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The Influence of *in situ* Synthesis Parameters on the Formation of ZnO Nanoparticles and the UPF Value of Cotton Fabric

Vpliv parametrov sinteze in-situ na tvorbo nanodelcev ZnO in vrednost UZF bombažne tkanine

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Abstract

The aim of this research was to investigate different parameters of the *in situ* synthesis of ZnO nanoparticles on cotton in order to achieve a high ultraviolet protection factor (UPF). In the first part of the research the influence of different reducing agents (Na_2CO_3, KOH, and NaOH) and their molar concentrations (0.1 M and 1 M) on the formation of ZnO nanoparticles and on the UPF values of cotton fabric were studied. The second part of the research was focused on the other parameters of *in situ* synthesis, such as the synthesis time ratio (time ratio between the treatment of the fabric in the precursor ($ZnCl_2$) and treatment after the reducing agent was added) and drying period duration after the *in situ* synthesis. Using UV/Vis spectroscopy, high UPF values (UPF 50+) were measured for cotton fabrics where *in situ* synthesis was performed using NaOH and KOH, both at 1 M molar concentration. Inductively coupled plasma mass spectrometry (ICP-MS) revealed a higher content of zinc on the fabric when NaOH was used. Scanning electron microscopy (SEM) showed that use of this reducing agent resulted in cotton fabric completely covered with small, round shaped nanoparticles. From the second part of the research, it was found that longer treatment times after the reducing agent was added produced functionalised cotton fabric with higher UPF values. The drying period duration after *in situ* synthesis did not significantly affect the UPF value of the fabric, but it did influence the morphology of the synthesised nanoparticles. With a longer drying time the nanoparticles were more rounded. The samples had poor wash fastness even after the first wash, which was found through low UPF values.

Keywords: *in situ* synthesis, nanoparticles, zinc oxide, UV radiation, cotton, UV protection

Izvleček

Namen raziskave je bil proučiti pogoje in situ sinteze nanodelcev cinkovega oksida na bombažni tkanini in doseči visok ultravijolični zaščitni faktor (UZF) funkcionalizirane tkanine. V prvem delu raziskave je bil proučevan vpliv vrste reducentov (Na_2CO_3, KOH, NaOH) in njihove molarne koncentracije (0,1M in 1M) na oblikovanje nanodelcev ZnO na bombažni tkanini. V drugem delu raziskave so bili proučevani še drugi dejavniki, kot so časovno razmerje sinteze (razmerje med časom obdelave tkanine v prekurzorju in obdelave po dodatku reducenta) in čas sušenja po sintezi in situ. Visoke vrednosti UZF (50+), ki so bile določene na UV/Vis- spektrofotometru, so bile dosežene pri sintezi in situ ZnO-ND z uporabo NaOH in KOH v molarni koncentraciji 1M. Masna-spektrometrična analiza induktivno sklopljene plazme (ICP-MS) je potrdila večjo vsebnost cinka na tkanini, kjer je bil za sintezo in situ uporabljen NaOH. Iz posnetkov vrstične elektronske mikroskopije (SEM) je bilo razvidno, da so bili z uporabo NaOH pri sintezi in situ oblikovani ZnO nanodelci okrogle oblike,

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ki so povsem oplaščili vlakna. V drugem delu raziskave je bilo ugotovljeno, da se nanodelci ZnO bolje oblikujejo in da ima funckionalizirana tkanina večje vrednosti UPF, ko je čas obdelave tkanine po dodatku reducenta daljši. Čas sušenja po sintezi in situ ni bistveno vplival na različne vrednosti UZF tkanine, je pa vplival na obliko nanodelcev, ki so se oblikovali na površini bombažnih vlaken. Z daljšim časom sušenja so se oblikovali nanodelci bolj pravilnih okroglih oblik. Funkcionalizirane tkanine niso imele dobre obstojnosti na pranje, kar je bilo ugotovljeno iz majhnih izmerjenih UPF-vrednosti funkcionaliziranih vzorcev bombažne tkanine po končanem pranju.
Ključne besede: sinteza in situ, nanodelci, cinkov oksid, UV-sevanje, bombaž, zaščita pred UV-sevanjem

1 Introduction

The modification of textile materials with nanoparticles has been the objective of several studies [1–7] aimed at producing finished fabrics with different performances. Zinc oxide (ZnO) is an excellent candidate to be used for the fabrication of protective and functional textile materials due to its photocatalytic self-cleaning, antibacterial, UV-shielding and electrical properties, while having mechanical, thermal and chemical stability [8]. Furthermore, ZnO is also considered to be a biosafe material [9]. The deposition of ZnO nanoparticles onto textile materials is predominantly performed using pre-prepared ZnO nanoparticles (*ex situ*), because of their known size and shape and the ease of their application onto materials (i.e., dipping, impregnation or spraying). However, the pre-prepared ZnO nanoparticles have poor adsorption onto textiles. Moreover, the nanoparticles tend to form agglomerates on the surface of the fibre, which reduces the functional properties of textiles. These two particular drawbacks were reduced by using gaseous plasma as a textile pretreatment [10–12]. An alternative to deposition of *ex situ* prepared ZnO nanoparticles is their synthesis directly on material, or so called *in situ* (on site) synthesis. It was found that the functionalisation of textiles with *in situ* synthesised nanomaterials is very effective in enabling a rather uniform distribution of nanoparticles, as well as their good adsorption and adhesion, therefore providing durable protective properties of fabrics [8]. In the field of *in situ* synthesis of ZnO on textile materials, few studies have been published [13–19]. Researchers have achieved good photocatalytic [17, 19], UV protective [13, 16, 18], and antimicrobial [15, 17, 18] properties on cotton fabrics, and permanent hydrophilic surface, lower yellowing and increased tensile strength of wool [14]. The functionalisation of cotton with *in situ* synthesised ZnO nanoparticles included the immersion of fabric in a Zn-acetate [13, 15] or Zn-nitrate solution [16–19] and the addition of a reducing agent (NaOH). The reaction that involves the formation of ZnO nanoparticles from Zn-salts includes two main steps [20]. The first step is nucleation (generation of ZnO nuclei), and the second is growth (ZnO crystal growth). After adding an alkali to the Zn-salt, $Zn(OH)_2$ particles form. Then, $Zn(OH)_2$ precipitates, and upon the appropriate hydrothermal conditions, dissociates into Zn^{2+} and OH^-; and when the ion formation exceeds a critical value, which is necessary for the formation of ZnO crystals, ZnO begins to nucleate and crystal growth begins. In the literature on the topic of the synthesis of ZnO on textiles we found some papers that included the word "*in situ*" in their title; however from their content it is clear that the process is not truly *in situ* synthesis but rather a seeding method [21–23]. In these papers, nanoparticles are formed in the bath and after the synthesis, the fabric is immersed in the bath for few hours (from 8 to 24 hours), at temperatures from 80 to 130 °C, to allow seeding of the nuclei and further growth of ZnO nanoparticles on the textile material. Even though the results of these studies are positive (textile substrates had a self-cleaning photocatalytic capacity, increased hydrophilicity and increased protection against UV radiation), the process is far from suitable for industrial application. Even more importantly, the synthesis is time-consuming and is performed at a high temperature. The aim of our research was to study how different parameters of *in situ* synthesis, such as the concentration of the reducing agent, synthesis time and drying time, influence the formation of ZnO nanoparticles on cotton fabric and affect the UV protection factor of the functionalised fabric.

2 Experimental

2.1 Material

Chemically bleached and mercerized cotton fabric (Tekstina tekstilna industrija Ajdovščina d. o. o.), zinc chloride ($ZnCl_2$, Honeywell), sodium carbonate (Na_2CO_3, Sigma Aldrich), potassium hydroxide (KOH, Grammol), sodium hydroxide (NaOH, Sigma Aldrich) were used in the research.

2.2 In situ synthesis process

In situ synthesis was performed at room temperature and a liquor ratio (LR) 1 : 100. The molarity of the precursor $ZnCl_2$ was the same for all samples (0.1 M), while the molarity of the reducing agent (Na_2CO_3, KOH, and NaOH) was 0.1 M and 1 M. The in situ synthesis process consisted of treating the cotton sample in precursor solution for a period of time at constant magnetic stirring (for 10, 20, 30 minutes), treating the sample after adding the reducing agent dropwise to the precursor solution for 10, 20, 30, 60 and 120 minutes, adjusting the drying period duration at 100 °C (for 10, 30, 60, 120, 240 minutes), rinsing the sample with distilled water, wringing and finally drying the sample at 100 °C for 5 minutes.

2.3 Durability to washing

Samples were washed in laboratory apparatus Gyrowash 815 (James Heal, Great Britain) in accordance with EN ISO 105-C06 standard. The wash bath contained 4 g/l ECE phosphate reference detergent B, the bath volume was 150 ml, the temperature of washing was 40 °C and the washing lasted for 45 minutes. Samples were washed without stainless steel globules which equals to 1 domestic washing and with added 10 stainless steel globules to perform washing equal to 5 domestic washings.

2.4 Analytical methods

Ultraviolet Protection Factor

The ultraviolet protection factor (UPF) of the untreated and functionalized fabric samples was determined according to the AATCC TM 183 standard and measurements were performed using a Varian CARY 1E UV/VIS spectrophotometer (Varian, Australia) containing a DRA-CA-301 integration sphere and Solar Screen software. The transmission of the ultraviolet radiation through the samples was measured in the spectral range between 280 and 400 nm, and the average transmittance (T) values with the wavelengths between 315 and 400 nm (UV-A), 280 and 315 nm (UV-B) and 280 and 400 nm (UV-R) were determined from the measurements. UPF was calculated according to the following equation:

$$UPF = \frac{\sum_{\lambda=280}^{400} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{\lambda=280}^{400} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda} \quad (1),$$

where E_λ is the relative erythermal spectral effectiveness, S_λ is the solar spectral irradiance, T_λ is the spectral transmittance of the specimen, and $\Delta\lambda$ is the measured wavelength interval in nm. The UPF rating and UVR protection categories were determined from the calculated UPF values according to the Australian/New Zealand Standard: Sun protective clothing – Evaluation and classification. The Australian/New Zealand Standard (AS/NZ 4399: 1996) defines criteria for assessing the UV protective effectiveness of textiles and evaluation for labelling textile products with a protective function. The standard classifies textile products into three categories of protection, namely, excellent, very good and good protection [24]. The values are in the range of 15 to 50 and the higher the value, the better the protection.

Scanning electron microscopy (SEM)

The morphology of nanoparticles on the cotton fibres was observed by SEM JSM-6060 LV (JEOL, Japan). Prior to the SEM analysis, samples were coated with a layer of gold to ensure sufficient electrical conductivity. SEM micrographs were taken at 1500x magnification.

Inductively coupled plasma mass spectroscopy (ICP-MS)

ZnO-functionalised cotton samples were analysed using mass spectrometry with inductive coupled plasma after microwave decomposition. Prior to ICP-MS analysis, each sample was weighted (approximately 100 mg) and digested using a microwave-assisted digestion system (CEM MDS-2000) in a solution of 7 ml nitric acid and 2 ml hydrogen peroxide. The digested samples were cooled to room temperature and then diluted with 2 %v/v nitric acid until their concentration was within the desired concentration range and were used in subsequent analyses. An Agilent Technologies 7500ce

ICP-mass spectrometry (MS) instrument, equipped with a MicroMist glass concentric nebuliser, and Peltier-cooled, Scott type spray chamber was used.

3 Results and discussion

3.1 The influence of the reducing agent and its molarity

In the first part of the research, different reducing agents and their molar concentrations were studied for *in situ* synthesis of ZnO nanoparticles. The synthesis process consisted of a 30-minute treatment of the fabric in a precursor solution ($ZnCl_2$) and a 60-minute treatment after the addition of the reducing agent (0.1 M Na_2CO_3, 1 M Na_2CO_3, 0.1 M KOH, 1 M KOH, 0.1 M NaOH, 1 M NaOH). After the *in situ* synthesis, samples were dried for 240 minutes, washed with distilled water, wrung and dried at 100 °C for 5 minutes. The 0.1 M concentration of all used reducing agents led to the formation of an uneven distribution of ZnO nanoparticles on the cotton fibres (Figures 1b, 1d, 1f). Here, some larger agglomerates are also noticeable. In the case when 1 M Na_2CO_3 was used as the reducing agent, the ZnO was formed in layers and not as nanoparticles (Figure 1c). Some cracking of the layers is visible. The formation of ZnO nanoparticles and their relatively good distribution on the cotton fibres was achieved using 1 M KOH as the reducing agent (Figure 1e). On this sample, only a few agglomerates have formed. Figure 1g shows the sample where 1 M NaOH was used as the reducing agent. Here, evenly distributed ZnO nanoparticles have completely coated the fibre surface and only a few larger agglomerates are visible.

The SEM images reveal that the choice of reducing agent has an influence on the morphology of the *in situ* synthesised ZnO nanoparticles and their distribution on the fibres. Consequently, the UV protection properties of the samples are affected. In Table 1, UPF, transmission of UVA and UVB radiation,

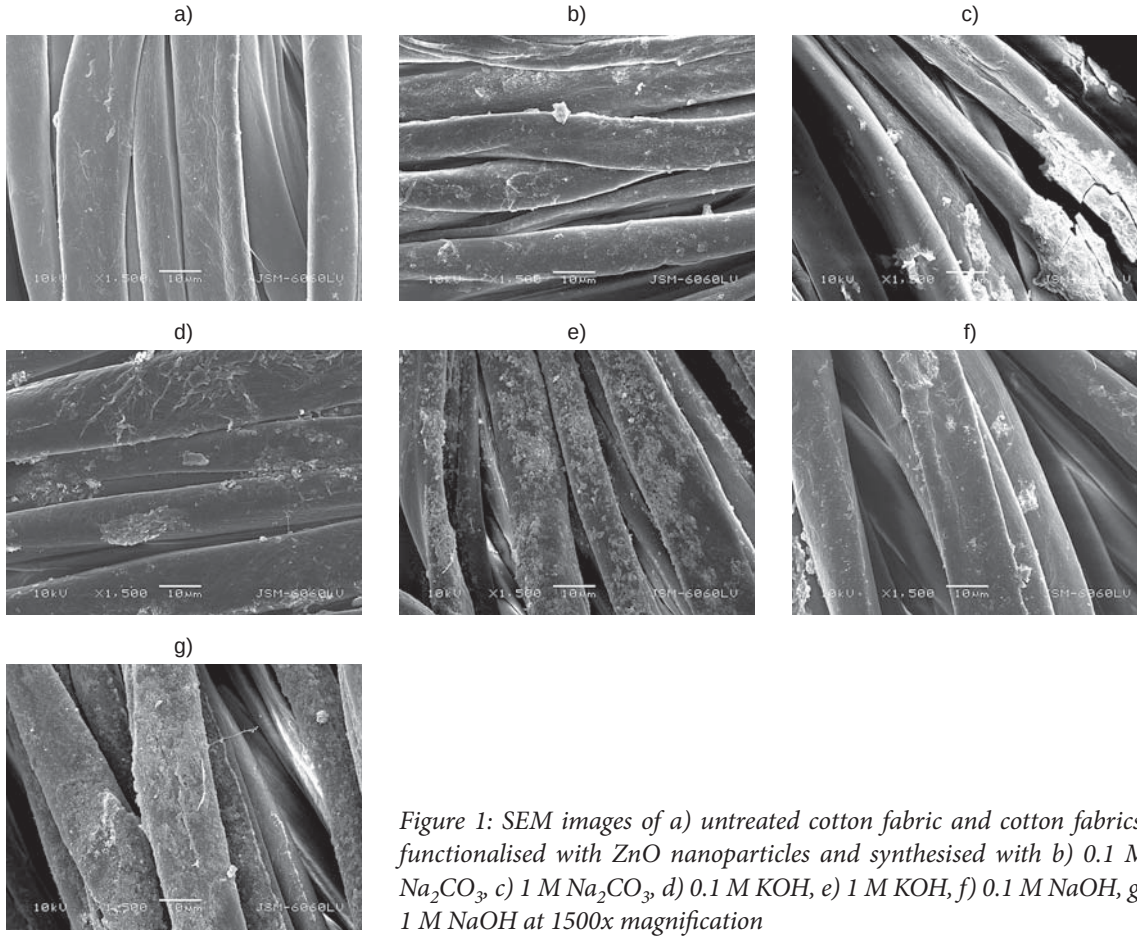

Figure 1: SEM images of a) untreated cotton fabric and cotton fabrics, functionalised with ZnO nanoparticles and synthesised with b) 0.1 M Na_2CO_3, c) 1 M Na_2CO_3, d) 0.1 M KOH, e) 1 M KOH, f) 0.1 M NaOH, g) 1 M NaOH at 1500x magnification

blocking of UVA and UVB radiation and protection category of the untreated and ZnO functionalised samples are presented. Untreated cotton has insufficient UV protection (UPF = 4.9). *In situ* synthesis of ZnO when 0.1 M KOH, NaOH and both molar concentrations of Na_2CO_3 were used as reducing agents does not significantly improve the UV protection of the cotton fabric. The UPF values of these samples remained under a value of 15; therefore, the samples do not provide sufficient UV protection according to the AS/NZ standard. High UV protection was achieved on the samples where 1 M KOH and NaOH were used as the reducing agents. The highest UPF value was achieved with the 1 M NaOH reducing agent (UPF=80.2), which places the sample into the excellent UV protection (50+) category. Excellent UV protection was also achieved on the sample where 1 M KOH was used as the reducing agent. The measured value of UPF was 58.4. Therefore, the results of the UV/Vis spectrophotometric measurements are in accordance with the SEM images. Samples where ZnO was formed in layers or there was only a small amount of nanoparticles visible on the samples did not provide sufficient UV protection, while the samples where an even distribution of a larger amount of nanoparticles was observed provided excellent UV protection.

From the results of the UV/Vis spectrophotometry and SEM analysis, we assumed that the sample where the NaOH reducing agent was used for the *in situ* synthesis of ZnO nanoparticles had a higher content of nanoparticles than the sample where the KOH reducing agent was used. With inductively coupled plasma mass spectrometry we confirmed our assumption (Table 2). Sample 1_NaOH with a higher UPF value (80.2), has a higher content of zinc (710.2 mg/kg) than the sample with a lower UPF value (58.4).

Table 2: Concentration of Zn (cZn) and UPF value of the samples when 1 M KOH and 1 M NaOH were used for the in situ synthesis

Sample	c_{Zn} [mg/kg]	UPF
1_KOH	590.0	58.4
1_NaOH	710.2	80.2

The literature describes that the *in situ* synthesis of ZnO nanoparticles on textiles provides good wash fastness [16]. However, our results indicate differently. In Figure 2 the results of the UPF values of washed samples 1_NaOH and 1_KOH are presented. The UPF values of both samples have decreased significantly after the first washing cycle. The UPF value of sample 1_KOH decreased from 58.4 to 10, and that of sample 1_NaOH decreased from 80.2 to 8.8. After five domestic washings, the UPF values of both samples are even lower. Our results indicate that the wash fastness of *in situ* synthesised ZnO nanoparticles on cotton is not good.

Table 1: Ultraviolet protection factor (UPF), transmission of UVA and UVB radiation (T(UVA) and T(UVB)), UVA and UVB blocking and protection category of the samples, where type and molar concentration of the reducing agent was changed

Sample	UPF	T (UVA) [%]	T (UVB) [%]	UVA blocking [%]	UVB blocking [%]	Protection category
Untreated	4.9	25.5	19.4	74.5	80.6	insufficient
0.1_Na_2CO_3 [a)]	5.8	23.1	15.8	76.9	84.2	insufficient
1_Na_2CO_3 [b)]	6.7	21.3	13.2	78.7	86.8	insufficient
0.1_KOH	6.1	22.6	15.1	77.4	84.9	insufficient
1_KOH	58.4	7.6	1.4	92.4	98.6	excellent
0.1_NaOH	5.7	23.3	16.2	76.7	83.8	insufficient
1_NaOH	80.2	7.4	0.9	92.6	99.1	excellent

[a)] 0.1_Na_2CO_3 – 0.1 M concentration of reducing agent

[b)] 1_Na_2CO_3 – 1 M concentration of reducing agent

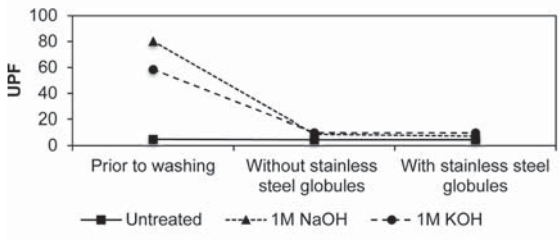

Figure 2: Ultraviolet protection factor (UPF) of the samples after one washing cycle without and with 10 stainless steel globules, which simulates one and five domestic washing cycles

3.2 The influence of synthesis time and drying time after the synthesis

To investigate how synthesis time influences the formation of ZnO nanoparticles and the UV protection of cotton fabric, different time ratios between the treatment of the fabric in precursor ($ZnCl_2$) and the treatment after the reducing agent (1 M NaOH) was added were combined, i.e., 10 : 10, 10 : 20, 10 : 30, 20 : 10, 20 : 20, 30 : 10, 30 : 30, and 30 : 60 minutes. The measured UPF values of the samples are presented in Table 4. The best UV protection was achieved on a sample where 30 minutes of treatment time in precursor was followed by 60 minutes of treatment time after adding the reducing agent. The measured UPF value of this sample was 80.2, which represents excellent UV protection. The second best UV protection provided by functionalised cotton fabric was achieved with a synthesis time ratio of 30 : 30. UV/Vis spectrophotometric measurements showed that this sample blocks 92.2% UVA and 97.7% UVB radiation, and has a UPF value of 39.3. A UPF value 35.5 was achieved by treating the fabric in a precursor for 10 minutes followed by a 30-minute treatment after the reducing agent was added. The UPF value of 29.2 was achieved on the sample where the treatment to synthesis time ratio was 30 : 10. As shown in Table 4, the samples that were treated for a longer period of time after the reducing agent was added to the reaction bath had higher UPF values than samples that were treated for a longer period of time in the precursor.

The results of the UV/Vis spectrophotometric measurements of the samples where the same synthesis time ratio was used (30 : 30) but different drying times were used (from 10 to 240 minutes) are presented in Table 5. Longer drying times did not result in significantly increased UPF values in the functionalised samples. The measured UPF values were in the range of 32 to 39 for all samples. Therefore, the drying time after *in situ* synthesis does not affect the UPF values of the functionalised samples. However, the drying time did influence the morphology of the ZnO nanoparticles (Figure 3). The samples presented in Figure 3 are the samples that were dried for the shortest period of time (10 minutes) (Figure 3a) and longest period of time (240 minutes) (Figure 3b). A significant difference in the morphology of the formed ZnO nanoparticles is noticeable. The nanoparticles were not fully formed into rounded shapes on the sample that was dried for 10 minutes after the *in situ* synthesis, while the nanoparticles on the sample that was dried for 240 minutes after the *in situ* synthesis were completely rounded.

Table 4: Ultraviolet protection factor (UPF), transmission of UVA and UVB radiation (T(UVA) and T(UVB)), UVA and UVB blocking and protection category of the samples according to the synthesis time

Synthesis time ratio [min][a)]	UPF	T (UVA) [%]	T (UVB) [%]	UVA blocking [%]	UVB blocking [%]	Protection category
10 : 10	22.0	10.5	4.0	89.5	96.0	good
10 : 20	29.7	9.2	3.4	90.8	96.6	very good
10 : 30	35.2	8.8	3.0	91.2	97.0	very good
20 : 10	19.7	10.8	4.4	89.2	95.6	good
20 : 20	28.7	9.1	3.0	90.9	97.0	very good
30 : 10	29.2	9.2	3.1	90.8	96.9	very good
30 : 30	39.3	7.8	2.3	92.2	97.7	very good
30 : 60	80.2	7.4	0.9	92.6	99.1	excellent

[a)] Time ratio between treatment of fabric in precursor and after adding the reducing agent.

Table 5: Ultraviolet protection factor (UPF), transmission of UVA and UVB radiation (T(UVA) and T(UVB)), UVA and UVB blocking and protection category of the samples with different drying times

Drying time [min]	UPF	T (UVA) [%]	T (UVB) [%]	UVA blocking [%]	UVB blocking [%]	Protection category
10	34.9	9.5	2.6	90.5	97.4	very good
30	36.9	9.0	3.2	91.0	96.8	very good
60	32.4	9.0	2.9	91.0	97.1	very good
120	39.8	8.4	2.3	91.6	97.8	very good
240	39.3	7.8	2.3	92.2	97.7	very good

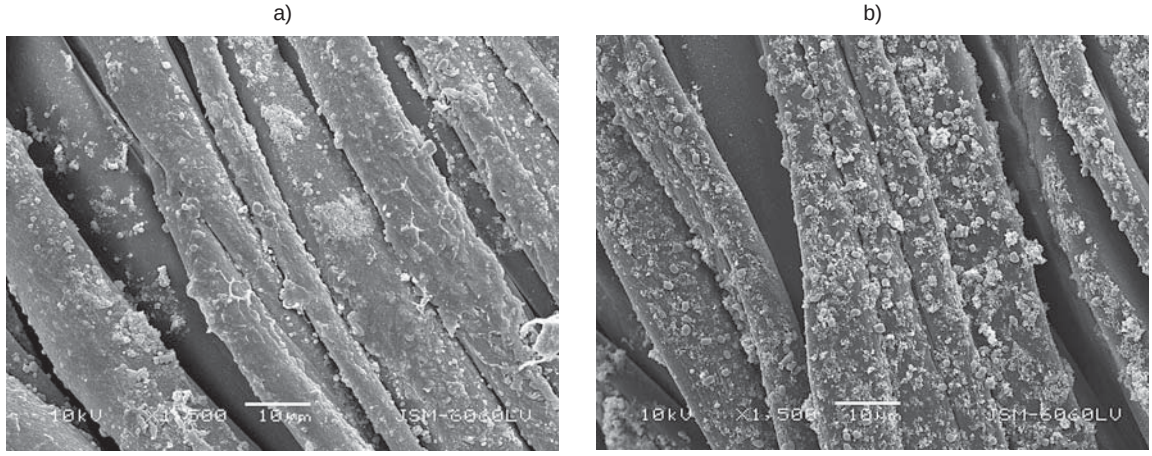

Figure 3: SEM images of the cotton samples with drying time: a) 10 minutes and b) 240 minutes

4 Conclusion

The parameters of the *in situ* synthesis of ZnO nanoparticles and the UV protection factor of the functionalised fabric were studied. The results show that the highest concentration of ZnO nanoparticles and their even distribution on the fibres, which results in highest UPF value of the functionalised fabric, is achieved when the *in situ* synthesis is performed with 1 M NaOH as a reducing agent. Such a sample provides excellent protection of the skin against UV radiation and could be potentially used for the production of UV protective textiles (i.e., clothes, parasols). The synthesis time ratio crucially affects the formation of ZnO nanoparticles on the fibre surface and consequently on the UPF value of cotton fabric. Higher UPF values of functionalised cotton fabrics are achieved when the treatment time after adding the reducing agent is prolonged. The drying time after the *in situ* synthesis does not significantly influence the UPF value of the functionalised cotton fabric, but it does influence the morphology of the formed ZnO nanoparticles. At a longer drying time, more rounded nanoparticles are formed. The results of this research showed that the *in situ* synthesis of nanoparticles did not increase the wash fastness of the functionalised cotton fabric. The results of the research have the potential to advance the development of UV protective textiles; however, due to the poor wash fastness, future research has to focus on achieving better adhesion of synthesised nanoparticles on cotton fabric, i.e., by plasma pretreatment of the fabric and/or the use of binders that could form a matrix to entrap the nanoparticles.

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