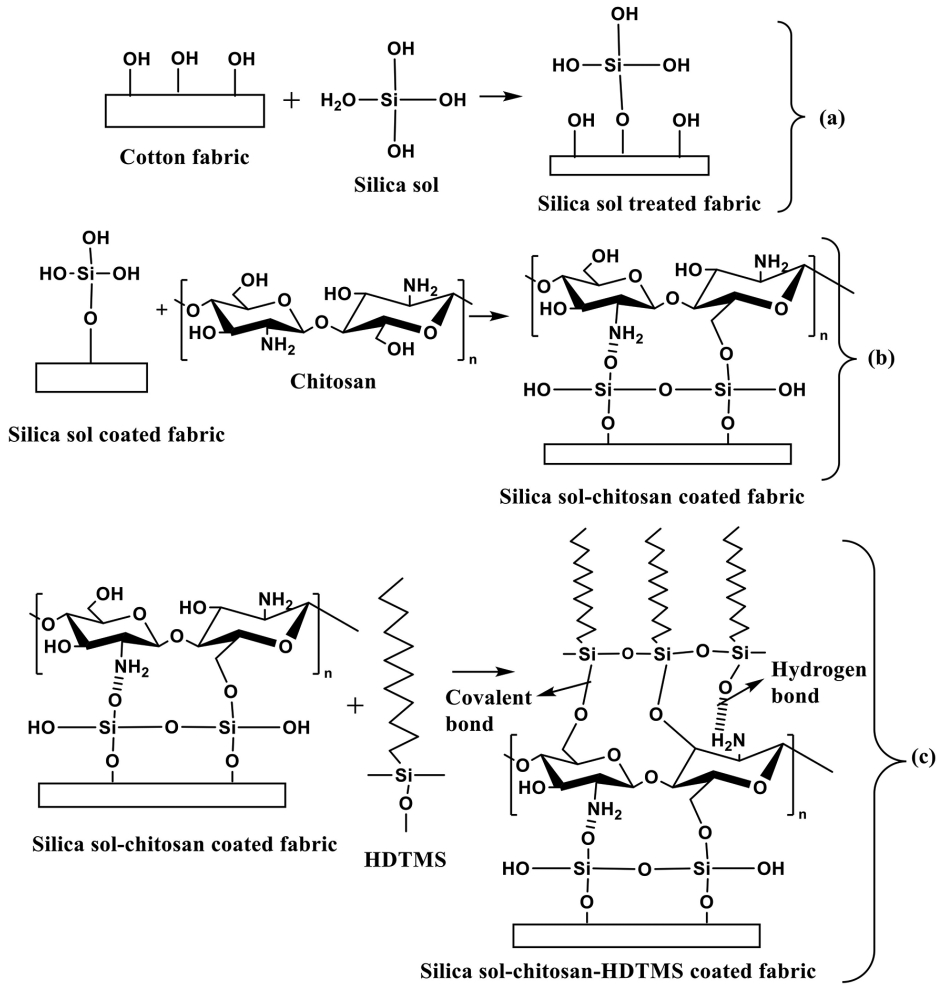


Figure 1: Potential reaction between: a) cotton fibre and silica sol; b) silica sol and chitosan; and c) chitosan and HDTMS

ed in available literature [33, 36]. The structure of chitosan contains hydroxyl and amine groups. Silica sol's hydroxyl group and chitosan's hydroxyl group established a covalent link, resulting in the silica nucleation. Although the amine group cannot create covalent bonds, it serves as an excellent hydrogen bonding partner. As a result, a hydrogen bond formed with the silica sol's hydroxyl group, as seen in Figure 1b, while a similar reaction was also observed by Budnyak [37]. Similar to the chitosan bonds with silica sol, HDTMS attached to chitosan through covalent and hydrogen bonds, as seen in Figure 1c [37].

FTIR spectra can be used to explain the binding mechanism. Figure 2 shows the FTIR spectra of materials that were uncoated, coated and dipped for 30 days. For hydrophilic groups (-OH groups and NH_2 groups), spectra in the range of 3200–3400 cm^{-1} was observed [38, 39]. After coating, there was a drop in the absorbance of spectra in the range of 3200–3400 cm^{-1}. This decrease may be the result of a condensation reaction among the hydroxyl groups of cotton and silica-sol, silica sol and chitosan, and chitosan and HDTMS, although the peak of -OH is still present even after coating, which indicates the presence of some hydroxyl group on the fabric surface even after HDTMS coating. The peak intensity in the range of 3200–3400 cm^{-1} was again raised after dipping the fabric in an aquas media for 30 days. This may be due to the breaking of hydrogen bond between hydroxyl group of HDTMS and NH_2 of chitosan, which results in an increase in hydrophilic groups (-OH and -NH_2). The breaking of bonds may be due to the prolonged direct contact of the samples with water. In water, hydrogen bonds break easily [40]. In addition, the unreacted OH group present on surface of coated fabric may absorb water molecules physically or by hydrogen bond [41, 43].

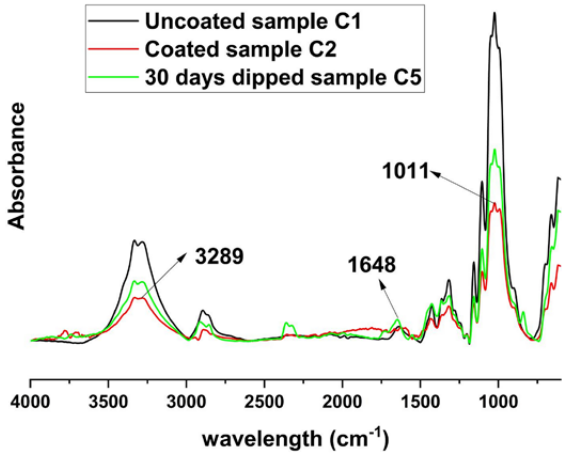


Figure 2: FTIR spectra of uncoated sample C1, coated sample C2 and sample C5 dipped for 30 days

Additionally, the spectra between 1600 cm^{-1} and 1700 cm^{-1} appeared for the sample dipped for 30 days, while the peak between 1600 cm^{-1} and 1700 cm^{-1} normally appeared for amine groups [34]. Moreover, the peaks in the range of 1600 cm^{-1} to 1700 cm^{-1} are further evidence that the hydrogen bond between HDTMS and chitosan were broken, exposing amine groups. The absorption Si-O-Si spectra of silica sol and HDTMS, and the C-O spectra of chitosan in the range of 1100–1000 cm^{-1} appear overlap with the untreated cotton C-O spectra (cellulosic bond), which is similar to the results of previously reported research [33, 43].

EDS analyses of uncoated sample C1, coated sample C2 and sample C5 dipped for 30 days were also performed to observe the stability of coating, and are presented in Figure 3. Only C and O atoms were detected on the surface of uncoated sample, while C, O, N and Si were detected for the coated sample and sample dipped for 30 days. Moreover, the presence

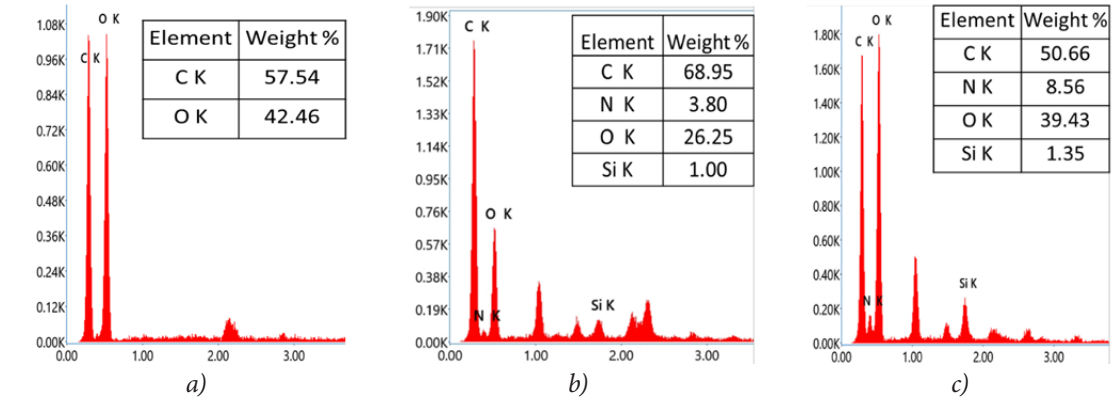


Figure 3: EDX spectra of: a) uncoated sample C1; b) coated sample C2; and c) sample C5 dipped for 30 days

of N atoms and Si atoms on the surface after 30 days of dipping confirmed coating stability.

The hydrophobicity of the fabric surface was determined by measuring the contact angle of the sample surface using a drop shape analyser. Table 3 and Figure 4 present the contact angle values for fabrics C1, C2, C3, C4 and C5. Table 3 shows that the contact angle of untreated cotton fabric was not measurable because the water droplet vanished immediately from the fabric's surface as soon as contact with the fabric surface was made. This may be due to the large number of hydrophilic groups present on cotton fibres, fine pores in the yarn and water wicking through the yarn's capillaries, which are ultimately responsible for the extreme hydrophilicity of untreated fabric [44]. It is evident that after being treated with silica sol, chitosan and HDTMS the water contact angle of the coated cotton surface C2 reached a value of 151.7°, which indicates superhydrophobic nature of the surface [21, 45].

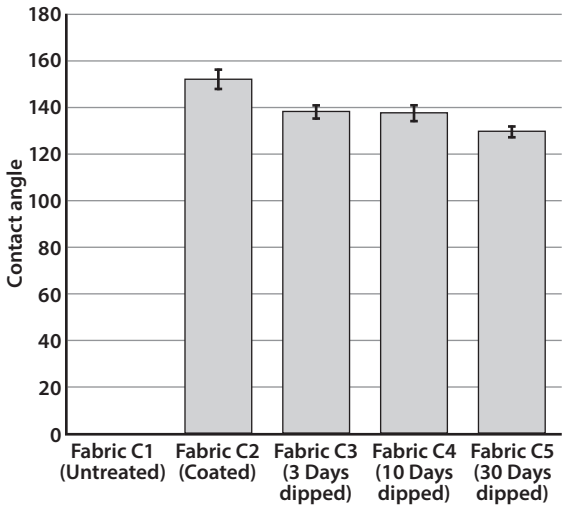
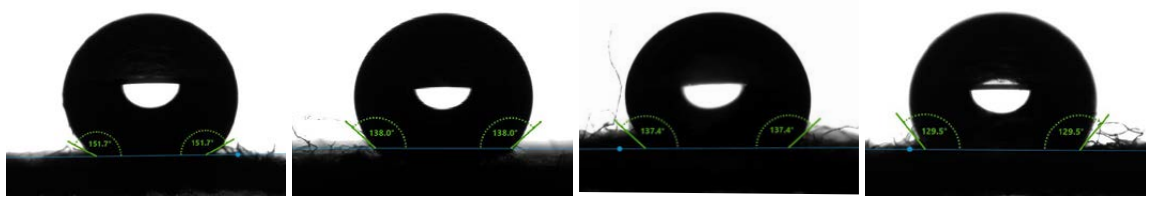


Figure 4: Water contact angle of untreated, treated and dipped cotton fabric

Table 3: Water contact angle of untreated, treated and dipped cotton fabric

Sample type	Contact angle (°)
C1	Not measurable
C2	151.7
C3	138.0
C4	137.4
C5	129.5

The sharp rises in contact angle may be due to the alteration of surface roughness of the fabric following the application of silicon sol, and a reduction in the surface energy of the cotton fabric surface due to subsequent treatment with HDTMS. Therefore, the combined effects of roughness and reduced surface energy lead to a highly hydrophobic surface [6, 33, 46]. The original tracing obtained from the drop shape analyser are presented in Figure 5 for the fabric surfaces of samples C2, C3, C4 and C5. It is evident from Figures 4 and 5 that the contact angle decreased significantly after three days of dipping in an aquas media i.e. 151.7° to 138°. Thereafter, the rate of reduction in the contact angle is relatively lower for the next 30 days. The contact angle was decreased after dipping in an aquas media. There are two probable reasons for the entire surface phenomena in this respect. First, the decrease in the contact angle after dipping was probably due to the cracks in the silica coating on the cotton fibre surface caused by the swelling of cotton. This is supported by earlier studies, which reported that the contact angle decreased after 25 to 30 washings, and the reduction may be due to cracks in silica film on the fibre surface caused by the swelling of cotton [33, 47]. The second reason is the absorption of water molecules by OH groups present on the coated



fabric C2	*fabric C3*	*fabric C4*	*fabric C5*
151.7°	*138°*	*137.4°*	*129.5°*
a)	*b)*	*c)*	*d)*

Figure 5: Contact angle of: a) treated sample; b) sample dipped for three days; c) sample dipped for 10 days; and d) sample dipped for 30 days

surface during long-term direct contact with water [41, 42]. Furthermore, any material intended for use as a biomaterial must be biocompatible and must also have a contact angle greater than 120° for at least a week after implantation in order to stop this tissue reaction [13, 17]. This is because tissue reactivity normally subsides after about a week [13]. The developed cotton fabric exhibited a contact angle of above 120° even after 30 days of dipping in an aquas media. It is thus possible to use this developed fabric as a wound healing/implant material.

The wicking effect of uncoated and coated cotton fabrics (C1 and C2, respectively) were observed by measuring the wicking height. Figure 6 and Table 4 show the wicking height of cotton fabrics that are uncoated (C1) and coated (C2), respectively. It is evident from Figure 6 and Table 4 that cotton fabrics that are not coated exhibit wicking behaviour and have a wicking height of 8 cm ± 1 cm. This might be caused by the capillaries that exist within the structure of the yarn (intra-yarn spaces) and between the yarns (inter-yarn spaces) [48, 49]. Conversely, the cotton fabric treated with silica sol, chitosan and HDTMS displayed zero evidence of wicking.

Table 4: Wicking performance of uncoated and coated cotton fabric

Fabric type	Maximum wicking height (cm)
Uncoated cotton fabric sample (C1)	8 ± 1
Coated cotton fabric sample (C2)	0

The coating on the fabric surface developed an impermeable barrier by blocking the pores and capillaries inside the yarns and the fabric's structure [50]. As a result, the obstructions limited the capillaries' ability to work in coated fabrics. Moreover, the blocked pore/capillaries can be useful for medical applications because the bacteria can not hide and grow inside the yarn structure of coated fabrics where the pores are blocked.

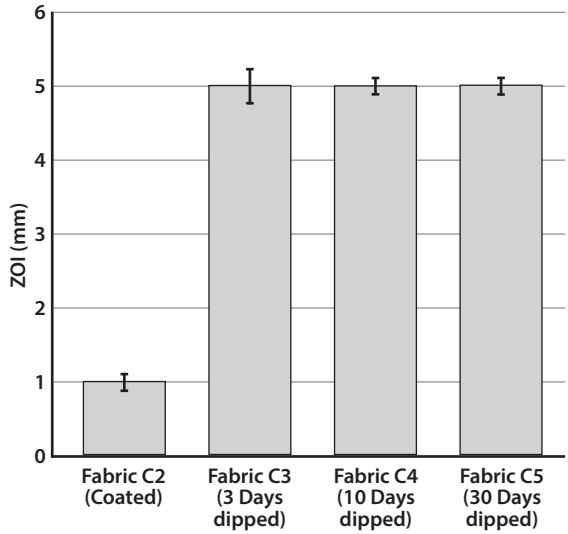
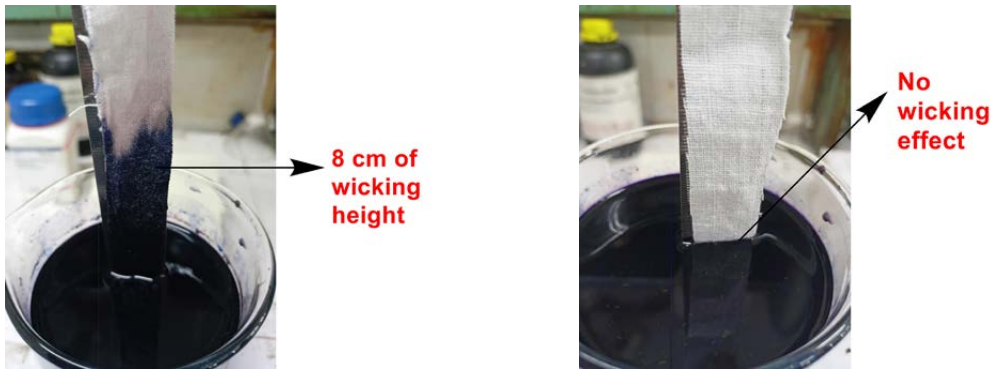


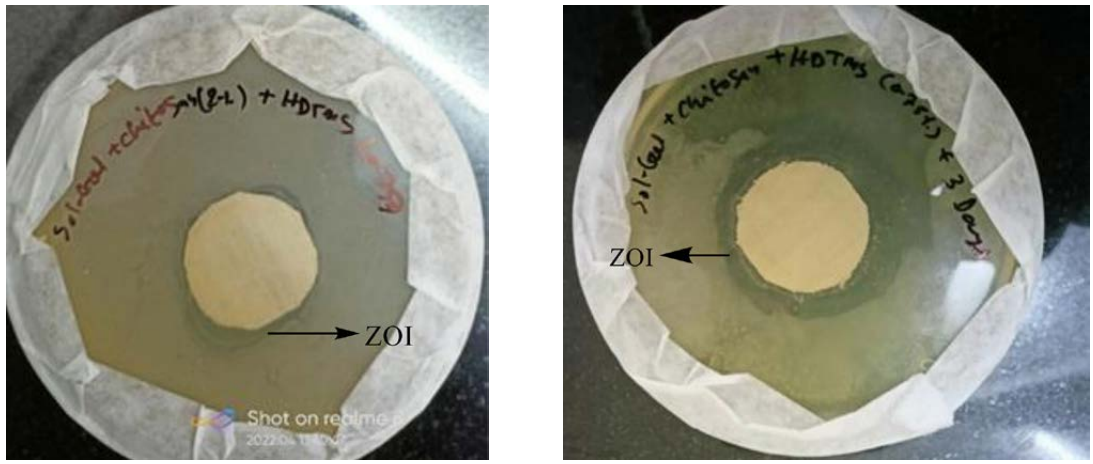
Figure 7: Zone of inhibition (ZOI) of treated and dipped fabric

The anti-bacterial activity of fabric C2, C3, C4 and C5 were measured with help of the agar-agar diffusion test method using *E. coli*. The zone of inhibition (ZOI) was calculated for all the samples and plotted in Figure 7. It was observed that the ZOI of fabric C2 (treated) was relatively low, at around 1 mm, while the ZOI increased in the case of dipped fabric C3, fabric C4 and fabric C5 relative to treated fabric C2. The ZOI of coated fabric sample C2 and



a) *b)*

Figure 6: Wicking of: a) uncoated cotton fabric (sample C1); and b) coated cotton fabric (sample C2)



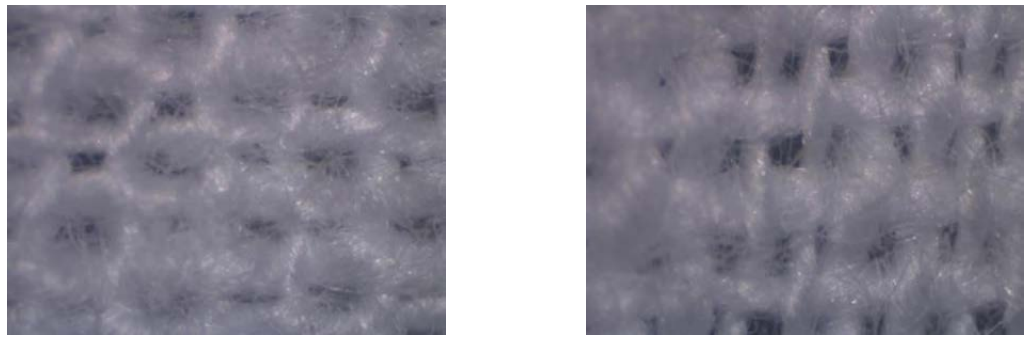
a) *b)*

Figure 8: ZOI of: a) treated fabric C2; and b) dipped fabric C3

dipped sample C3 are also shown in Figure 8. The increase in the ZOI of the dipped fabric samples (C3, C4 and C5) may be due to the breakage of the hydrogen bond between the -NH_2 of chitosan and the -OH of HDTMS. The hydrogen bond breaks due to long-term direct contact with water. Hydrogen bonds break easily in water [40]. The breakage of the hydrogen bond thus leads to the exposure of the NH_2 of chitosan. The exposure of NH_2 after dipping was also confirmed by FTIR, which showed the increased intensity of the NH_2 spectra at 1648 cm^{-1} (Figure 2). Moreover, when NH_2 was exposed to an aquas media, it became cationic in nature and thus killed bacteria [34].

However, both the coated fabric sample (C2) and dipped fabric samples (C3, C4 and C5) demonstrated antibacterial activity due to the presence of chitosan. There are two types of proposed mechanisms by which chitosan exhibits antibacterial property. In one method, the polycationic nature of the amino group (NH_2) in chitosan interferes with the metabolism system of bacteria by attaching to the cells of bacteria. In the other method, the chitosan binds with DNA to inhibit the synthesis of mRNA [34, 51]. Hence, the improved antibacterial activity of coated samples after dipping in an aquas media may be useful in addressing the antibacterial requirements of biomaterial [9–12].

The surface morphology of textile fabrics before and after coating are observed by using a Leica image analyser and SEM. The Leica image of fabric before and after coating are shown in Figure 9. The SEM images of uncoated sample C1, coated sample C2 and dipped sample C5 are shown in Figure 10. Higher roughness was observed on the SEM image of coated cotton fabrics C2 than on the untreated cotton fabric C1, which confirmed the attachment of chitosan and silicon nanoparticles. Moreover, the roughness of dipped sample C5 increased relative to coated sample. This may be due to the cracks in silica coating caused by the swelling of fibre during long-term direct contact with water [33].



a) *b)*

Figure 9: Leica images of: a) untreated fabric C1; and b) treated fabric C2

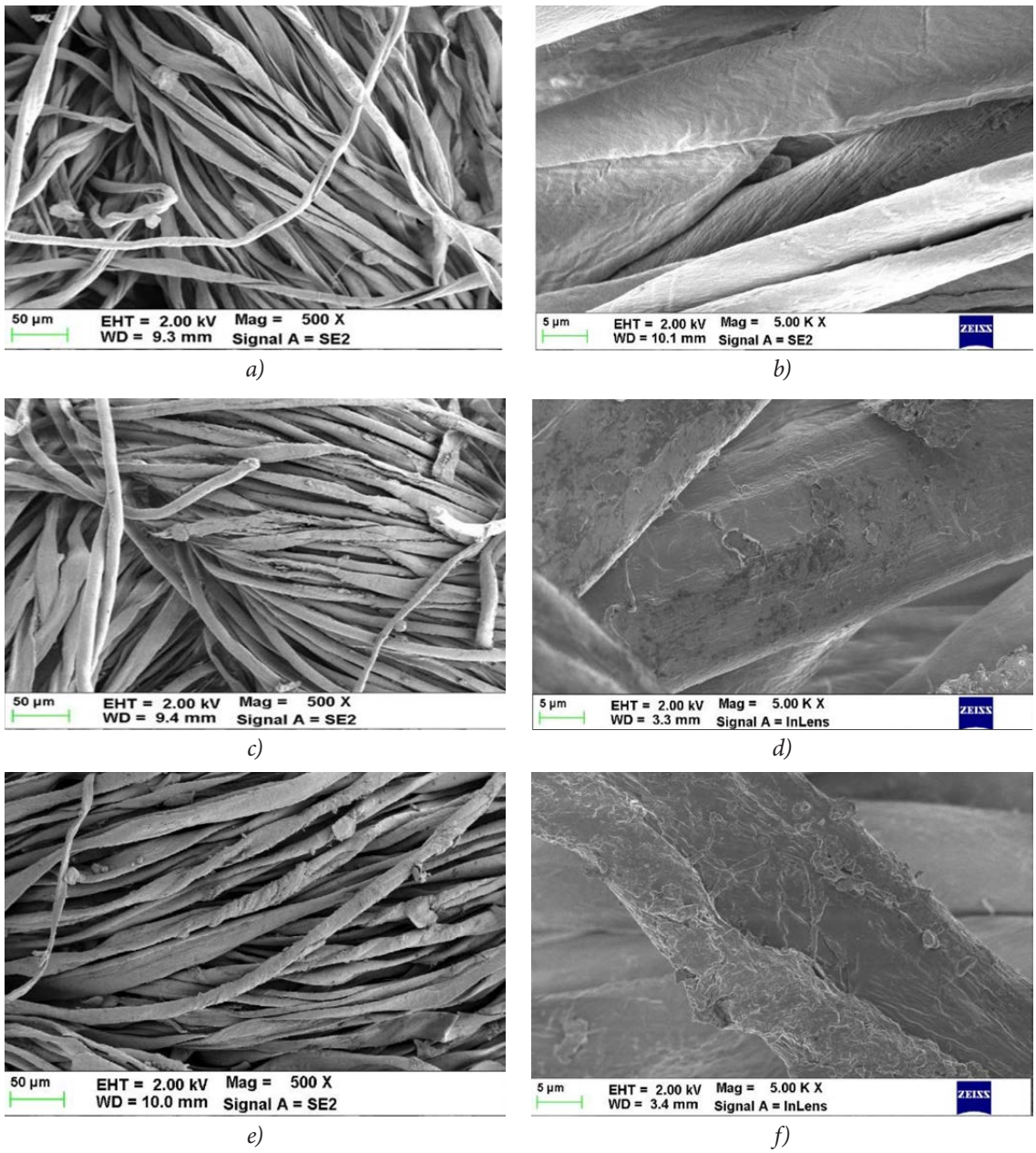


Figure 10: SEM images of: a) untreated fabric C1; b) untreated fabric C1 with higher magnification; c) treated fabric C2; d) treated fabric C2 with higher magnification; e) dipped fabric C5; and f) dipped fabric C5 with higher magnification

The tensile strength of yarn unravelled from treated fabric sample C2 and sample C5 dipped for 30 days was measured and is presented in Table 5. After 30 days of dipping, the yarn's tensile strength decreased by 6.4%. The degradation of cotton fibre in the aquas media may be responsible for this drop in tensile strength.

Table 5: Tensile strength of coated sample (C2); and sample (C5) dipped for 30 days (yarn)

Sample type	Breaking force (N)
C2	3.1 ± 0.3
C5	2.9 ± 0.4

The tearing strength of uncoated fabric sample C1 and coated fabric sample C2 were evaluated and are

presented in Table 6. It is evident from Table 6 that tearing strength decreased by about 2% after coating. Therefore, coating does not have a significant effect on tearing strength ($p > 0.05$).

Table 6: Tearing strength of uncoated and coated sample

Type of sample	Average tearing strength (N)
Uncoated fabric sample C1	15.34
Coated fabric C2	15.08

The stiffness of uncoated fabric sample C1 and coated fabric sample C2 was observed by measuring the bending length and is presented in Table 7. The bending length increased by 10% after coating. Therefore, the stiffness of the fabric is only marginally affected by coating ($p > 0.05$).

Table 7: Bending length of uncoated and coated sample

Type of sample	Average bending length (cm)
Uncoated fabric sample C1	1.8 ± 0.1
Coated fabric sample C2	2.0 ± 0.1

4 Conclusion

The developed cotton fabric exhibited a highly hydrophobic nature when coated with silica sol, chitosan and HDTMS, while the value of the contact angle of the treated fabric was around 151.7°. However, after three, 10 and 30 days of dipping in an aquas media, the contact angle decreased to 138°, 137.4° and 129.5° respectively, meaning a highly hydrophobic nature was maintained even after 30 days. Moreover, the treated fabric indicates zero wicking due to the blocking of pores. In terms of antibacterial activity, coated fabric demonstrated a low antibacterial activity with a ZOI of approximately 1 mm. However, the antibacterial activity was enhanced when the fabric was dipped in an aquas media for three, 10 and 30 days, with a ZOI of 5 mm. It is likely that the decrease in contact angle was due to cracks in the silica coating and the absorption of water molecules by -OH groups present on the coated surface. An increase in ZOI (1 mm to 5 mm) was seen as a result of the breakage of the hydrogen bond between chitosan and HDTMS, leading to the exposure of NH_2 groups of chitosan. The developed hydrophobic cotton fabric, with antibacterial capabilities even after 30 days of dipping in an aquas media, may be beneficial for developing natural biocompatible textile materials that may be used as wound healing/implant materials.

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