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Original scientific paper

Biodegradation of cotton fabric impregnated with TiO₂ nanoparticles

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Abstract: Commercial P25 TiO₂ nanoparticles are widely exploited as an efficient photocatalyst. In the textile domain, these nanoparticles are used for the production of self-cleaning, highly UV protective textiles, with an antimicrobial activity. The disposed textile products may end up in a landfill where they are subjected to the biodegradation process. Considering the importance of the later, this study discusses the biodegradation behaviour of cotton fabric impregnated with commercial P25 TiO₂ nanoparticles. Photocatalytic activity of TiO₂ nanoparticles immobilized on cotton fabric was proved by the photodegradation of dyes C.I. Acid Orange 7 and methylene blue in aqueous solution. Biodegradation of fabrics was assessed by soil burial test in periods of 3, 9 and 18 days. Chemical and morphological changes induced by biodegradation were analyzed by FTIR, SEM and EDS. A colour of the samples gradually changed from white to yellow/brown due to rotting. SEM analysis revealed a severe destruction of the control and impregnated cotton fibres after 18 days of soil burial which was in line with visual appearance of completely damaged fabrics. The results confirmed that biodegradation behaviour of both the control and impregnated sample was equivalent, indicating that P25 TiO₂ nanoparticles did not inhibit the biodegradation process of cellulose.

Keywords: cotton; TiO₂ nanoparticles; biodegradation; dye photodegradation; UV protection.

INTRODUCTION

Various goods with immobilized metal and metal oxide nanoparticles (NPs) can be already found on the market. Although Ag NPs are enormously exploited due to their antimicrobial action against a wide range of microorganisms,^{1–3} the

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commercialization of products with TiO₂ NPs should not be underestimated. Excellent photocatalytic activity, UV protective properties, high stability and relatively low price made them attractive for numerous applications (photovoltaic cells, treatment of effluents, manufacturing of cosmetic products, self-cleaning ceramics and glass, etc). These features are also utilized for manufacturing of textiles with high UV protective, self-cleaning and antimicrobial efficiency.⁴⁻⁶ The commercially available P25 powdered TiO₂ NPs (Degussa and Aeroxide) are the most commonly consumed TiO₂ NPs and they can be considered as *de-facto* standard titania photocatalyst.⁷ Generally, TiO₂ NPs in anatase crystalline form exhibit extraordinary photocatalytic activity. However, it has been shown that P25 TiO₂ NPs possess absolutely superior photocatalytic activity, which is attributed to their specific anatase/rutile crystalline structure.⁴ The addition of rutile significantly improves the photocatalytic activity of anatase phase.⁸ Namely, when anatase and rutile phase are in the close contact, photo-excited electrons and holes are preferentially trapped in the anatase and rutile phases, inhibiting an unfavourable electron-hole recombination.^{8,9} Although the mechanism of their action is well established, little is known on their environmental impact and health safety at this point. These aspects gained much attention recently, but the specific nature of NPs that highly differ from the behaviour of equivalent bulk materials makes such research very complex and time consuming. The environmental impact of NPs in general is strongly affected by their size, shape, chemical composition, surface structure and area, charge, solubility and aggregation state¹⁰ and hence, an extensive and systematic research on the interaction of the NPs with various ecosystems should be encouraged.¹¹

Keeping in mind the significance of biodegradation of textile products in post-exploitation period, we made many efforts in the last several years to learn more on the possible influence of Ag, TiO₂ and TiO₂/Ag NPs on biodegradation behaviour of cotton and cotton/PET fabrics in soil.¹²⁻¹⁶ Since the biodegradation trends vary with a nature of the substrate and applied NPs, it is very important to understand that some general conclusion will be drawn in the future only on the ground of the results acquired from the plenty of individual case studies. The reported studies so far indicated that the complexity is even larger than expected as the temperature, the humidity and the type of soil, including the type of enzymes involved, also play an important role in biodegradation processes of textiles in the soil.^{14,17,18} As anticipated, the results confirmed that Ag NPs in various forms inhibit the biodegradation of cotton and cotton/PET fabrics due to outstanding antimicrobial activity.^{12-15,17} Recently, Milošević *et al.* reported that Ag/TiO₂ NPs also suppress the biodegradation of cotton and cotton/PET fabrics in the soil.¹⁵ It is well established that antimicrobial activity of TiO₂ NPs is initiated by UV irradiation. Therefore, it was surprising that cotton fabrics loaded with colloidal TiO₂ NPs synthesized by acidic hydrolysis of TiCl₄ hindered the

biodegradation process, which was carried out in the dark.¹⁴ The latest study pointed out that the biodegradation behaviour of the cotton fabric corona pre-treated and impregnated with the same TiO₂ NPs insignificantly differed from the control sample.¹⁶

To our knowledge, a biodegradation behaviour of cotton fabrics loaded with P25 TiO₂ NPs, which are dominant in textile nanocomposites studied in literature and commercial textile products, has not been reported yet. Therefore, the aim of this study was to consider their influence on biodegradation of cotton fabric in soil by the standard soil burial test. Chemical and morphological changes were assessed by FTIR and SEM, respectively. As already mentioned, P25 TiO₂ NPs impart photocatalytic and UV protective properties to textile materials. In order to demonstrate that TiO₂ NPs in applied concentrations are truly efficient from that point of view, UV protection efficiency and discoloration of selected textile dyes (C.I. Acid Orange 7 and methylene blue) from aqueous solution were also evaluated.

EXPERIMENTAL

Materials and methods

Desized and bleached cotton (CO) woven fabric (117.5 g/m², 52 picks/cm, 27 ends/cm, thickness of 0.26 mm) was kindly supplied by the Slovenian textile company Tekstina d.d. Ajdovščina (Ajdovščina, Slovenia). The samples were cleaned from impurities before the impregnation with Aeroxide P25 TiO₂ NPs in a manner described elsewhere.¹⁹

CO fabric was dipped into 0.1 M dispersion of TiO₂ NPs (liquor to fabric ratio 20:1) for 5 min and after squeezing at a pressure of 2 kg/cm², it was dried at room temperature. Dry fabric was rinsed twice (5 min) with deionised water and dried again at room temperature. This fabric is denoted as a CO+TiO₂.

The UV protection factor (UPF value) of the control and impregnated CO fabrics was measured by UV/Vis spectrophotometer Cary 100 Scan (Varian). The UV protection factor (UPF) was automatically calculated based on recorded data in accordance with Australia/New Zealand standard AS/NZS 4399:1996 using a Startek UV fabric protection application software, version 3.0 (Startek Technology).

Photocatalytic activity of TiO₂ NPs deposited onto CO fabric was studied by measuring the removal of dyes C.I. Acid Orange 7 (AO7) and methylene blue (MB) from aqueous solution under UV illumination (Ultra-Vitalux lamp, 300 W, Osram). A 0.5 g of the CO fabric was dipped into 25 mL of AO7 and MB solutions (10 mg/L) and illuminated for 30, 60, 90, 120, 180, 240, 300, 360 and 1440 min. The AO7 and MB concentrations were calculated based on spectrophotometric measurements (UV/Vis spectrophotometer Cary 100 Scan, Varian) at λ_{\max} of 664 and 484 nm, respectively.

Biodegradation of the CO and the CO+TiO₂ fabrics was accomplished by a soil burial test according to ISO 11721-1:2001 and ISO 11721: 2003 standards. In this standard procedure, a container was filled with commercial grade compost. The water content of the soil was 60±5 % of its maximum moisture retention capacity. It was held constant during the experiment by spraying with water. The pH of the soil was between 4.0 and 7.5. The samples were buried in the soil for 3, 9 and 18 days. After certain incubation times, the samples were rem-

oved from the soil and rinsed with running tap water. Afterwards, they were immersed in 70 % ethanol for 30 min and dried at room temperature.

The presence of TiO₂ NPs on the surface of the CO fibres after impregnation was detected by field emission scanning electron microscopy (FESEM, Tescan Mira3 FEG). In addition, energy-dispersive X-Ray spectroscopy (EDS) of the fibres was performed using a JEOL JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK). Morphological changes of CO and CO+TiO₂ fabrics induced by the biodegradation process after 3, 9 and 18 days of exposure to the soil microflora were analyzed by JEOL JSM 5610 and 6060 LV scanning electron microscope equipped with EDS. The samples were coated with a thin layer of Au before the analysis.

The wettability of CO and CO+TiO₂ fabrics was studied using a thin-layer wicking test of wettability (TLW) which was carried out in the horizontal direction according to Chibowski and Gonzales-Caballero.²⁰

Fourier-transform infrared (FTIR) spectra were obtained by a Spectrum GX I spectrophotometer (Perkin Elmer, Great Britain) equipped with an attenuated total reflection (ATR) cell and a diamond crystal ($n = 2.0$). The spectra were recorded over a range of 4000 to 600 cm⁻¹ using 32 scans at a resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

A successful impregnation of CO fabric with P25 TiO₂ NPs was confirmed by FESEM and EDS analyses. Large amounts of agglomerated TiO₂ NPs across the surface of CO fibre can be seen in FESEM image (Fig. 1a). Peaks corresponding to Ti are also visible in EDS spectrum of the CO+TiO₂ fabric which is presented in Fig. 1b.

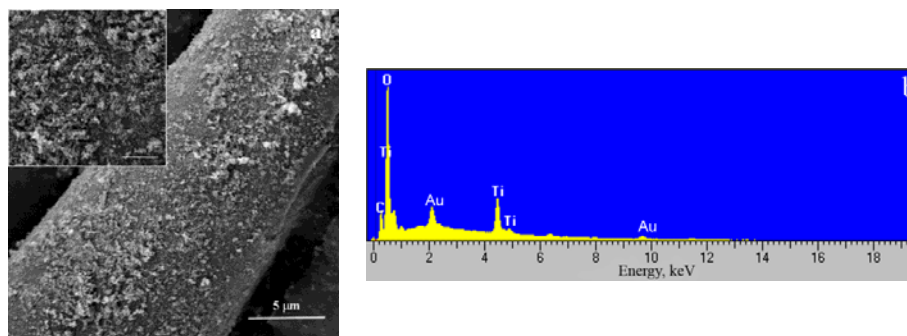


Fig. 1. FESEM image (a) and EDS spectrum (b) of the CO+TiO₂ fiber.

The influence of TiO₂ NPs on the wickability of the impregnated CO fabric was evaluated on the basis of the results obtained by TLW measurements. The time at which the water penetrated a certain distance was plotted as a function of the wetted surface and the results are presented in the Fig. 2. Apparently, the impregnation of CO fabric with TiO₂ NPs resulted in decreased wickability. The rate of thin-layer wicking of water into the CO+TiO₂ fabric was slower compared to the control CO fabric. Taking into account that wickability and wettability are

closely related,²¹ the obtained results indicate that TiO₂ NPs created the hydrophobic effect. Such finding is in a good correlation with literature data.^{14,16,22}

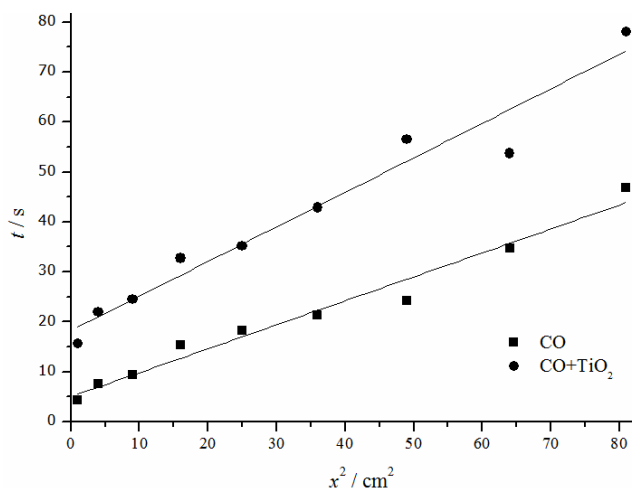


Fig. 2. Rate (x^2/t) of thin-layer wicking of water into CO and CO+TiO₂ fabrics.

Growing depletion of ozone layer requires adequate UV protection which can be utilized with TiO₂ NPs due to their ability to absorb UV irradiation. The UV protection of textiles is commonly expressed as UV protection factor (UPF) or UPF rating. It is recommended that UPF rating for garments should not be less than 40 to 50+. In this study, the UPF values of CO and CO+TiO₂ fabrics were 5.24 ± 0.21 and 83.79 ± 12.32 , respectively. The UPF rating of only 5 in the case of CO fabric means that it does not provide UV protection. In contrast, the impregnated fabric ensured maximum UPF rating of 50+.

The photocatalytic activity of TiO₂ NPs immobilized onto CO fabric was evaluated by monitoring the discoloration of aqueous solutions of dyes AO7 and MB under the lamp which simulated the sunlight. The dependence of c/c_0 vs. time of illumination for the CO and the CO+TiO₂ fabrics is shown in Fig. 3. Fig. 3a reveals that the control CO fabric caused the removal of AO7 dye by approximately 10 % after 24 h of exposure to illumination. On the other hand, MB was almost completely removed from the solution in the same period. Such results are attributed to the absorption of dyes which was more prominent in the case of MB as it is cationic dye. The photographs of the CO and the CO+TiO₂ fabric samples after the repeated illumination cycles (Fig S-1, Supplementary material to this paper) proved that photodegradation did not occur in the presence of CO fabric. It is evident that both CO samples were orange/blue coloured after 24 h of illumination. In contrast, CO+TiO₂ fabric remained white, independently of investigated dye, which indicates the photodegradation of both AO7 and MB dyes. The AO7 dye was totally removed from the solution after 3.5 h, while in the case

of the MB dye, the complete discoloration of the solution occurred after 3 h. The obtained results confirmed that the amount of deposited TiO₂ NPs was sufficient for the efficient removal of AO7 and MB dyes from aqueous solutions.

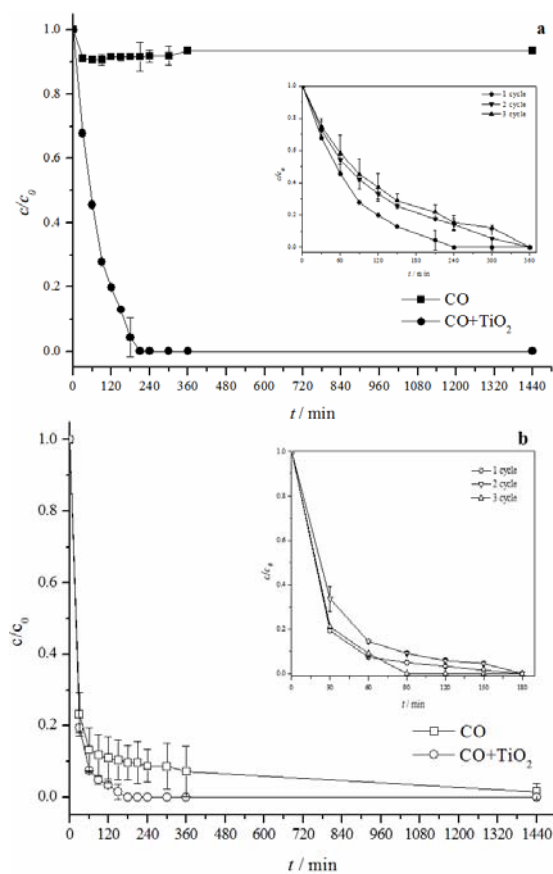


Fig. 3. Removal of dyes AO7 (a) and MB (b) from aqueous solutions in the presence of the CO and the CO+TiO₂ fabrics under sun-like illumination (inset: repeated illumination cycles with CO+TiO₂ fabric).

In order to examine the durability of photocatalytic activity of TiO₂ NPs in the impregnated CO+TiO₂ fabric, the discoloration procedure was repeated two more times under the same experimental conditions. The changes in relative AO7 and MB concentrations after repeated illumination cycles for the CO+TiO₂ fabric are presented as insets in Fig. 3. Obviously, the CO+TiO₂ fabric preserved excellent photocatalytic activity in repeated cycles, but its efficiency slightly decreased for the AO7 dye though it can be still considered as satisfactory. Such results demonstrate that the CO+TiO₂ fabric is stable and it could be exploited several times.

Biodegradation of the CO and the CO+TiO₂ fabrics was evaluated by the soil burial test. CO fabrics consist of cellulosic fibers that are prone to action of bacteria and fungi during the biodegradation process. The photographs of the CO

and the CO+TiO₂ fabrics before and after 3, 9 and 18 days of soil burial are shown in Fig. 4. Apparently, there is no significant difference in appearance between the control and impregnated fabric. The yellowish/brown colour of both samples appeared already after 3 days spent in soil. The prolongation of incubation time in soil led to a further darkening of the samples due to severe rotting. It can be also noticed that both fabrics lost their form after 18 days of soil burial, *i.e.*, they were disintegrated into pieces. Such macroscopic, visually detectable changes are caused by the changes in fibre morphology, crystallinity and chemical structure.



Fig. 4. Photographs of the CO and the CO+TiO₂ fabrics before and after 3, 9 and 18 days of soil burial.

Morphology of CO and CO+TiO₂ fibres before burial and after excavation from the soil after 3, 9 and 18 days were assessed by SEM analysis (Fig. 5). On the other hand, EDS analysis provided the data on the surface elemental composition of the CO+TiO₂ fibres before and after the soil burial test (Fig. S-2 of the Supplementary material).

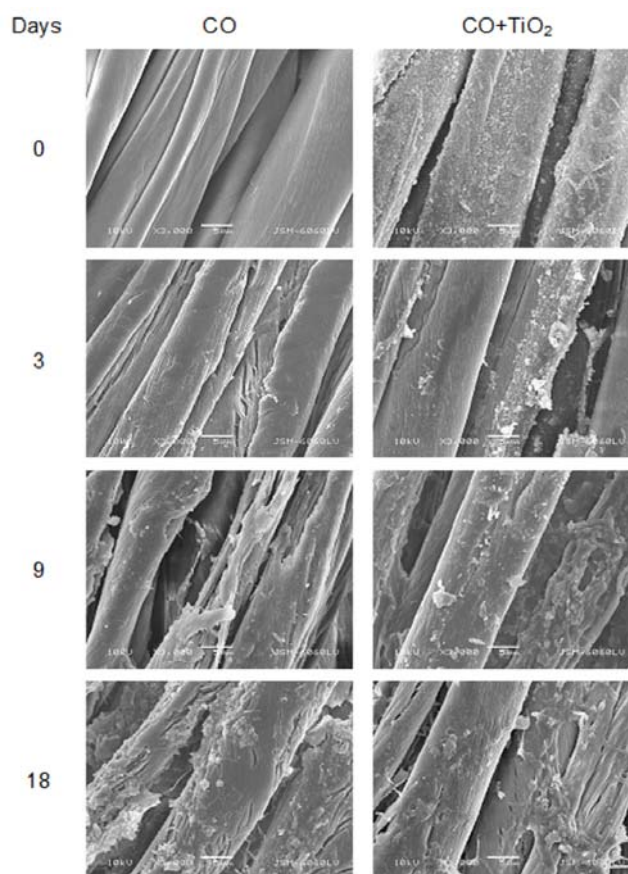


Fig. 5. SEM images of the CO and the CO+TiO₂ fabrics before and after 9 and 18 days of soil burial.

The indications of fibres damage were apparent already after 3 days of burial. Deep cracks can be observed on both CO and CO+TiO₂ fibres. The damage was slightly more pronounced on the CO fibres indicating higher biodegradation rate. As expected, further prolongation of burial time brought about more severe fibre destruction which is in line with the photos shown in Fig. 4 and previous results.¹⁶ The presence of considerable fibre defibrillation was also reported by Milošević *et al.* and Primc *et al.*^{15,23} The SEM images of the CO+TiO₂ fibres reveal considerable decrease in amounts of deposited TiO₂ NPs with a burial time, which implies the leaching of TiO₂ NPs into the soil environment. On the other hand, the EDS results showed that Ti was detected on the CO+TiO₂ fibre surface even after 18 days of burial. It is clear that both the CO and the CO+TiO₂ fibres underwent the equivalent destruction. This indicates that TiO₂ NPs did not affect the biodegradation process.

It is generally accepted that TiO₂ NPs exhibit antimicrobial activity when they are exposed to UV light. However, some studies indicated that TiO₂ NPs can interact with bacteria even in the absence of UV light.^{24,25} Lazić *et al.* also demonstrated that CO fabric impregnated with 0.1 M colloid of anatase TiO₂ NPs (with significantly smaller dimensions than currently applied P25 TiO₂ NPs) which were synthesized by acidic hydrolysis of TiCl₄, exhibited similar biodegradation behaviour as the control sample within 20 days of testing.¹⁴ However, unlike in the current study, the former samples were not destroyed within this time interval and impregnated sample in the following weeks showed a resistivity towards biodegradation. This collision in the results implies that the structure, size and shape of TiO₂ NPs may highly influence their behaviour in soil. On the other hand, weaker degradation is attributed to lower temperature and humidity, as well as to different soil type in previous study. Commonly, microorganisms in soil are more active at elevated temperature and humidity. So far reported results undoubtedly convinced us that these parameters are extremely important in biodegradation process.¹⁴⁻¹⁸ It is suggested that cuticle layer of the CO fiber is digested first.²⁶ The action of various microorganisms is supposed to be different. Fungi penetrate through the second wall until they reach fibre lumen where they grow. In fact, mycelium grows towards the fibre wall secreting the enzymes which cause the degradation.²⁶ In contrast, the action of bacteria is oriented in opposite direction: from the fibre surface towards fibre interior. Tomšič *et al.* assumed that fungi play the main role in biodegradation of cellulose fibres since bacteria need medium with larger moisture.¹³ In other words, CO fabric should be saturated throughout the whole biodegradation process.

The chemical changes induced by biodegradation were examined by FTIR analysis. The FTIR spectra of CO and CO+TiO₂ samples before and after 3, 9 and 18 days of soil burial are presented in Fig. 6. The characteristic absorption bands for cellulosic fibres can be clearly read from these spectra and they were discussed in detail in our previous work.^{15,16} The emergence of intensive absorption bands at 1641 and 1535 cm⁻¹ corresponding to amide I and II in excavated samples are attributed to secondary amides originating from the proteins that were produced during the growth of microorganisms and they remain irreversibly bound to the fibres.^{12,13} The intensity of these bands gradually increased with a prolongation of the burial time for both the CO and the CO+TiO₂ samples. The clear presence of these bands in the CO+TiO₂ fabric revealed that TiO₂ NPs did not significantly affect the biodegradation process in soil. Since the existence of these bands was reported and discussed in many studies so far, they can be adopted as an indicator of microbial growth and thus, the degree of fibre deterioration.^{12,13,15,16,23}

Rough conclusions on the alterations in crystallinity of cellulose caused by biodegradation process can be drawn also on the basis of FTIR measurements.

The degree of crystallinity is commonly expressed as a crystallinity index (I_k). In accordance with methods proposed by O'Connor *et al.*, Nelson and O'Connor, and Hulleman *et al.* in the current study, I_k was determined from the proportion of intensity of absorption bands at 1429 (CH₂ bending) and 893 cm⁻¹ (C–O stretching), at 1372 (vibration of C–H group of cellulose ring) and 2900 cm⁻¹ (C–H stretching) as well as at 1280 (C–H bending) and 1200 cm⁻¹ (–OH bending)^{27–29}. The I_k changes of cellulose in the CO and the CO+TiO₂ fabrics caused by biodegradation after 3, 9 and 18 days of soil burial are presented in Fig. 7. Evidently, the degree of crystallinity increased within 18 days of soil burial for both samples. Such finding is attributed to initial attack of amorphous fibre regions by microorganisms.^{13,18} It is believed that further exposure to the action of microorganisms would result in deterioration of both amorphous and crystalline regions of the fibre.¹⁸ Obtained results are in accordance with the reported data.¹⁶

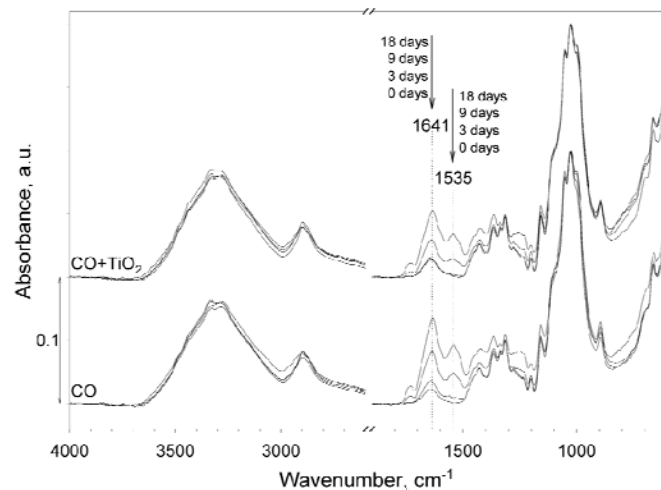


Fig. 6. FTIR spectra of the CO and the CO+TiO₂ fabrics before and after 3, 9 and 18 days of soil burial.

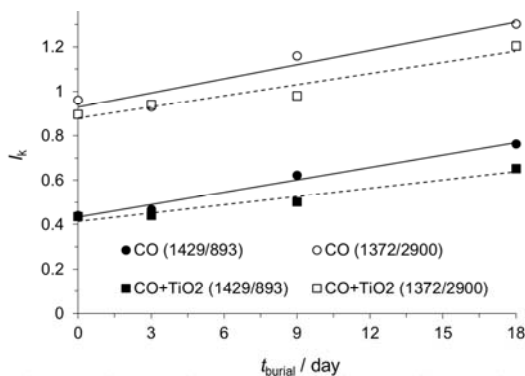


Fig. 7. Dependence of crystallinity index, I_k , from burial time of the CO and the CO+TiO₂ samples. Method of I_k determination: ● and ■ are proportions of intensity of the bands at 1429 and 898 cm⁻¹, □ and ○ are proportions of intensity of the bands at 1372 and 2900 cm⁻¹.

CONCLUSION

The commercial P25 TiO₂ nanoparticles present on the fibres of the impregnated cotton fabric decreased the fabric wickability, provided maximum UPF rating and excellent photocatalytic activity.

After 18 days of soil burial, both the control cotton fabric and impregnated fabric were disintegrated into pieces. The observed defibrillation and degradation of the control and impregnated fibres during the biodegradation in the soil environment showed that presence of the P25 TiO₂ nanoparticles did not significantly influence the biodegradation process. Furthermore, the detected amide groups from the generated proteins and increased crystallinity index with a prolonged burial time, for both the control and impregnated fabrics, suggested that TiO₂ nanoparticles did not obstruct the growth of the microorganisms. Obtained results clearly demonstrated that P25 TiO₂ nanoparticles did not hinder the biodegradation of cotton fabric which is very beneficial from the environmental standpoint.

SUPPLEMENTARY MATERIAL

The additional data are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

БИОДЕГРАДАЦИЈА ПАМУЧНЕ ТКАНИНЕ ИМПРЕГНИРАНЕ НАНОЧЕСТИЦАМА TiO₂

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Комерцијалне наночестице P25 TiO₂ се широко употребљавају као катализатор. У области текстила се ове честице често користе у производњи самочистећег текстила са УВ заштитом и антимикробном активношћу. Одбачени текстилни производи могу завршити на депонијама где долази до њихове биодеградиције. Узимајући ово у обзир, у раду је дискутовано понашање памучне тканине импрегниране комерцијалним наночестицама P25 TiO₂ приликом процеса биодеградиције. Фотокаталитичка активност наночестица TiO₂ имобилисаних на памучној тканини је доказана праћењем фотодеградиције воденог раствора боја *C.I. Acid Orange 7* и метиленско плаво. Биодеградиција памучне тканине је испитана методом закопавања у земљу на период од 3, 9 или 18 дана. Хемијске и морфолошке промене настале услед биодеградиције материјала су испитане FTIR, SEM и EDS анализом. Боја узорака се променила из беле у жуто/браон услед процеса труљења. SEM анализа је указала на изражено оштећење контролног узорка и импрегни-

раниh vlakana nakon 18 dana staјања u zemљи, што је u skladu sa izgledom raspadnutih tkanina. Takoђе је utvrђeno da prisustvo nanочестица P25 TiO₂ nema negativan uticaj na sposobnost biodegradacije pamučne tkanine.

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