ANTIBACTERIAL ACTIVITY AND DURABILITY OF SOME REGENERATED CELLULOSIC FABRICS TREATED WITH Zn, Cu AND Ag METAL SALTS AFTER REPEATED LAUNDERING

OĞUZ DEMİRYUREK and TUĞBA TULUNAY

Erciyes University, Faculty of Engineering, Department of Textile Engineering,
Melikgazi Kayseri, Turkey
✉ *Corresponding author: Oğuz Demiryürek, oguzdemiryurek@gmail.com*

In this study, the antibacterial activity and durability against repeated laundering of Modal[®], Promodal[®], Tencel[®], Viscose[®] and Viloft[®] knitted fabrics were studied. The fabrics were treated with zinc, copper and silver metal salts using the exhaustion technique, and then washed 10 times to determine wash durability against pathogenic bacteria, such as *E. coli* and *S. aureus*. The bacteriodynamic activity of the treated fabrics was evaluated in accordance with the ASTM E2149-01 test method. The amounts of the metal ions on the fabrics (applied and residual after washing) were analyzed by XRF. In conclusion, all metal ion treatments yielded satisfactory results as to antibacterial activity. The durability of Cu treated fabrics after repeated laundering cycles was higher than that of Ag and Zn treated fabrics. However, the antibacterial activity of Ag and Cu treated fabrics was higher in comparison with that of Zn treated fabrics.

Keywords: Modal[®], Promodal[®], Tencel[®], Viscose[®], Viloft[®], antibacterial, XRF, laundering, zinc, copper, silver, metal salts

INTRODUCTION

Antimicrobial functional textiles are being developed for hygienic and medical purposes, while the number of research works on this topic has increased considerably over the last few years.[1] Fibres that provide a large surface area and absorb humidity generate a suitable medium for microbial proliferation.[2] Antibacterial textiles are designed to avoid the loss of performance properties of the fabrics as a result of microbial fibre degradation, significantly limit the incidence of bacteria and prevent the transfer and spread of pathogenic germs.[1,3] Antibacterial textiles can be developed by using naturally antibacterial fibres and/or by applying antibacterial finishes onto the fabric.

If bacteria form a parasitic association with other organisms, they are classified as pathogens.[4] Pathogenic bacteria reproduce rapidly in humid environment and they can be classified as gram-positive or gram-negative. *S. aureus*, *S. epidermidis* and *Corynebacterium* are the most common gram-positive bacteria, whereas *E. coli*, *K. pneumonie* and *P. vulgaris* are the most prevalent gram-negative bacteria.[5] *S. aureus* has long been recognized as one of the most important types of bacteria causing skin and soft tissue infections, such as abscesses (boils), furuncles and cellulitis. *S. aureus* can also cause other serious infections, such as bloodstream infections, pneumonia, or bone and joint infections.[6] *E. coli* bacteria are found in the environment, food and the intestines of people and animals. Some kinds of *E. coli* can cause diarrhea, while others cause urinary tract infections, respiratory illnesses and other diseases.[7]

There are various studies about antibacterial applications on textiles. Some of them report on the use of metals,[8] such as silver,[9-14] copper and zinc oxide,[15] stainless steel wires wrapped around naturally antibacterial fibres,[16] others describe the use of chitosan[17-19] or triclosan[20] to treat fabrics or weaving fabrics from SeaCell fibre.[21] Other research has reported on applying antibacterial metal salts to fabrics.[22-27]

In general, the antibacterial properties against some selected pathogenic bacteria were found to increase.

In our literature survey, we remarked that researchers have mostly focused on cotton textiles. There are few studies about the antibacterial properties of regenerated cellulosic fabrics. Moreover, to our knowledge, no study has been conducted to compare the antibacterial properties of novel and conventional regenerated cellulosic fabrics. For this purpose, in this investigation, Modal®, Promodal®, Tencel®, Viscose® and Viloft® knitted fabrics, which are generally used for manufacturing underwear or socks, have been selected and treated with metal salts, such as $Zn(NO_3)_2$, $CuSO_4$ and $AgNO_3$ by the exhaustion technique. Then, the samples were washed 10 times to determine the laundering durability of the antibacterial treatments against gram-positive and gram-negative pathogenic bacteria, such as *S. aureus* and *E. coli*.

EXPERIMENTAL

The fibres used in the study are illustrated in Figure 1. These fibres are man-made regenerated cellulosic fibres. Viscose, Viloft and Modal fibres are produced by reacting cellulose with carbon bisulphide (CS_2). The combination of regenerated cellulose and coagulation of cellulose-xanthate results in the shell-core structure of viscose fibres.[28] High Wet Modulus fibres (HWM), such as Modal, are produced by

including amines and polyether glycols into the coagulation bath. The CS_2 amount in the coagulation bath and the duration of the bath are different from the viscose process. Thus, the cross-section of Modal fibres has a shell form and, as a result, the strength of these fibres is higher than that of viscose.[29] Tencel (Lyocell) fibres are produced by a more environmentally friendly procedure consisting in spinning a solution of non-derivative cellulose in a solvent, where the cellulose is dissolved directly in the organic solvent (N-methylmorpholine-N-oxide), without the formation of derivatives.[28] This fibre has a high crystallinity degree and molecular orientation, compared to viscose. However, it presents fibrillation under mechanical stress because of the weak bonds between the macromolecules.[30] Viloft fibre is a novel fibre representing modified viscose. The chemical composition of this fibre is identical with that of viscose, however, its cross-section and surface characteristics are different. Viloft has a crenulated surface and rectangular cross-section. Promodal is the blend of Modal and Tencel fibres. Although all the fibres investigated here are cellulosic, the differences with their structure may lead to various levels of retention of metal salts and their removal during washing.

Single-jersey knitted fabrics from the above fibres were supplied by a textile company. The basic raw material properties of the regenerated cellulosic fabrics are listed in Table 1. The fabrics were treated with $Zn(NO_3)_2$, $CuSO_4$ and $AgNO_3$ metal salts. The chemical formulas of the metal salts are shown in Figure 2.

a) Modal　　　　　　　　b) Promodal[31]　　　　　　　　c) Tencel[32]
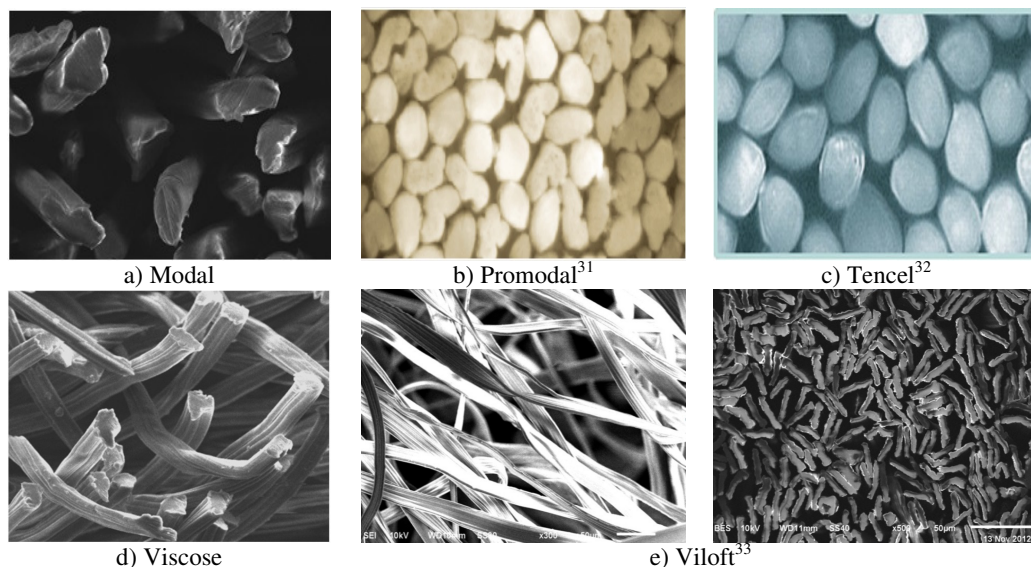
d) Viscose　　　　　　　　　　　　　　　　e) Viloft[33]

Figure 1: Cross-section view of fibres used in the study

Table 1
Properties of regenerated cellulosic fabrics

Fabric	Weight (g/m^2)	Thickness (mm)	Yarn count (tex)
Modal	138.8	0.53	19.7
Promodal	132.8	0.54	19.7
Tencel	147.5	0.58	19.7
Viscose	155.1	0.60	19.7
Viloft	143	0.64	19.7

a) $Zn(NO_3)_2$ b) $CuSO_4$ c) $AgNO_3$
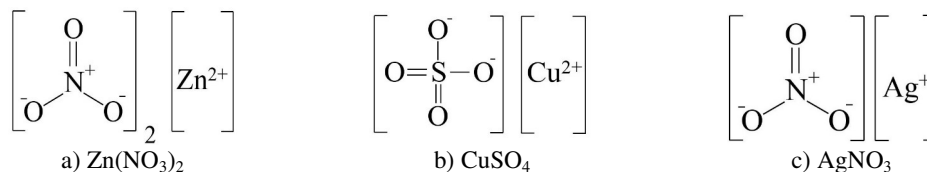
Figure 2: Chemical formulas of metal salts used

A:Fabric
B: Distilled water
C: $Zn(NO_3)$ or $CuSO_4$ or $AgNO_3$
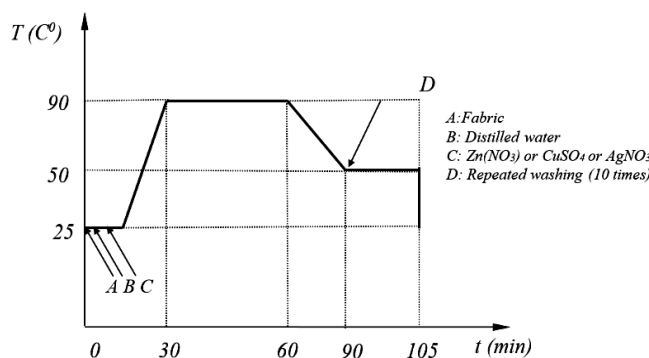D: Repeated washing (10 times)

Figure 3: $Zn(NO_3)_2$, $CuSO_4$ and $AgNO_3$ treatments of fabrics

The treatment procedure with the zinc, copper and silver metal salts is shown in Figure 3. The fabric samples were treated with $CuSO_4$, $Zn(NO_3)_2$ and $AgNO_3$ at 1% concentration in glass bottles at 95 °C for 30 min, at a M/L ratio of 1/15. After the treatment, each fabric sample was washed 4 times at a water temperature of 50 °C without detergent during 15 minutes. Then, in the 5th and 6th cycle, the samples were laundered according to TS EN ISO 6330[34] standard (Table 4N, 40 °C, with Reference detergent 3). The following 4 washing cycles (7th-10th) were carried out at 50 °C during 15 minutes without using detergent. The samples were dried under standard atmosphere conditions (20 ± 2 °C and 65% ± 2 RH) after each washing cycle.

Cultures of *Escherichia coli* (ATCC 11229)[35] and *Staphylococcus aureus* (ATCC 25923)[36] bacteria were used in the study. Before the antimicrobial tests, the bacteria obtained from a fresh culture were grown in nutrient broth at 37 °C for 18 hours. The bacteriodynamic activity and the bactericidal effect of the treated fabrics against the selected bacterial species were assessed according to ASTM E2149-01[37] test method. A sterile fabric sample (0.5 g) was immersed into 10 mL of nutrient broth inoculated with the desired microbe for 3 hours at 37 °C. The number of colonies in the tubes was counted by serial dilution at point 0 and after a contact time of 3 h. The reduction percent of the selected test bacteria on each treated sample was expressed as:

$$R (\%) = 100[(c_0\text{-}c)/c_0] \qquad (1)$$

where c_o (cfu) is the number of microbial colonies on the treated fabric at zero time and c (cfu) is the number of microbial colonies after three hours. R (%) is the reduction in bacterial population.[38]

The metal ion quantity on both washed and unwashed fabric samples was detected by X-ray fluorescence spectroscopy (XRF) using a Perkin Elmer AA800. Thus, the laundering durability of the antibacterial fabrics could be determined.

RESULTS AND DISCUSSION
Antibacterial test results

The antibacterial test results of $Zn(NO_3)_2$, $CuSO_4$ and $AgNO_3$ treated fabric samples are

displayed in Tables 2, 3 and 4, respectively. These tables present the numbers of bacterial colonies (*Escherichia coli* and *Staphylococcus aureus*) in the tubes, counted by serial dilution, at 0 and 3 hours of contact time, with the untreated fabrics and the metal salt treated fabrics before and after 10 washing cycles. No antibacterial effect was observed on the untreated fabrics, since the number of bacterial colonies increased. The maximum antibacterial effect was recorded on the silver treated fabrics, whereas the minimum – on the zinc treated ones.

The antibacterial test results for $Zn(NO_3)_2$ applied on fabrics are shown in Table 2 and Figure 4. Here, the untreated cellulosic fabrics did not resist bacterial colonization and therefore the bacterial count increased on each fabric type. Applying the 1% $Zn(NO_3)_2$ treatment gave satisactory results and the antibacterial activity of these fabrics decreased the bacterial population (100%). Although repeated laundering of these fabrics caused a decrease in ion count, all the fabrics again showed a satisfactory antibacterial effect. After 10 washing cycles, Tencel fabrics showed the maximum antibacterial resistance of 100%. The bacterial population decreased on the other fabrics (Promodal, Viloft, Viscose and Modal) as well. This could be explained by the specific surface area of the fibres to which Zn^{+2} ions could attach. The fibrillation or the weak bonds between the macrofibrils in Tencel fibres contributed to a higher specific area, with more sites available for the ions to attach.

Viloft fabric ranked the second as to its antibacterial effect – with 75.86%. Viloft fibre is a modified viscose fibre, which has crenulated surface and higher specific area than viscose fibre. Promodal is a blend of Tencel and Modal fibres, which explains that it is the third fibre with regard to its antibacterial effect (63.75%) after repeated laundering cycles. The minimum antibacterial effect was observed for Modal fabric (34.72%).

Table 3 and Table 4, as well as the corresponding figures, Figure 5 and Figure 6, respectively, exhibit the antibacterial test results for $CuSO_4$ and $AgNO_3$ treated fabrics, respectively. As may be noted, the untreated fabrics did not display any antibacterial property and the bacterial colonies increased in number. However, the 1% metal salt treated fabrics gave satisfactory results, as all the fabrics displayed 100% antibacterial activity against for both *E. coli* and *S. aureus* bacteria, before and after 10 washing cycles.

Table 2
Antibacterial test results of $Zn(NO_3)_2$ treated fabrics

Fabric	Treatment	*Escherichia coli*			*Staphylococcus aureus*		
		Bacterial count/mL		Decrease	Bacterial count/mL		Decrease
		Initial	After 3 h	(%)	Initial	After 3 h	(%)
Modal	No treatment	7,000,000	12,300,000	Increase	8,300,000	13,200,000	Increase
	1% $Zn(NO_3)_2$	7,100,000	0	100	8,100,000	0	100
	1% $Zn(NO_3)_2$ +10 wash cycles	9,300,000	4,700,000	49.46	7,200,000	4,700,000	34.72
Promodal	No treatment	8,500,000	13,900,000	Increase	9,500,000	14,100,000	Increase
	1% $Zn(NO_3)_2$	8,100,000	0	100	9,200,000	0	100
	1% $Zn(NO_3)_2$ +10 wash cycles	9,300,000	0	100	8,000,000	2,900,000	63.75
Tencel	No treatment	10,200,000	14,500,000	Increase	9,800,000	13,500,000	Increase
	1% $Zn(NO_3)_2$	6,700,000	0	100	8,000,000	0	100
	1% $Zn(NO_3)_2$ +10 wash cycles	8,200,000	0	100	6,900,000	0	100
Viscose	No treatment	7,800,000	11,000,000	Increase	7,900,000	12,100,000	Increase
	1% $Zn(NO_3)_2$	9,200,000	0	100	10,200,000	0	100
	1% $Zn(NO_3)_2$ +10 wash cycles	8,900,000	1,200,000	86.51	8,700,000	4,300,000	50.57
Viloft	No treatment	6,900,000	9,800,000	Increase	8,900,000	11,300,000	Increase
	1% $Zn(NO_3)_2$	8,100,000	0	100	9,000,000	0	100
	1% $Zn(NO_3)_2$ +10 wash cycles	8,200,000	900,000	89.02	8,700,000	2,100,000	75.86
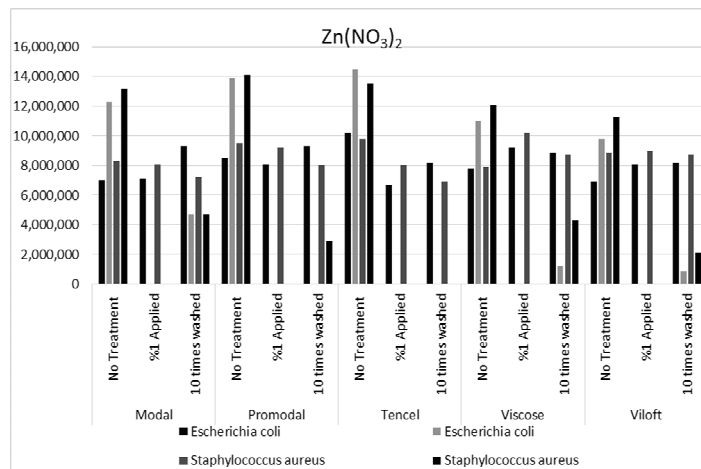
Figure 4: Antibacterial activity of $Zn(NO_3)_2$ treated fabrics

Table 3
Antibacterial test results of $CuSO_4$ treated fabrics

Fabric	Treatment	*Escherichia coli*			*Staphylococcus aureus*		
		Bacterial count/mL		Decrease	Bacterial count/mL		Decrease
		Initial	After 3 h	(%)	Initial	After 3 h	(%)
Modal	No treatment	7,000,000	12,300,000	Increase	8,300,000	13,200,000	Increase
	1% $CuSO_4$	5,900,000	0	100	9,000,000	0	100
	1% $CuSO_4$ +10 wash cycles	6,200,000	0	100	6,600,000	0	100
Promodal	No treatment	8,500,000	13,900,000	Increase	9,500,000	14,100,000	Increase
	1% Cu SO_4	9,000,000	0	100	6,800,000	0	100
	1% $CuSO_4$ +10 wash cycles	9,100,000	0	100	8,200,000	0	100
Tencel	No treatment	10,200,000	14,500,000	Increase	9,800,000	13,500,000	Increase
	1% $CuSO_4$	9,100,000	0	100	6,900,000	0	100
	1% $CuSO_4$+10 wash cycles	6,800,000	0	100	7,000,000	0	100
Viscose	No treatment	7,800,000	11,000,000	Increase	7,900,000	12,100,000	Increase
	1% $CuSO_4$	6,500,000	0	100	8,300,000	0	100
	1% $CuSO_4$+10 wash cycles	8,000,000	0	100	9,000,000	0	100
Viloft	No treatment	6,900,000	9,800,000	Increase	8,900,000	11,300,000	Increase
	1% $CuSO_4$	7,000,000	0	100	5,900,000	0	100
	1% $CuSO_4$+10 wash cycles	7,900,000	0	100	6,300,000	0	100

XRF spectroscopy

The antibacterial activity is strictly related to the presence of metal ions on the washed or unwashed fabrics. Thus, the amount of metal ions on the fabrics was evaluated by the XRF spectroscopy. For this purpose, firstly, the atomic weight ratios of Zn^{+2}, Cu^{+2} and Ag^+ ions in $Zn(NO_3)_2$, $CuSO_4$ and $AgNO_3$ molecules, respectively, applied to the fabrics, were calculated in order to determine the theoretical amount of ions applied on the fabrics. Secondly, the ion amounts on the fabrics were observed by XRF spectroscopy to determine the amounts actually present on the fabrics. Thirdly, the application ratio of the metal ions on the fabrics were calculated by dividing the actual ion amounts by the theoretical ion amounts. For example, the atomic weight of Zn^{+2} in the $Zn(NO_3)_2$ molecule is 0.4797; that of Cu^{+2} in the $CuSO_4$ molecule is 0.3981 and that of Ag^+ in the $AgNO_3$ molecule is 0.6350. These values are the theoretical ion weights. The ion amounts applied

to the fabrics, determined by XRF spectroscopy, and the application ratios are tabulated in Tables 5, 6 and 7 for Zn^{+2}, Cu^{+2} and Ag^+ ions, repectively.

The theoretical Zn^{+2} weight ratio applied to the fabrics was calculated to be 0.4797 by considering the atomic weights. By XRF spectroscopy, the actual Zn^{+2} weight ratio was determined for both washed and unwashed 1% $Zn(NO_3)_2$ treated fabrics. In Table 5, the XRF results and the application ratio are presented. For example, the amount of Zn^{+2} on the 1% $Zn(NO_3)_2$ treated fabrics was found to be 0.0890 on Modal. This value was divided by theoretical amount (0.4790) and multiplied by 100. As a result, the application ratio of 18.55% was obtained.

Table 4
Antibacterial test results of AgNO₃ treated fabrics

| Fabric | Treatment | *Escherichia coli* | | | *Staphylococcus aureus* | | |
| | | Bacterial count/mL | | Decrease | Bacterial count/mL | | Decrease |
		Initial	After 3 h	(%)	Initial	After 3 h	(%)
Modal	No treatment	7,000,000	12,300,000	Increase	8,300,000	13,200,000	Increase
	1% AgNO₃	7,100,000	0	100	8,100,000	0	100
	1% AgNO₃ +10 wash cycles	9,300,000	0	100	7,200,000	0	100
Promodal	No treatment	8,500,000	13,900,000	Increase	9,500,000	14,100,000	Increase
	1% AgNO₃	8,100,000	0	100	9,200,000	0	100
	1% AgNO₃ +10 wash cycles	9,300,000	0	100	8,000,000	0	100
Tencel	No treatment	10,200,000	14,500,000	Increase	9,800,000	13,500,000	Increase
	1% AgNO₃	6,700,000	0	100	8,000,000	0	100
	1% AgNO₃ +10 wash cycles	8,200,000	0	100	6,900,000	0	100
Viscose	No treatment	7,800,000	11,000,000	Increase	7,900,000	12,100,000	Increase
	1% AgNO₃	9,200,000	0	100	10,200,000	0	100
	1% AgNO₃ +10 wash cycles	8,900,000	0	100	8,700,000	0	100
Viloft	No treatment	6,900,000	9,800,000	Increase	8,900,000	11,300,000	Increase
	1% AgNO₃	8,100,000	0	100	9,000,000	0	100
	1% AgNO₃ +10 wash cycles	8,200,000	0	100	8,700,000	0	100
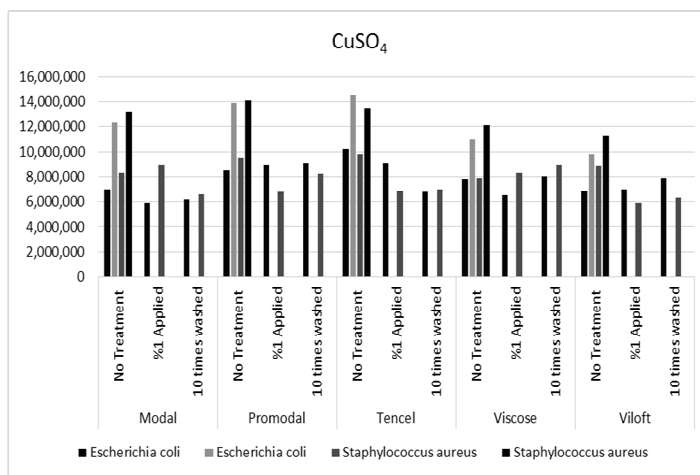
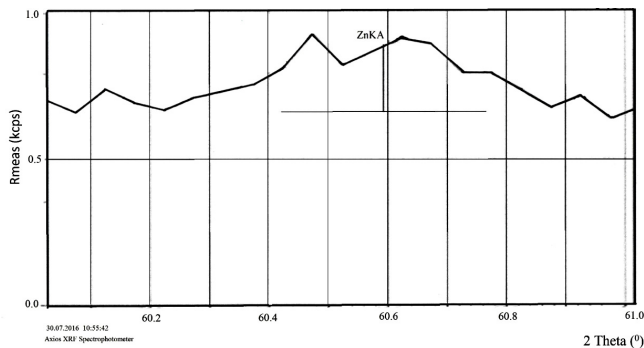Figure 5: Antibacterial activity of CuSO₄ treated fabrics
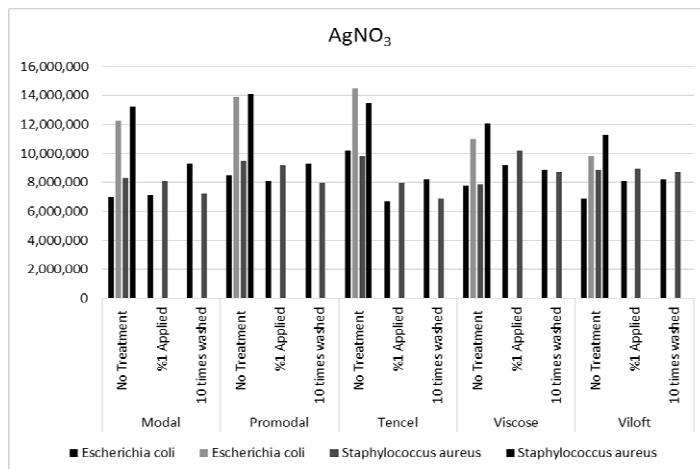
Figure 6: Antibacterial activity of $AgNO_3$ treated fabrics

As may be noted in Table 5, the maximum application ratio was found to be 47.40% for Tencel. According to their ion application ratio, the fabrics can be ranked in decreasing order as follows: Tencel, Viloft, Promodal, Viscose and Modal. This order is in agreement with the results on the antibacterial activity of the fabrics displayed in Table 2. It can be related with the specific surface area of the fibres from which the fabrics were made. Because of fibrillation in Tencel fibres, a higher specific area was available for the ions to attach. Thus, the maximum amounts of ions was noted on Tencel fibres and, as a result, this fabric showed the maximum antibacterial activity – of 100% (Table 2).

Table 5
XRF results and Zn^{+2} amounts on fabrics (theoretical Zn^{+2} weight ratio: 0.4797)

Fabric	Zn^{+2} amount on 1% $Zn(NO_3)_2$ finished fabrics	Application ratio (%)	Zn^{+2} on fabrics treated with 1% $Zn(NO_3)_2$ + 10 wash cycles	Residual Zn^{+2} ratio after 10 wash cycles (Durability) (%)
Modal	0.0890	18.55	0.0188	3.92
Promodal	0.1565	32.62	0.0343	7.15
Tencel	0.2274	47.40	0.1014	21.14
Viscose	0.1483	30.91	0.0183	3.81
Viloft	0.1668	34.77	0.0230	4.79

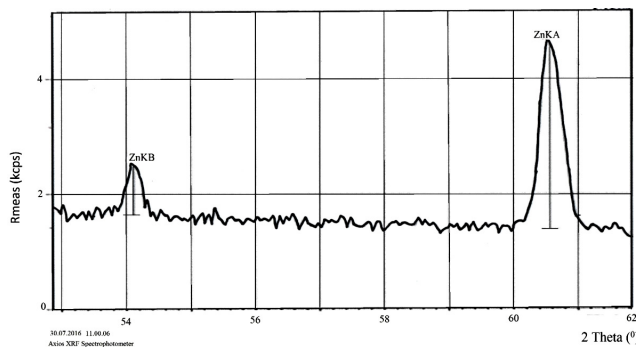Figure 7: XRF results for $Zn(NO_3)_2$ treated Modal fabric washed 10 times

Figure 8: XRF results for $Zn(NO_3)_2$ treated Tencel fabric washed 10 times

The residual Zn^{+2} ratio after 10 washing cycles is also displayed in Table 5. As expected, the amount of Zn^{+2} decreased compared with the initial amount on the finished fabrics for all the samples. This ratio can also be called durability. It may be remarked that the maximum durability was achieved for Tencel fabrics. The durability of Modal-Promodal and Viloft-Viscose were close to each other. These results imply that the ion attachment to the fibres is more superficial in Viloft, Viscose, Modal and Promodal fabrics than in Tencel. Thus, the maximum durability to washing was achieved for Tencel fabrics. The XRF results for Modal and Tencel fabrics after ten washing cycles are shown in Figure 7 and Figure 8, respectively. The peaks of the curve in the figures indicate the amount of Zn on the fabrics. It can clearly be seen that the amount of Zn on Tencel fabrics is higher than that on Modal fabrics.

The theoretical Cu^{+2} weight ratio applied to the fabrics by the 1% $CuSO_4$ treatment was calculated to be 0.3981 by considering the atomic weights. In Table 6, the XRF results and the application ratio are presented. In this table, the maximum application ratio was found to be of 53.90% for Tencel, again. According to their ion application ratio, the fabrics can be ranked in decreasing order as follows: Tencel, Promodal, Viloft, Viscose and Modal. This ranking confirms the results on the antibacterial activity of the fabrics displayed in Table 3.

Table 6
XRF results and Cu^{+2} amounts on fabrics (theoretical Cu^{+2} weight ratio: 0.3981)

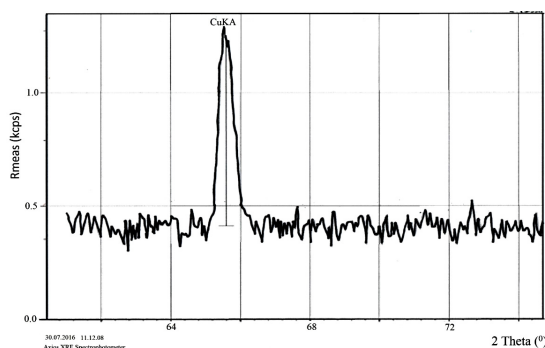| Fabric	Cu^{+2} amount on 1% $CuSO_4$ finished fabrics	Application ratio (%)	Cu^{+2} amount on fabrics treated with 1% $CuSO_4$ + 10 wash cycles	Residual Cu^{+2} ratio after 10 wash cycles (Durability) (%)
Modal	0.1069	26.85	0.0472	11.86
Promodal	0.2366	59.43	0.1243	31.22
Tencel	0.3026	76.01	0.2146	53.90
Viscose	0.1773	44.53	0.1122	28.18
Viloft	0.2195	55.13	0.1219	30.62

Figure 9: XRF results for $CuSO_4$ treated Modal fabric washed 10 times
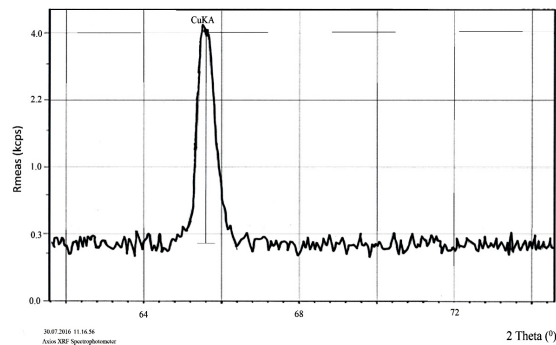
Figure 10: XRF results for CuSO₄ treated Tencel fabric washed 10 times

The residual Cu^{+2} ratio after 10 washing cycles is also displayed in Table 6. The Cu^{+2} ratio decreased compared to the initial amount on the finished fabrics for all fabric types, however, this decrease is not drastic, compared to the results for Zn^{+2} exhibited in Table 5. The maximum durability was achieved for Tencel fabrics – of 53.9%. In addition, the durability of Promodal, Viscose and Viloft fabrics gave satisfactory results. It can be inferred that the durability of Cu^{+2} ions on the fabrics is higher than that of Zn^{+2}.
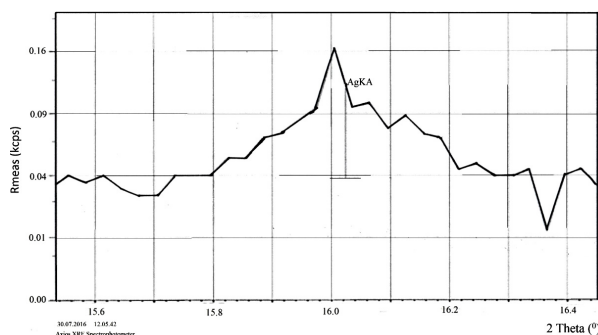
XRF data for Modal and Tencel fabrics after ten washing cycles are shown in Figure 9 and Figure 10, respectively. The peaks indicate the amount of Cu on the fabrics. It can clearly be seen

that the amount of Cu on Tencel fabrics is higher than that on Modal fabrics.

The theoretical Ag^+ weight ratio applied to the fabrics by the 1% $AgNO_3$ treatment was calculated to be 0.6350 by considering the atomic weights. Table 7 presents the XRF results and the application ratio of Ag^+ on the fabrics. The maximum application ratio was found to be of 50.72% for Tencel. The results for the other fabrics were close to each other. The residual Ag^+ ratio after 10 washing cycles is also displayed in Table 6. The Ag^+ ratio decreased compared to the initial amount on the fabrics for all fabric types. The maximum durability was achieved for Tencel fabrics – of 28.41%. The durability of Promodal was also satisfactory, while the results for the other fibres were low.

Table 7
XRF results and Ag^+ amounts on fabrics (theoretical Ag^+ weight ratio: 0.6350)

Fabric	Ag^+ amount on 1% $AgNO_3$ finished fabrics	Application ratio (%)	Ag^+ amount on fabrics treated with 1% $AgNO_3$ + 10 wash cycles	Residual Ag^+ ratio after 10 wash cycles (Durability) (%)
Modal	0.1421	22.37	0.0114	1.80
Promodal	0.1558	24.53	0.0620	9.76
Tencel	0.3221	50.72	0.1804	28.41
Viscose	0.1315	20.70	0.0139	2.19
Viloft	0.1487	23.41	0.0168	2.65

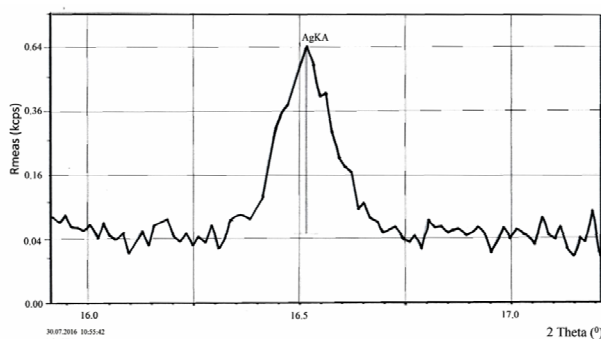Figure 11: XRF results for AgNO₃ treated Modal fabric washed 10 times

Figure 12: XRF results for AgNO$_3$ treated Tencel fabric washed 10 times

The XRF results for Modal and Tencel fabrics after ten washing cycles are shown in Figure 11 and Figure 12, respectively. The peaks of the curve indicate the amount of Ag on the fabrics. It can be clearly seen that the amount of Ag on Tencel fabrics is higher than that on Modal fabrics.

CONCLUSION

From the present study, the following conclusions can be drawn:

- Untreated regenerated cellulosic fabrics did not show antibacterial activity. The metal salt treatment induced an antibacterial effect on all the cellulosic fabrics. Despite the fact that the repeated laundering decreased the metal ion amount on all the regenearated fabrics, the antibacterial effect of the copper and silver treated fabrics was maintained at 100%. However, the antibacterial activity of the zinc treated fabrics was comparatively lower.

- Since Cu^{+2} and Zn^{+2} bond to the fibre with two electrons, while Ag^+ with only one, the application ratio of Cu^{+2} and Zn^{+2} were found to be higher than that of Ag^+. Despite the low durability of the silver treatment after repeated laundering, the antibacterial activity of the silver treated fabrics reached 100%. This can be explained by the higher bactericidal effect of silver, compared to that of other metals. The durability of $CuSO_4$ treated fabrics is higher than that of Zn^{+2} and Ag^+ ion treated ones. It can be inferred that the fibre-Cu^{+2} bonds are stronger than those with Zn^{+2} and Ag^+.

- Although all the fabrics were cellulosic, the differences in the structure of the fibres led to different levels of retention of metal salts and of their removal during washing. Viscose and Viloft fibres have a core-shell structure, whereas Modal has a fully shell structure. Thus, the metal ions bonded to Viscose and Viloft fabrics more than to Modal. The antibacterial effect of Modal-Promodal and Viloft-Viscose were close to each other for all metal treatments. This implies that the ion-fibre bonding is more superficial in Viloft, Viscose, Modal and Promodal, while it is more intrinsic in Tencel. Since Promodal is a blend of Tencel and Modal fibres, the application and durability results obtained ranged between those of the last two fabrics. Having crenulated surface, which results in higher specific surface area compared to that of viscose, Viloft fabrics recorded higher application ratio and durability than those of Viscose.

- The application ratio and durability of Tencel fabrics were higher than those of the other fabrics. Fibrillation in Tencel fibres led to a higher specific area available for the ions to attach to the macrofibrils. As a result, Tencel fibres exhibited the maximum antibacterial effect.

REFERENCES

[1] D. Höfer, in "Biofunctional Textiles and the Skin. Current Problems in Dermatology", edited by U. C. Hipler and P. Elsner, Basel, Karger, 2006, vol. 33, pp. 42-50.

[2] U. Wollina, M. B. Abdel-Naser and S. Verma, in "Biofunctional Textiles and the Skin. Current Problems in Dermatology", edited by U. C. Hipler and P. Elsner, Basel, Karger, 2006, pp. 1-16, Karger.

[3] H. K. Rouette, "Lexikon für Textilveredlung", Dülmen, Laumann, 1995.

[4] J. Wearing, "Bacteria", Crabtree Pub., USA, 1991, pp. 5-58.

[5] T. Tulunay, MSc Thesis, Erciyes University, Turky, 2016.

[6] Minnesota Department of Health, "Causes and Symptoms of *Staphylococcus aureus*" (available at: http://www.health.state.mn.us/divs/idepc/diseases/staph/basics.html).

[7] Center for Disease Control and Prevention, "*Escherichia coli*" (available at: https://www.cdc.gov/ecoli/).

[8] B. Tang, L. Sun, J. L. Li, J. Kaur, H. J. Zhu *et al.*, *Dyes Pigments*, **113**, 289 (2015).

[9] V. G. Nadiger and S. R. Shukla, *J. Text. Inst.*, **107**, 1543 (2016).

[10] J. Z. Praskalo-Milanovic, M. M. Kostic, S. I. Dimitrijevic-Brankovic and P. D. Skundric, *J. Appl. Polym. Sci.*, **117**, 1772 (2010).

[11] F. C. Yang, K. H. Wu, M. J. Liu, W. P. Lin and M. K. Hu, *Mater. Chem. Phys.*, **113**, 474 (2009).

[12] J. Zheng, F. Song, X. L. Wang and Y. Z. Wang, *Cellulose*, **21**, 3097 (2014).

[13] H. M. M. Ibrahim and M. S. Hassan, *Carbohyd. Polym.*, **151**, 841 (2016).

[14] J. U. Kim, M. S. Gong and J. G. Kim, *Cellulose Chem. Technol.*, **52**, 475 (2018).

[15] N. Ditaranto, R. A. Picca, M. C. Sportelli, L. Sabattini and N. Cioffi, *Surf. Interface Anal.*, **48**, 505 (2016).

[16] E. Alay, K. Duran and A. Korlu, *AATCC J. Res.*, **3**, 29 (2016).

[17] Z. C. Yu, J. F. Zhang, C. W. Lou, H. L. He, A. P. Chen *et al.*, *J. Text. Inst.*, **106**, 1203 (2015).

[18] H. K. Shin, M. Park, Y. S. Chung, H. Y. Kim, F. L. Jin *et al.*, *Macromol. Res.*, 21, 1241 (2013).

[19] W. Zhang, X. L. Dai, J. J. Zhou and G. Zhu, *Fiber Polym.*, **18**, 290 (2017).

[20] M. Orhan, D. Kut and C. Gunesoglu, *Indian J. Fibre Text.*, **32**, 114 (2007).

[21] U. C. Hipler, *Mycoses*, **51**, 39 (2008).

[22] G. Y. Zhang, Y. Liu, H. Morikawa and Y. Y. Chen, *Cellulose*, **20**, 1877 (2013).

[23] Y. Yu, Z. H. Jiang, G. Wang, G. L. Tian, H. K. Wang *et al.*, *Wood Sci. Technol.*, **46**, 781 (2012).

[24] T. Nakashima, Y. Sakagami, H. Ito and M. Matsuo, *Text. Res. J.*, **71**, 688 (2001).

[25] Q. Q. Zhou, J. C. Lv, L. Cai, Y. Ren, J. Y. Chen, *et al.*, *J. Text. Inst.*, **108**, 1371 (2017).

[26] M. Shateri-Khalilabad and M. E. Yazdanshenas, *Text. Res. J.*, **83**, 993 (2013).

[27] H. E. Emam, A. P. Manian, B. Siroka, H. Duelli, P. Merschak *et al.*, *Surf. Coat. Tech.*, **254**, 344 (2014).

[28] T. Kreze and S. Malej, *Text. Res. J.*, **73**, 675 (2003).

[29] B. H. Öztürk and T. Beckhtold, *Cellulose*, **15**, 101 (2008).

[30] Y. Umur, *Journal of Uludag University Engineering-Architecture Faculty*, **15**, 121 (2010).

[31] Lenzing, "Promodal" (available at: http://lenzinginnovation.lenzing.com/fileadmin/template/ pdf/usa_ProModal_folder.pdf).

[32] Danenong, "Modal-Micro modal" (available at: http://www.daenong21.com/en/product/sub3_1.asp?main=3&sub=31).

[33] O. Demiryurek and D. Uysalturk, *Text. Res. J.*, **83**, 1740 (2013).

[34] Turkish Standards Manual, Institute of Turkish Standards, TS EN ISO 6330, Ankara, Turkey.

[35] ATCC Standards Manual, ATCC Standards Development Organization, 11229, Manassas, United States.

[36] ATCC Standards Manual, ATCC Standards Development Organization, 25923, Manassas, United States.

[37] ASTM Standards Manual, ASTM International, E2149-0, West Conshohocken, United States.

[38] M. Tutak and F. Gun, *Fiber Polym.*, **12**, 457 (2011).