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Vpliv barvanja bombaža z reaktivnim barvilom na adsorpcijo srebra

Izvirni znanstveni članek

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Izvleček

V raziskavi smo proučili vpliv reaktivnega barvila na bombažni tkanini na adsorpcijo srebra protimikrobnega sredstva RucoBac AGP, ki smo ga na tkanino nanašali po izčrpalnem postopku. Primerjalno smo RucoBac AGP nanesli tudi na tkanine, obdelane v slepi kopeli, ki je vsebovala vsa pomožna sredstva razen barvila. Funkcionaliziranim tkaninam smo določili vsebnost srebra, protimikrobno učinkovitost in pralno obstojnost. Proučili smo tudi vpliv obdelave bombaža s srebrom na belino in barvo bombaža. Raziskava je pokazala, da barvanje z reaktivnim barvilom vpliva na povečanje adsorpcije srebra na beljeno/mercerizirano bombažno tkanino in posledično na njeno protimikrobno učinkovitost. Spremembe beline in barve tkanine so opaznejše pri funkcionalizaciji tkanine z višjo koncentracijo RucoBac-a AGP.

Ključne besede: bombaž, reaktivno barvilo, nanodelci, srebro, adsorpcija

Influence of Dyeing Cotton with Reactive Dye on Adsorption of Silver

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Abstract

The influence of reactive dyeing on the silver adsorption of antimicrobial agent RucoBac AGP on a cotton fabric was investigated for the research purpose. RucoBac AGP was applied on a cotton fabric using the exhaustion method. For a comparison, RucoBac AGP was applied on fabrics treated in a blank dyebath which contained all auxiliaries except for the dye. The quantity of silver, the antibacterial efficiency and wash-fastness were determined for functionalized fabrics. The whiteness and colour change of silver treated cotton fabrics were investigated as well. The research results show that dyeing with a reactive dye causes higher adsorption of silver on a bleached/mercerized cotton fabric and its antimicrobial efficiency. The changes in the whiteness and colour of the fabric are more visible when treating cotton with a higher concentration of RucoBac AGP.

Keywords: cotton, reactive dye, nanoparticles, silver, adsorption

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1 Uvod

Tekstilni materiali so zaradi svoje velike površine in zmožnosti zadrževanja vlage odlično okolje za razvoj mikroorganizmov. Ti lahko na tekstilijah povzročajo milejše, estetske nevšečnosti, a tudi resnejše, z zdravjem povezane težave [1]. Tekstilni materiali s protimikrobnim učinkovanjem se uporabljajo za medicinske, vojaške in tehnične tekstilije, tekstilije za šport in prosti čas ter posteljno perilo [2–4]. Priprava kovinskih delcev nanovelikosti omogoča razvoj novih biocidov [5]. Pri nanotehnoloških raziskavah v tekstil-

1 Introduction

Due to their large surface area and ability to retain moisture, textile materials provide an excellent environment for the microorganism growth. Microorganisms can cause from a milder, aesthetic unpleasantness to a serious, health-related problem [1]. Textile materials with an antimicrobial effect are used for medical, military and technical textiles, textiles for sports and leisure, and bedding [2–4]. The preparation of metal nanoparticles enables the development of new biocides [5]. At nanotechnology researches in textiles, different forms of silver were used, e.g. metal silver nanoparticles, silver chloride (AgCl) and composite particles of silver and titanium dioxide (Ag-TiO$_2$) [6–22]. In the case of antimicrobial efficiency, the surface coating of nanosilver on titanium dioxide maximizes the number of particles per unit area in comparison with the use of an equal mass fraction of pure silver [23, 24]. When dealing with researches of deposition of silver onto different substrates, it is important to understand the adhesion of particles, which is dependent on the interaction mechanism with a material. The mechanism of nanoparticle adhesion has not been completely explained yet, since there are many different opinions among the theorists on the subject. Thus, it is generally considered that attractive forces and chemical bonds play an important role in the adhesion of particles [25]. The physical or mechanical adhesion of nanoparticles mostly occurs due to van der Walls or electrostatic forces, while the chemical adhesion of particles is a consequence of ionic, covalent, metallic and hydrogen bonds [26]. Moreover, the nanoparticles can penetrate into certain parts of the substrate, such as pores, holes and crevices, and they lock mechanically to the substrate. This adhesion mechanism, which is called mechanical interlocking, has been understood from the perspective of surface roughness effects [27]. The increased adsorption of nanoparticles on textile materials can be achieved by using different techniques of nanoparticle applications, e.g. exhaustion procedure, the use of a matrix and a prolonged treatment time of textiles in the silver nanoparticles containing bath [6, 14, 17]. The

stvu so bile uporabljene različne oblike srebra, kot so kovinski nanodelci, srebrov klorid (AgCl) ter kompoziti srebra in titanovega dioksida (Ag-TiO$_2$) [6–22]. Pri protimikrobni aktivnosti se pri površinsko vezanem srebru na TiO$_2$ poveča število srebrovih nanodelcev na enoto površine v primerjavi z uporabo enakega masnega deleža čistega srebra [23, 24].
Pri raziskovanju nanašanja delcev na različne substrate je pomembno razumevanje adhezije delcev, ki je odvisna od mehanizma interakcij z materialom. Mehanizem adhezije nanodelcev še vedno ni popolnoma razjasnjen, zato med teoretiki obstaja o tej temi veliko različnih mnenj. Vendar pa na splošno velja, da na adhezijo vplivajo privlačne sile in kemijske vezi [25]. Fizikalna oz. mehanska adhezija delcev na površino substratov je v večini primerov posledica van der Waalsovih ali elektrostatskih sil, medtem ko je kemijska adhezija delcev na površino substratov posledica ionskih, kovalentnih, kovinskih ali vodikovih vezi [26]. Poleg adhezije delcev na površino substrata lahko srebrovi nanodelci penetrirajo v določene dele substrata, kot so pore, luknje, žlebiči in medvlakenski prostori, kjer se lahko povsem mehansko vežejo na substrat. Takšno mehansko vezanje nanodelcev je še posebno značilno za površinsko bolj hrapave substrate [27]. Adsorbcijo nanodelcev na tekstilije lahko povečamo z uporabo različnih načinov nanosa nanodelcev, kot so izčrpalni postopek, uporaba sredstev za zamreženje ali podaljšan čas obdelave tekstilije v kopeli, ki vsebuje nanodelce [6, 14, 17]. Povečanje adsorpcije nanodelcev na tekstilije lahko dosežemo tudi s predpripravo tekstilije, kot je npr. uporaba plazemske tehnologije [7–9]. Ugotovljeno je bilo, da na povečanje adsorpcije nanodelcev srebra vpliva tudi barvanje bombaža z redukcijskimi barvili [28].
V raziskavi smo beljeno/mercerizirano bombažno tkanino funkcionalizirali z barvanjem in nanodelci srebra. Namen naše raziskave je bil proučiti vpliv barvanja bombažne tkanine z reaktivnim barvilom na povečanje adsorpcije srebra iz kopeli. V ta namen smo raziskavo opravili na slepo barvani in z reaktivnim barvilom barvani bombažni tkanini. Tkaninam smo določali protimikrobno učinkovitost in pralno obstojnost tkanin, obdelanih z nanodelci. Proučili smo tudi vpliv funkcionalizacije bombaža s srebrom na belino in barvo bombaža.

2 Eksperimentalni del

Vzorce beljene/mercerizirane bombažne tkanine, v vezavi platno (119,2 g/m^2, osnova: 52 niti/cm, votek: 26 niti/cm) smo barvali oz. slepo barvali in jih nato obdelali s protimikrobnim sredstvom. Tkanine smo barvali z bireaktivnim barvilom Cibacron deep red S-B (Ciba) pri kopelnem razmerju 1 : 20. Barvalna kopel je vsebovala 0,5 % barvila, 30 g/l Na_2SO_4 (Carlo Erba) in 8 g/l Na_2CO_3 (Carlo Erba). Po barvanju so sledile naknadne obdelave: izpiranje z destilirano vodo, nevtralizacija z 1 ml/l CH_3COOH 30 % (Sigma-

increased adsorption of nanoparticles onto textiles can also be achieved by using the plasma technology as a surface pre-treatment [7–9]. It was established that the dyeing of cotton with a vat dye increases the adsorption of silver nanoparticles [28].

For the research, a bleached and mercerized cotton fabric was functionalized with dyeing and silver nanoparticles. The purpose of our research was to investigate the influence of reactive dyeing on the adsorption of silver on a cotton fabric. The quantity of silver, the antibacterial efficiency and wash fastness were determined for blank dyed and dyed cotton fabrics treated with nanosilver. The influence of functionalization with silver on the whiteness and colour of cotton was investigated as well.

2 Experimental

The samples of a bleached/mercerized cotton fabric in plane weave (119.2 g/m^2, warp: 52 threads/cm, weft: 26 threads/cm) were first dyed or blank dyed, and then treated with an antimicrobial agent. The cotton samples were dyed with a bi-reactive dye Cibacron deep red S-B (Ciba). The liquor ratio 20 : 1, 0.5% of dye, 30 g/l Na_2SO_4 (Carlo Erba) and 8 g/l Na_2CO_3 (Carlo Erba) were used. After the dyeing, the samples were after-treated, i.e. rinsed with distilled water, neutralized with 1 ml/l CH_3COOH 30% (Sigma-Aldrich) and soaped with 1 g/l Cibapon R (Ciba). The samples were finally rinsed with cold distilled water. The dyeing procedure and after-treatments are presented in Figure 1.

As the antimicrobial treatment of cotton, a commercial form of nanoparticles RucoBac AGP (Rudolph Chemie) [29] was used. RucoBac AGP (RB) is a hygienic finish for all fibre types. It is highly a concentrated hygiene and freshness system complying with the Öko-Tex standard 100. RB is a nano-dispersion of titanium dioxide (TiO_2) as the carrier of the active component silver chloride (AgCl). The recommended concentration of RB is 0.2–0.5%. For our research, the lowest recommended concentration, i.e. 0.2%, was used. For a comparison, 0.1% of RB was used, which represents a half of the lowest concentration recommend-

-Aldrich), miljenje z 1 g/l Cibapon R (Ciba) in ponovno izpiranje z destilirano vodo. Diagram barvanja in naknadnih obdelav je predstavljen na sliki 1.

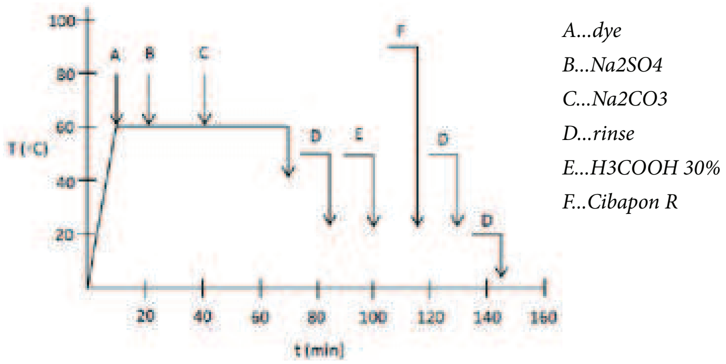

Figure 1: Dyeing procedure for Cibacron deep red S-B and after-treatments

Za protimikrobno obdelavo smo uporabili trgovsko obliko nanodelcev RucoBac AGP (Rudolph Chemie), ki je higienska apretura za vse vrste vlaken [29]. RucoBac AGP (RB) zagotavlja higieno in svežino tekstilij ter je skladen z Öko-Tex 100. RB je nanodisperzija kompozita titanovega dioksida (TiO_2) v kombinaciji z aktivno komponento srebrovega klorida (AgCl). Priporočena koncentracija RB je od 0,2 do 0,5 %. Za raziskavo smo uporabili najnižjo priporočeno koncentracijo RB (0,2 %). Za primerjavo smo uporabili tudi 0,1 % RB, kar pomeni za polovico nižjo koncentracijo od najnižje, ki jo predpisuje izdelovalec sredstva. Vzrok za tako odločitev je bilo preverjanje možnosti doseganja dobrega protibakterijskega učinka bombažne tkanine z uporabo zelo nizke koncentracije srebrovega kompozita. RB smo na vzorce tkanine nanašali po izčrpalnem postopku pri naslednjih pogojih: kopelno razmerje (KR) = 1 : 10, T = 50 °C in t = 30 min. Sledilo je štiriminutno sušenje tkanin pri 130 °C. RucoBac AGP smo nanašali na slepo barvane in barvane bombažne tkanine.

Funkcionalizirane vzorce smo 10-krat prali v Launder-o-metru pri naslednjih pogojih: KR = 1 : 50, T = 60 °C, t = 30 min, 5 g/l standardiziranega pralnega sredstva (ECE phosphate reference detergent B) in 2 g/l Na_2CO_3 [30]. Po pranju je sledilo dvakratno izpiranje z destilirano vodo in desetminutno izpiranje pod tekočo vodo. Vzorce smo posušili na zraku pri sobni temperaturi.

Na tkaninah smo z analizno metodo masne spektroskopije z induktivno sklopljeno plazmo (ICP-MS) spremljali količino adsorbiranega srebra in primerjali slepo barvane in barvane vzorce. Analizo ICP-MS smo opravili pred pranjem vzorcev in po njem.

Protimikrobno učinkovitost različno funkcionaliziranih nepranih in pranih bombažnih tkanin smo ugotavljali po metodi ASTM: E 2149-01 [31], ki je priporočena metoda izdelovalca RucoBac-a AGP, na *Staphylococcus aureus* (ATCC 25923), *Escherichio coli* *ed by the agent producer. The reason for such a decision was to verify the possibility in achieving good antibacterial efficiency of a cotton fabric with the use of a very low concentration of a silver composite. The exhaustion method was used for the deposition of RB onto blank dyed and dyed cotton samples. The liquor ratio was 10 : 1, and the treatment time 30 min at 50 °C. Afterwards, the samples were dried at 130 °C for 4 min.*

The samples were tested for wash-fastness in an AATCC Atlas Launder-O-Meter Standard Instrument. The samples were washed repetitively 10 times at 60 °C in a solution of 5 g/l standard detergent (ECE phosphate reference detergent B) and 2 g/l Na_2CO_3 [30]. The duration of washing cycles was 30 min. After the washing, the samples were rinsed twice in cold distilled water, held under cold tap water for 10 min, wrung out and dried at a room temperature.

The quantity of silver on cotton samples was determined using inductively coupled plasma mass spectroscopy (ICP-MS). Blank dyed and reactive dyed cotton samples were compared. The ICP-MS analysis was applied before and after the washing of samples.

The antimicrobial effectiveness of different functionalized unwashed and washed samples was determined according to the test method ASTM: E 2149-01 [31], recommended by the producer RucoBac AGP, against Staphylococcus aureus (ATCC 25923), Escherichia coli (ATCC 25922), Streptococcus faecalis (ATCC 27853) and Pseudomonas aeruginosa (ATCC 27853). The bacterial reduction (R) was calculated using Equation 1; where A is the Colony-forming unit (CFU) per millilitre for the flask containing the treated substrate after 1 hour contact time and B is the CFU per millilitre for the flask to determine A before the addition of the treated substrate (time "0"). The value of bacterial reduction must exceed 60% for a fabric to have satisfactory antimicrobial effectiveness.

The whiteness index and whiteness tint were determined for blank dyed samples based on the CIE measurements of reflectance values by using the spectrophotometer Spectraflash 600 Plus-CT (Datacolor). The measurements were made under the following conditions: size of measurement port 9 mm, observation angle

(ATCC 25922), *Streptococcus faecalis* (ATCC 27853) in *Pseudomonas aeruginoso* (ATCC 27853). Bakterijsko redukcijo (R) smo izračunali po enačbi 1:

$$R\,(\%) = \frac{B - A}{B} \times 100, \qquad (1)$$

kjer je *A* število bakterijskih kolonij v suspenziji po enournem stiku suspenzije s substratom in *B* število bakterijskih kolonij v suspenziji brez stika s substratom. Vrednost bakterijske redukcije za zadovoljivo protimikrobno delovanje mora biti višja od 60 %.

Slepo barvanim vzorcem smo z uporabo spektrofotometra Spectraflash 600 Plus-CT (Datacolor) na podlagi meritev CIE barvnih vrednosti določili stopnjo in odtenek beline. Meritve smo opravili pri naslednjih pogojih: velikost odprtine 9 mm, kot opazovalca 10°, standardna svetloba D 65 in izklopljena zrcalna komponenta. Stopnjo beline (WI) smo izračunali po enačbi 2 [32].

$$\mathrm{WI} = \mathrm{Y} + 800 \cdot (\mathrm{x}_{n,10} - \mathrm{x}) + 1700 \cdot (\mathrm{y}_{n,10} - \mathrm{y}), \qquad (2)$$

kjer je *Y* standardizirana barvna vrednost, *x, y*, sta standardizirana barvna deleža, $x_{n,10}$, $y_{n,10}$ sta vrednosti belega standarda.

Odtenek beline (TV) smo izračunali po enačbi 3.

$$\mathrm{TV} = 900 \cdot (\mathrm{x}_{n,10} - \mathrm{x}) - 650 \cdot (\mathrm{y}_{n,10} - \mathrm{y}) \qquad (3)$$

Vrednosti *WI* in *TV* smo določili za slepo barvane neobdelane in z RucoBac-om AGP funkcionalizirane vzorce.

Tkaninam, obarvanim z reaktivnim barvilom, smo določili barvo, ki smo jo ovrednotili s pomočjo refleksijskega spektrofotometra Spectraflash 600 Plus-CT in z uporabo barvnega sistema CIE $L^*a^*b^*$. Barvo vzorcev smo določili tako neobdelanim kot z RucoBac-om AGP funkcionaliziranim vzorcem. Meritve smo opravili pri enakih pogojih kot meritve beline, le s to razliko, da je bila zrcalna komponenta vklopljena. Barvno razliko med neobdelanim barvanim vzorcem in z RucoBac-om AGP funkcionaliziranim vzorcem smo izračunali po enačbi 4 [33]:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}\,, \qquad (4)$$

kjer je ΔL^* razlika v svetlosti, Δa^* razlika na rdeče-zeleni osi in Δb^* razlika na rumeno-modri osi med standardom in vzorcem.

3 Rezultati z razpravo

V preglednici 1 so predstavljeni oznake in opisi obdelave preiskovanih bombažnih vzorcev.

Table 1: Marking and description of cotton samples

Sample marking	Sample description
B	Blank dyed sample
B_0.1	Blank dyed sample, treated with 0.1% RucoBac AGP
B_0.1_w	Blank dyed sample, treated with 0.1% RucoBac AGP, washed
B_0.2	Blank dyed sample, treated with 0.2% RucoBac AGP
B_0.2 _w	Blank dyed sample, treated with 0.2% RucoBac AGP, washed
D	Dyed sample
D_0.1	Dyed sample, treated with 0.1% RucoBac AGP
D_0.1_w	Dyed sample, treated with 0.1% RucoBac AGP, washed
D_0.2	Dyed sample, treated with 0.2% RucoBac AGP
D_0.2_w	Dyed sample, treated with 0.2% RucoBac AGP, washed

Table 2: Quantity of Ag (mg/kg) and antimicrobial efficiency, expressed as bacterial reduction (R), of bleached/mercerized cotton fabrics

Sample	Ag (mg/kg)	R (%)			
		S. aureus	*E. coli*	*S. faecalis*	*P. aeurginosa*
B	0	—	—	—	—
B_0.1	1.50 ± 0.30	—	—	—	—
B_0.1_w	0.42 ± 0.08	—	—	—	—
B_0.2	6.70 ± 1.30	—	98	—	—
B_0.2 _w	1.20 ± 0.20	—	—	—	—
D	0	—	—	—	—
D_0.1	8.90 ± 1.80	100	100	100	100
D_0.1_w	2.20 ± 0.40	—	—	—	—
D_0.2	15.00 ± 3.00	100	100	100	100
D_0.2_w	2.30 ± 0.50	—	—	—	—

B...blank dyed, D...dyed, 0.1…0.1% ...RucoBac AGP, 0.2…0.2% RucoBac AGP, w...washed, –...reduction less than 60%

10°, standard light D 65 and excluded specular. The whiteness index (WI) was calculated using Equation 2 [32], where Y denotes the tristimulus value of the sample, x, y denote the chromaticity coordinates of the sample and $x_{n,10}$, $y_{n,10}$ denote the chromaticity coordinates of a white standard.

V preglednici 2 so podani rezultati analize ICP-MS in protimikrobne analize preiskovanih vzorcev.

Iz preglednice 2 je razvidno, da se količina srebra na bombažni tkanini povečuje z naraščajočo koncentracijo RB v kopeli. Slepo barvan vzorec, ki je bil obdelan z 0,1 % RB, vsebuje 1,5 ± 0,3 mg/kg srebra, medtem ko slepo barvan vzorec, obdelan z 0,2 % RB, vsebuje 6,7 ± 1,3 mg/kg srebra. Enako opazimo tudi pri barvanih

The whiteness tint (TV) was calculated using Equation 3.
The values of WI and TV were determined for blank dyed untreated and RucoBac AGP functionalized samples.
The colour of samples dyed with a reactive dye was determined based on the CIELAB colour system measured with the spectrophotometer Spectraflash 600 Plus-CT. The colour of samples was determined for untreated samples and for samples functionalized with RucoBac AGP. The measurements of colour were made under the same conditions as the measurements of whiteness with the exception of the specular being included. The colour difference (ΔE) between the untreated dyed sample and dyed sample functionalized with RucoBac AGP was calculated using Equation 4 [33], where ΔL* is the difference in lightness, Δa* is the difference on the red-green axis and Δb* is the difference on the yellow-blue axis between a standard and a sample.*

3 Results and discussion

The markings and descriptions of cotton samples are presented in Table 1.
The results of the ICP-MS and antimicrobial analysis of samples are presented in Table 2.
The quantity of silver on a cotton fabric is increasing with a higher concentration of RucoBac AGP (RB) used in the bath (cf. Table 2). The blank dyed sample treated with 0.1% RB contains 1.5 ± 0.3 mg/kg of silver, while the blank dyed sample treated with 0.2% RB contains 6.7 ± 1.3 mg/kg of silver. The same trend is noticed on the samples dyed with a reactive dye. The quantity of silver on cotton is different when comparing blank dyed and reactive dyed samples. The dyed samples contain a much higher quantity of silver than the blank dyed samples. In the case of treating cotton with 0.1% RB, the quantity of silver on a dyed sample is by almost six times higher than on a blank dyed sample (from 1.5 ± 0.3 mg/kg to 8.9 ± 1.8 mg/kg) and by two times higher in the case of treatment with 0.2% RB (from 6.7 ± 1.3 mg/kg to 15 ± 3 mg/kg of silver). RB is a nanodispersion composite of titanium dioxide (TiO_2) in the combination of an active component of

vzorcih. Vsebnost srebra se na bombažnih vzorcih poveča tudi tedaj, ko smo vzorec pred obdelavo z RB barvali z reaktivnim barvilom. Barvani vzorci vsebujejo bistveno večjo količino srebra kot slepo barvani vzorci. Tako se pri obdelavi vzorca z 0,1 % RB vsebnost srebra na barvanem vzorcu poveča skoraj šestkratno (na 8,9 ± 1,8 mg/kg) in pri obdelavi z 0,2 % RB se poveča dvakratno (na 15 ± 3 mg/kg). RB je nanodisperzija kompozita titanovega dioksida (TiO_2) v kombinaciji z aktivno komponento srebrovega klorida (AgCl) [29]. Ob prisotnosti vlage srebrovi kationi reagirajo s funkcionalnimi hidroksilnimi skupinami celuloznih vlaken ter se nanje vežejo z elektrostatskimi vezmi. Reaktivna barvila so anionska barvila, ki priskrbijo sulfonske kisle skupine, na katere se lahko veže kationsko protimikrobno sredstvo [34]. Zato je mogoče sklepati, da se RB veže na bombažno vlakno prek sulfonskih skupin kovalentno vezanega barvila, kot tudi prek delno ioniziranih hidroksilnih in karboksilnih skupin, prisotnih na vlaknu. Vzorci, ki vsebujejo manj kot 6 mg/kg srebra, ne kažejo zadostne protimikrobne učinkovitosti. Slepo barvan vzorec, obdelan z 0,2 % RB (vzorec B_0.2), kaže odlično protimikrobno učinkovitost na *Escherichio coli*, vendar pa vsebnost 6,7 ± 1,3 mg/kg srebra ne zadošča za doseganje učinkovite protimikrobne zaščite vzorca na druge bakterije. Barvana vzorca D_0.1 in D_0.2, ki vsebujeta 8,90 ± 1,80 oz. 15,00 ± 3,00 mg/kg srebra, pa že kažeta odlično protimikrobno učinkovitost proti *Staphylococcus aureus*, *Escherichii coli*, *Streptococcus faecalisu* in *Pseudomonas aeruginosi*.
Vpliv pranja na obstojnost funkcionalizacije bombaža z RB je razviden iz rezultatov analize ICP-MS v preglednici 2. Po desetkratnem pranju pri 60 °C v Launder-o-metru se količina srebra na bombažnih vzorcih zmanjša ne glede na to, ali so bili slepo barvani ali barvani z barvilom. Rezultati so v skladu z rezultati drugih raziskovalcev, ki so prav tako ugotovili, da se s pranjem srebro s tkanin odstrani. Oprani vzorci nimajo protimikrobne učinkovitosti, saj vsebujejo premalo srebra (od 0,42 ± 0,08 mg/kg do 2,30 ± 0,50 mg/kg).
Nanos RB na beljeno/mercerizirano bombažno tkanino vpliva na belino vzorca. Z višanjem koncentracije RB v kopeli se stopnja beline (WI) slepo barvanih vzorcev znižuje, odtenek beline (TV) pa ostaja nespremenjen (preglednica 3). Tako znaša WI neobdelanega slepo barvanega vzorca 81,44, slepo barvanega vzorca, funkcionaliziranega z 0,2 % RB, pa 79,81. Obdelava bombaža z RB vpliva tudi na barvo barvanega vzorca (preglednica 4). Z naraščajočo koncentracijo RB v kopeli postajajo barvani vzorci temnejši, bolj rdeči in bolj rumeni. Barvna razlika med neobdelanim barvanim vzorcem (vzorec D) in barvanim vzorcem, obdelanim z 0,1 % RB (vzorec D_0.1), znaša ΔE* = 1,49. Barvna razlika je po uporabi 0,2 % RB večja in znaša ΔE* = 1,73.

silver chloride (AgCl) [29]. In the presence of moisture, silver cations react with hydroxyl functional cellulosic groups and are attached to each other electrostatically. The presence of a reactive dye on cotton and the introduction of additional covalently bound sulfonic acid groups will facilitate the uptake of a cationic antimicrobial agent [34]. Therefore, it is possible to conclude that RB is bound to the cotton surface through sulfonic groups of a covalently bound dye and through partially ionized hydroxyl and carboxyl groups present on the fibre. The samples containing less than 6 mg/kg of silver do not show satisfactory antimicrobial efficiency. The blank dyed sample treated with 0.2% RB (Sample B_0.2) shows excellent antimicrobial efficiency against Escherichia coli, whereas the quantity of silver 6.7 ± 1.3 mg/kg was not sufficient for the antimicrobial protection against other bacteria. The dyed samples D_0.1 and D_0.2, containing 8.90 ± 1.80 mg/kg and 15.00 ± 3.00 mg/kg, respectively, already show excellent antimicrobial efficiency against Staphylococcus aureus, Escherichia coli, Streptococcus faecalis and Pseudomonas aeruginosa.

The ICP-MS measurements of the silver quantity determined on cotton RB functionalized fabrics before and after ten repetitive washings (cf. Table 2) show poor wash-fastness of RB regardless if samples were blank dyed or dyed with a reactive dye. These results are in accordance with the results of other researchers who have also established that silver is removed with washing. The washed samples do not show antimicrobial efficiency since they contain too low quantity of silver (from 0.42 ± 0.08 mg/kg to 2.30 ± 0.50 mg/kg).

The application of RB on a bleached/mercerized cotton fabric influences the fabric whiteness. By increasing the concentration of RB in the bath, the whiteness index (WI) decreases while the whiteness tint (TV) remains the same (cf. Table 3). For an untreated blank dyed sample, WI is 81.44 and 79.81 for a blank dyed sample functionalized with 0.2% RB.

The treatment of cotton with RB also influences the colour of reactive dyed sample (cf. Table 4). By increasing the concentration of RB, the dyed samples become darker, redder and yellower. The colour difference of the untreated

Table 3: Whiteness index (WI) and tint (TV) of blank dyed cotton fabrics

Sample	WI	TV
B	81.44	−0.25
B_0.1	80.61	−0.25
B_0.2	79.81	−0.23

B ... slepo barvan, 0.1 ... 0,1% RucoBac AGP, 0.2 ... 0,2% RucoBac AGP

*Table 4: CIEL*a*b* values of colour coordinates and colour differences (ΔE*) of dyed cotton fabrics*

Sample	L*	a*	b*	ΔE*
D	45.41	50.42	0.55	–
D_0.1	44.28	50.43	1.52	1.49
D_0.2	44.10	50.60	1.67	1.73

D ... barvan, 0.1 ... 0,1% RucoBac AGP, 0.2 ... 0,2% RucoBac AGP

4 Sklepi

Proučevali smo vpliv barvanja z reaktivnim barvilom na adsorpcijo srebra na beljeno/mercerizirano bombažno tkanino. Kot vir nanodelcev srebra smo uporabili nanodisperzijo RucoBac AGP, ki smo jo na tkanino nanašali po izčrpalnem postopku. Vpliv adsorpcije srebra na tkanino smo proučili s primerjavo rezultatov analize metode ICP-MS slepo barvanih in barvanih tkanin, na katere smo nanašali RucoBac AGP v dveh koncentracijah. Vsebnost srebra na tkaninah smo spremljali tudi po desetkratnem pranju. Z mikrobiološkimi testi smo ugotavljali protimikrobno učinkovitost različno funkcionaliziranih nepranih in pranih bombažnih tkanin. Iz rezultatov smo ugotovili, da barvani vzorci vsebujejo bistveno večjo količino srebra kot slepo barvani vzorci. Barvani vzorci, obdelani z RucoBac-om AGP, kažejo odlično protimikrobno učinkovitost na *Staphylococcus aureus*, *Escherichio coli*, *Streptococcus faecalis* in *Pseudomonas aeruginoso.* Višja količina srebra na tkanini pomeni tudi boljšo protimikrobno učinkovitost. Po desetkratnem pranju se vsebnost srebra na vzorcih zmanjša ne glede na način funkcionalizacije. S spektrofotometrom smo določili belino in odtenek beline slepo barvanih vzorcev ter barvne vrednosti barvanih vzorcev. Pri uporabi višje koncentracije RucoBac-a AGP je opazna sprememba v belini in barvi vzorca, kar pa ne poslabša videza tkanine. Barvanje z reaktivnimi barvili se je izkazalo kot učinkovita in preprosta metoda za doseganje povečanja adsorpcije srebra na bombažni substrat, s čimer se doseže zadostna protimikrobna učinkovitost tekstilije že z zelo nizkimi koncentracijami srebra v kopeli, *dyed sample (Sample D) and the dyed sample treated with 0.1% RB (Sample D_0.1) is DE* = 1.49. After treating the dyed sample with 0.2% RB, the colour difference is even higher (DE* = 1.73).*

4 Conclusions

The influence of reactive dyeing on the adsorption of silver on a bleached/mercerized cotton fabric was investigated. The source of silver nanoparticles was nano-dispersion RucoBac AGP. The exhaustion method was used to load RucoBac AGP in two concentrations on a cotton fabric. The adsorption of silver on cotton was investigated on blank dyed and reactive dyed samples by comparing the ICP-MS results. The quantity of silver on cotton was examined after ten repetitive washings. Microbiological tests were used to examine the antimicrobial efficiency of differently functionalized unwashed and washed samples. From the result, it can be concluded that the reactive dyed samples contain higher quantity of silver than the blank dyed samples. The dyed samples treated with RucoBac AGP also show excellent antimicrobial efficiency against Staphylococcus aureus, Escherichia coli, Streptococcus faecalis and Pseudomonas aeruginosa. A higher quantity of silver on a fabric gives better antimicrobial efficiency. The results also show poor wash-fastness of RucoBac AGP regardless of the treatment. The whiteness index and tint of blank dyed samples and colour values of reactive dyed samples was determined using a spectrophotometer. When using a higher concentration of RucoBac AGP, there is a noticeable change in the whiteness and colour of the sample, while the change does not impair the appearance of the fabric.

The dyeing with a reactive dye has proved to be an effective and a simple method in increasing the silver nanoparticle adhesion on a cotton substrate in order to achieve sufficient antimicrobial efficiency of a textile using a very low concentration of silver in the bath, which also has a severe impact on reduced water pollution with silver nanoparticles.

kar seveda močno vpliva na zmanjšano onesnaževanje odpadnih voda s srebrom.

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