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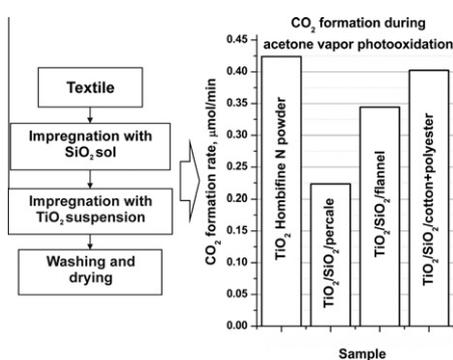
Effect of preparation method of functionalized textile materials on their photocatalytic activity and stability under UV irradiation

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HIGHLIGHTS

- ▶ Highly photoactive TiO₂ based textile materials were developed.
- ▶ Al₂O₃ and SiO₂ were used as binding and protective agents.
- ▶ Activity was tested in the acetone vapor photooxidation.
- ▶ H₂O, CO and CO₂ were detected as the gaseous degradation products.

GRAPHICAL ABSTRACT



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ABSTRACT

Cotton textiles and cotton/polyester blends were modified by impregnation with Al₂O₃ or SiO₂ as the binding agent and TiO₂ as the photocatalyst. The photocatalytic activity of the synthesized materials was measured in a flow reactor under steady-state conditions. The effect of the preparation procedure on the photostability of the textile materials under prolonged UV irradiation as well as the photocatalytic activity during acetone vapor photooxidation was investigated. It was demonstrated that impregnation with commercially available SiO₂ water sol and TiO₂ Hombifine N is a good method for preparing highly photocatalytically active textile materials that have activity comparable to that of TiO₂ Hombifine N powder. In contrast, modification with either SiO₂ prepared from tetraethyl orthosilicate by the sol-gel process or Al₂O₃ and TiO₂ Hombifine N led to significantly lower photoactivity of the textiles.

Self-degradation of the functionalized textiles under long-term UV irradiation was observed, and H₂O, CO and CO₂ were determined to be the gaseous degradation products by IR spectroscopy. One of the most active prepared materials displayed a decrease in tensile strength of 80% after UV irradiation for a month.

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1. Introduction

Heterogeneous photocatalytic oxidation (PCO) is regarded as an efficient method to decompose traces of organic pollutants [1]. Titanium dioxide has been a major focus in this area of research during the last decades due to its attractive characteristics such as low cost, chemical stability and high photoactivity. Many types of organic compounds can be decomposed efficiently both in air

and in water by TiO₂-mediated photocatalytic oxidation [2]. Highly photocatalytically active TiO₂ is typically manufactured as a powder. Titanium dioxide P25 from Evonik (Degussa), Germany, has been used as a reference sample in many investigations. Therefore, it is necessary to fix TiO₂ on certain types of support (e.g., porous ceramics, glass beads, organic porous materials, etc.) for practical use in filters. The development of good porous materials for TiO₂ deposition remains a problem.

Currently, the production of photoactive textiles incorporated with photocatalyst particles is of great interest. Much research devoted to the preparation and investigation of such materials has

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been reported in recent years [3–5]. Cotton [6], polyester [7,8], cotton/polyester [9], wool [10,11], nylon [12] and carbon-containing [13] textiles and fibers have been used for deposition of TiO₂ nanoparticles. Several methods to prepare photoactive TiO₂-containing textiles, such as spray [14,15] and dip-coating techniques, have been reported. TiO₂ sols prepared using titanium organic precursors [10] or suspensions of commercially available TiO₂ powder (e.g., P25) [16] were used for the impregnation of textiles in the dip-coating method. Other researchers [17] have applied a treatment under solvothermal conditions to enhance the crystallinity of the TiO₂ formed from an organic titanium precursor by a sol-gel process. SiO₂ has often been selected as a binder to protect the textile from the high oxidation potential of irradiated TiO₂ nanoparticles [3].

The photoactivity of modified textiles was investigated in the decontamination of organic dyes [8,18,19], discoloration of wine or coffee stains [10,20] and degradation of gaseous pollutants [12,16,21,22]. Antibacterial activity of these modified textiles was also observed [5,23,24]. The analysis of the oxidation products formed during the degradation of organic compounds and the investigation of their stability under long-term UV irradiation has not received sufficient attention.

The goal of this work is to investigate the effect of the preparation method of textiles with an incorporated photocatalyst on their photoactivity and stability. The photocatalytic activity of the prepared materials was tested in an acetone vapor oxidation in a flow-circulating reactor, and the CO₂ formation rate was used to compare their activity. The investigation of the self-degradation of the materials under long-term UV irradiation was a major focus.

2. Materials and methods

2.1. Materials

Percalé (P, cotton), flannel (F, cotton), a cotton textile (C, cotton) and cotton/polyester blends (CP1, 35% cotton and 65% polyester; CP2, 50% cotton and 50% polyester; CP3, 60% cotton and 40% polyester) were used for the photocatalyst immobilization as purchased. Both cotton textiles and cotton/polyester blends were chosen because of their different behaviors in the binder and TiO₂ deposition and different stabilities under UV irradiation. Additionally, the chosen materials had different surface porosities and, as a consequence, different resistances against air flow. This last parameter is important for their use in commercial air purifiers. All of the textiles were washed out thoroughly with distilled water before use. A detailed description of all of the materials is presented in the Supporting information (SI) section (table 1).

SiO₂ and Al₂O₃ were applied as the binders. These materials were used to protect the textiles from degradation under UV light and to adsorb the additional organic admixtures from the air. Boehmite, which has a crystallite size of 3.1–3.4 nm, was used as the Al₂O₃ source. Unless otherwise stated in the text, commercially available SiO₂ water sol (Kremnesol KZ-L, specification TU 6-00-0209604-019-89, SiO₂ particles size 6.0–10.5 nm, pH 9.5–10.8, Russia) with a standard concentration of 330–340 g/l was used in the SiO₂ deposition. To obtain the desirable SiO₂ water sol concentration, a standard concentration of SiO₂ sol was diluted with distilled water. In some cases, SiO₂ was prepared by the sol-gel process using tetraethyl orthosilicate (TEOS), isopropanol, distilled water and 0.1 M HCl. All the chemicals used were of high grade of purity.

Commercially available TiO₂ Hombifine N (Sachtleben Chemie GmbH) was chosen as a photocatalyst due to its high photoactivity in gas-phase oxidation [25,26] and high surface area ($S_{\text{BET}} \sim 350 \text{ m}^2/\text{g}$).

2.2. Preparation of functionalized textiles

The functionalized materials were prepared using the impregnation of different structured textiles with suspensions of the binder and the photocatalyst. A brief description of the preparation procedures is presented in Fig. 1. The synthesis of the functionalized textiles was performed on a “large scale” (up to 10 m² of each sample) on the processing line in the Kazan Chemical Scientific and Research Institute.

The composition of the impregnation solution (the concentrations of the binder and TiO₂ and pH) and the sequence of the impregnations were parameters that could be adjusted during the preparation. The impregnations with the binder and TiO₂ were performed both subsequently (the first bath with only the SiO₂ colloidal solution followed by the second bath with the TiO₂ suspension) and simultaneously (one bath with Al₂O₃ or SiO₂ and the TiO₂ suspension).

As a result, a series of 15 samples was prepared. Materials were referred to as “sample N” where N is a number in the range from 1 to 15. The TiO₂ Hombifine N was marked as **sample 0**.

Samples 1 and 2 were prepared by the “1 bath” procedure with a water suspension of 3% Al₂O₃ and 5% TiO₂ (pH = 4.4). **Samples 3–6** were prepared by the “2 bath” procedure with 10% SiO₂ in the first bath (pH = 10.8) and 6% TiO₂ in the second bath (pH = 0.3). **Samples 7–9** were prepared by the “1 bath” procedure with 18% SiO₂ and 15% TiO₂ (pH = 5.2). **Samples 10–12** were prepared by the “1 bath” procedure with a water-alcohol suspension of 9.5% SiO₂ prepared from TEOS and 8.5% TiO₂ (pH = 3.3). **Samples 13–15** were prepared by the “2 bath” procedure with 10% SiO₂ in the first bath (pH = 10.8) and 2% TiO₂ in the second bath (pH = 2.2). The contents mentioned above are weight percentages of the compound in the suspension.

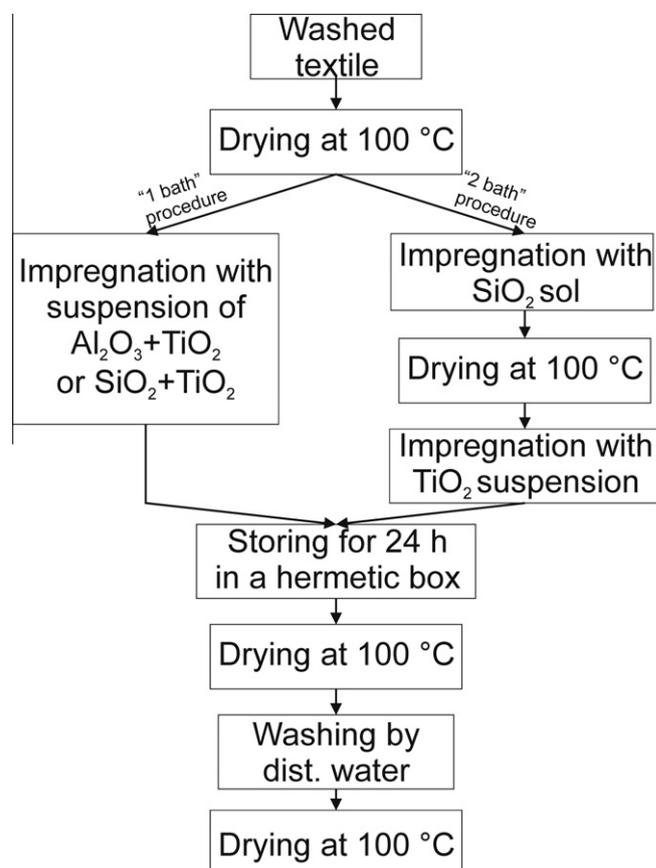


Fig. 1. Brief description of the preparation procedures.

In the “2 bath” method, the pH of the first bath was 10.8, which corresponded to the pH of commercially available SiO₂ water sol. The pH of the second bath was either 0.3 or 2.2 and was adjusted by H₂SO₄. A lower pH value (**samples 3–6**) resulted in better deposition of the TiO₂ nanoparticles and higher activity [27], but the textile degradation was also high. A higher pH value (**samples 13–15**) resulted in lower hydrolysis of the textiles, but their photocatalytic activity was also lower, as demonstrated in the Section 3.2. In the “1 bath” procedure, the pH value was chosen to obtain the most stable impregnating suspension.

2.3. Characterization of materials

Atomic absorption analysis with an Optima 4300 DV spectrometer was used to determine the contents of Al, Si and Ti in the synthesized materials. The contents of Al₂O₃, SiO₂ and TiO₂ were recalculated on the basis of these results. The morphology of the samples was studied by scanning electron microscopy (SEM) using a LEO-430 spectrometer (Carl Zeiss). Before scanning, the samples were coated with a thin layer of Cu by thermal evaporation in a vacuum.

2.4. Kinetic measurements

The photocatalytic activity of the prepared materials was tested in the oxidation of acetone vapor in a flow-circulation reactor under steady-state conditions. A detailed description of the reactor design is presented in our previous work [28]. The irradiated area of the textile sample in the photoreactor was 7 cm². Irradiation was performed using a Philips PL-S 9 W UV-A lamp ($\lambda_{\text{max}} \sim 370$ nm, sample irradiance ~ 2.1 mW/cm²). The emission spectrum of the light source used is presented in the SI section (Fig. 2). The other operational parameters were the reactor temperature, 40 °C; relative humidity (RH), 30–35%; inlet acetone concentration, 16–25 $\mu\text{mol/l}$; and volumetric flow rate (U), 30 cm³/min.

The rate of CO₂ formation during the oxidation of acetone vapor was used to compare the photocatalytic activities of the synthesized textile materials. The CO₂ and acetone concentrations were

measured using a gas cell installed in the cell compartment of a Nicolet 380 (Thermo) FTIR spectrometer. The measurements were performed in a pulse regime, i.e., the inlet acetone concentration was constant, but a special valve switched the FTIR gas cell between the inlet and outlet gas mixtures of the flow-circulation reactor.

The photocatalytic activity of every sample was measured for at least 12 h. First, the sample was irradiated in the reactor for 6–7 h without acetone vapor, and the CO₂ concentration was measured in the inlet and outlet air streams. For example, the CO₂ and acetone concentration profiles during the kinetic experiment in the flow-circulating reactor for **sample 8** are presented in Fig. 2. In this case, a small rate of CO₂ formation (approximately 0.03 $\mu\text{mol/min}$) was observed without acetone vapor, and this value constantly decreased during the illumination. The cause of CO₂ formation is the oxidation of some organic compounds adsorbed on the surface of the fibers and the photodestruction of the polymeric structure of the textile material. Following irradiation, all the samples were snow-white in color.

Then, a constant acetone vapor concentration was established in the inlet air stream and new CO₂ concentrations were measured periodically in the inlet and outlet streams until a stable difference in CO₂ concentrations was achieved. A difference in the rate of CO₂ formation with and without acetone was used to measure the photocatalytic activity of the textile material.

The rate of CO₂ formation was calculated according to the following formula: $W_{\text{CO}_2} = \Delta C_{\text{CO}_2} \cdot U$, where ΔC_{CO_2} is the difference in CO₂ concentrations in the outlet and inlet air streams of the reactor and U is the volumetric flow rate.

As a reference experiment, commercially available TiO₂ (Hombifine N) was deposited on a glass plate with an area of 7 cm² from the water suspension with subsequent drying at 110 °C [29]. The amount of deposited TiO₂ was ~ 1 mg/cm².

A static reactor 0.3 L in volume installed in the cell compartment of a Nicolet 380 FTIR spectrometer was used for the analysis of the gaseous products formed from self-degradation of the functionalized textiles under UV irradiation. For this purpose, a piece of sample with an area of 7 cm² was placed in the reactor

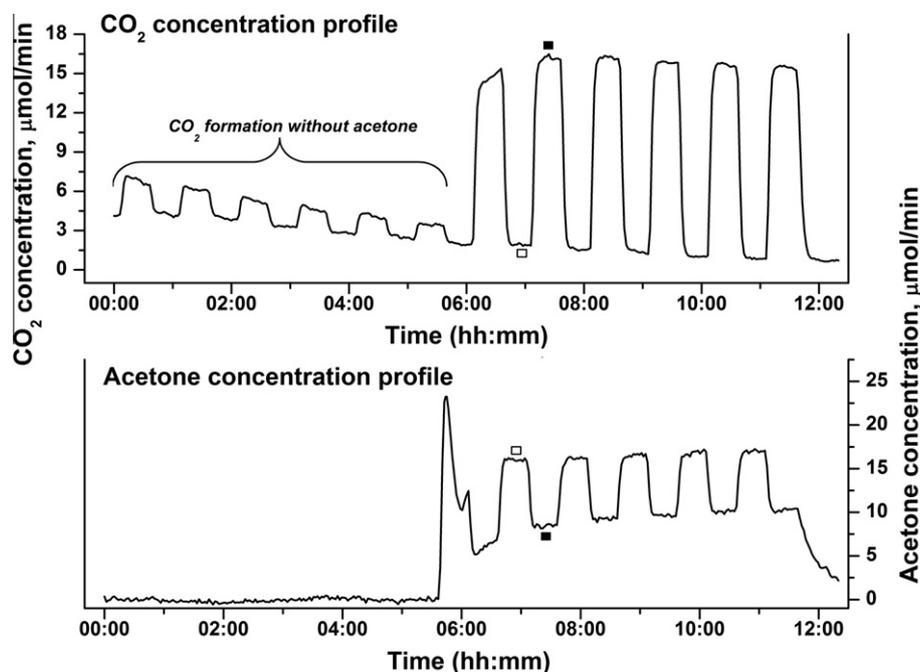


Fig. 2. The CO₂ and acetone concentration profiles during the kinetic experiment for **sample 8**. □ marks the inlet concentration of CO₂ or acetone, ■ marks the outlet concentration of CO₂ or acetone.

Table 1
Characteristics of the synthesized materials.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Procedure	1 bath		2 bath				1 bath			1 bath			2 bath		
Textile used	P	CP1	P	F	CP1	CP2	P	F	CP1	P	F	CP1	F	C	CP3
Al ₂ O ₃ content, wt.%	4.5	7.1													
SiO ₂ content, wt.%			18.2	13.9	7.5	8.8	0.4	8.0	0.8	7.8	11.4	6.6	14.0	6.3	10.4
TiO ₂ content, wt.%	1.0	1.7	1.9	5.3	3.6	3.3	2.0	10.3	4.0	4.6	7.7	3.9	3.6	1.7	0.8

and irradiated for 45–65 h with a highly powerful UV diode purchased from Nichia Co. (Japan). The UV diode provided UV-A light with $\lambda_{\text{max}} \sim 373$ nm, and the sample irradiance was 3.5 mW/cm². The emission spectrum of the UV diode is presented in the SI section (Fig. 3). To analyze the degradation products, IR spectra of the gas phase in a static reactor were taken periodically.

2.5. Measurements of tensile strength

A special test bench was manufactured for long-term irradiation of the materials. It was equipped with ten Philips Cleo Performance 80 W UV lamps and subjected to UV irradiation of at least 3.6 mW/cm² intensity. UVA light in range 320–400 nm constituted the main part of the emission spectra in this case, as well as in the cases of kinetic and self-degradation experiments described above. A more detailed description of the applied test bench and light emission spectrum is presented in the SI section.

The tensile strength, the force in Newtons for rending, was determined using a “Schopper” testing device for the initial and impregnated textiles before and after UV irradiation for 7 or 30 days. The measurements were performed according to the Russian National Standard (GOST 3813-72). The degradation extent was evaluated by the comparison of the tensile strength of non-irradiated and irradiated textiles, textiles coated only with SiO₂ and textiles coated with SiO₂ and TiO₂.

3. Results and discussion

3.1. Textiles functionalization

Cotton-based textiles and cotton/polyester blends with different textures and densities were modified by the impregnation method using TiO₂ Hombifine N. Because the irradiated TiO₂ surface possesses a high oxidation potential and could destroy textile fibers, Al₂O₃ and SiO₂ were also applied to protect the textile from photodegradation.

Table 1 presents the content of deposited solids of the synthesized samples. The content of the solids of the samples depends on the composition of the textile support. For example, in **samples 3–6**, the total amount of deposited solids (SiO₂ and TiO₂) for the cotton textile-based materials (**samples 3–4**) was approximately 2 times higher than that for the materials based on cotton/polyester blends (**samples 5–6**). This difference indicates that the adhesion of TiO₂ and binder occurs better in the cotton fibers.

Among all the materials, the cotton textile flannel demonstrated the best ability to capture and hold the solid nanoparticles. We hypothesize that the flannel is best because of its double-napped texture, which is obtained by rubbing the fabric with a fine metal brush to create fine fibers from the loosely spun yarns. The TiO₂ content for the flannel samples was in the range of 3.6–10.3 wt.%. Comparing the different procedures used to prepare the materials, it could be concluded that the “2 bath” procedure provided a higher amount of SiO₂ and TiO₂ attached to the textile.

Comparing the different procedures used to prepare the materials, it could be concluded that the “2 bath” procedure provided a higher amount of SiO₂ and TiO₂ attached to the textile.

3.2. Kinetic experiments

3.2.1. Experiments in the flow reactor

The effect of the preparation method of the material on its activity was investigated in a flow-circulating reactor. The steady-state rates of CO₂ formation during acetone vapor PCO for **samples 0–15** are presented in Fig. 3. The data are grouped according to preparation methods of the samples. The CO₂ rate for the acetone oxidation over TiO₂ Hombifine N powder is also presented in Fig. 3 as a reference sample.

The photocatalytic activity of the sample depends on the method of its synthesis and type of textile support. The samples prepared with Al₂O₃ revealed much lower activity in comparison with the SiO₂ water sol-treated samples. Using SiO₂ prepared from TEOS by the sol–gel process (**samples 10–12**) also led to very low activity. It seems that the TiO₂ particles were blocked in the SiO₂ matrix formed. Considering the other samples in each series, it could be concluded that photocatalytic activity correlates with the TiO₂ content in the sample. For example, in the case of the 3rd series, the photocatalytic activity, as well as the TiO₂ content, increased in the order of **samples 7, 9, and 8**.

One important result is that the activity of some of the synthesized materials obtained from commercially available SiO₂ sol and TiO₂ suspension is comparable with the activity of TiO₂ powder. For example, the steady-state value of the formation rate of CO₂ for **samples 5, 6 and 8** was approximately 0.4 μmol/min, while this value was 0.42 μmol/min for TiO₂ Hombifine N (**sample 0**). This result means that the TiO₂ particles uniformly coated the surface of the textile fibers and that the SiO₂ nanoparticles did not block the TiO₂ surface. All of the samples demonstrated good TiO₂ powder fixation without filling the air with dust, even during intense clapping of the textile material between the hands.

3.2.2. Experiments in the static reactor

Long-term experiments in the static reactor without the acetone vapor admixture were performed to determine the identity of the products formed during self-degradation of the textile materials under UV irradiation. Analysis of the FTIR spectra of the gas phase revealed that only H₂O, CO₂ and CO were formed during self-degradation of the materials. Corresponding gas-phase IR spectrum is presented in the SI section (Fig. 5).

Kinetic curves of the CO and CO₂ accumulation are presented in Fig. 4. The preparation procedure and the type of textile used affect the CO and CO₂ formation rates.

Samples 4–6, prepared by the “2 bath” method, revealed a higher rate of CO₂ formation during the self-degradation experiments compared with **samples 8–9**, prepared by the “1 bath” method. Treatment with sulfuric acid, as was applied to **samples 4–6**, increased the acidity of the TiO₂ nanoparticle surface. The increase in acidity resulted in an increase in photocatalytic activity [27] and simultaneous enhancement of textile self-degradation due to hydrolysis. The lowest CO₂ accumulation rate was observed in **sample 8**. The CO kinetic curves for this sample, unlike for the other samples, reached a maximum (168 ppm) after ~30 h of irradiation.

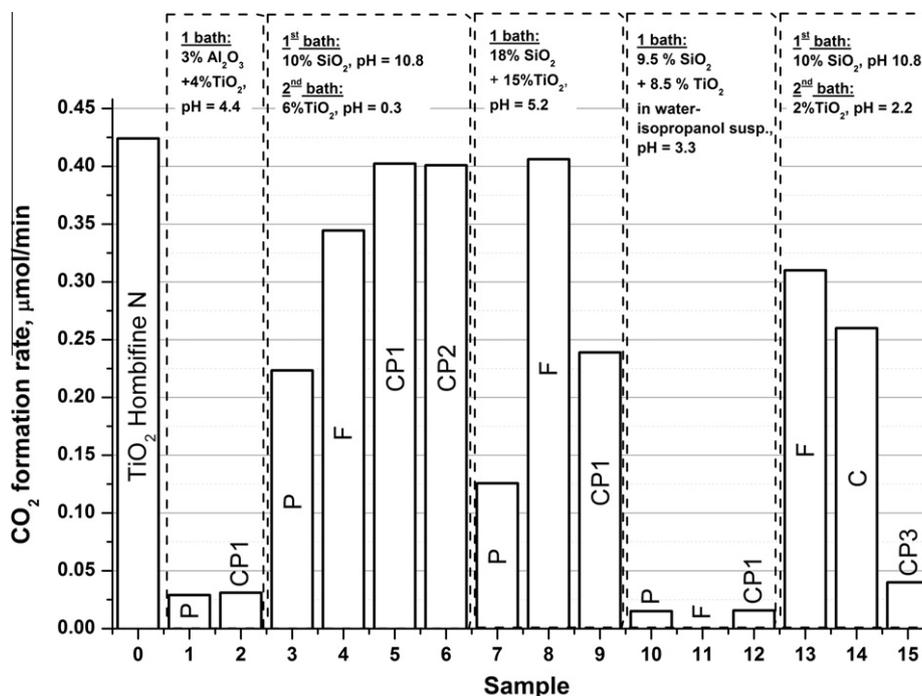


Fig. 3. Results of the kinetic experiments in a flow reactor over the synthesized textiles.

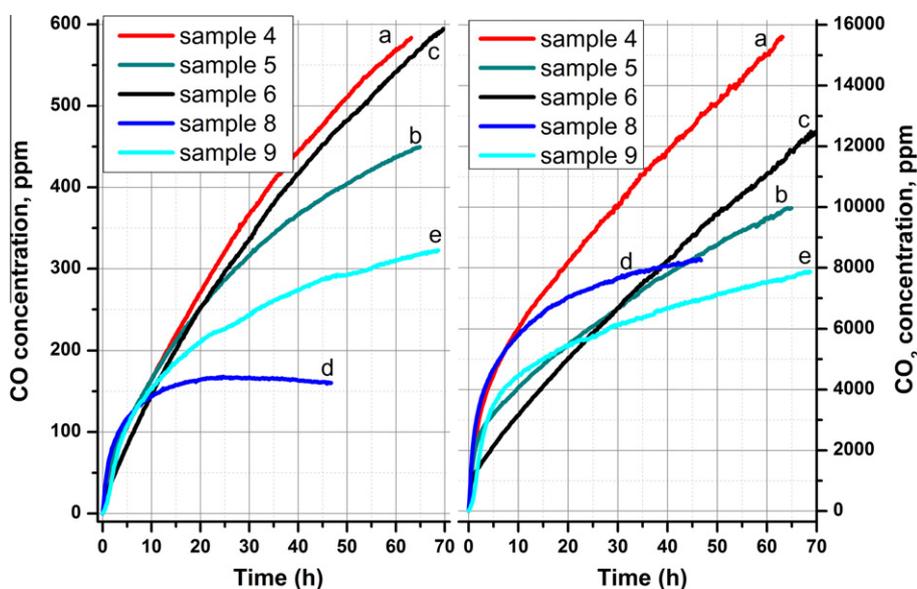


Fig. 4. CO and CO₂ kinetic curves during UV irradiation of **samples 4** (a), 5 (b), 6 (c), 8 (d) and 9 (e).

Unfortunately, the most active samples demonstrated high rates of self-degradation. The structure of the textiles in such materials was almost completely destroyed after UV irradiation for 1.5–2 months (**samples 3–6** and **7–9**). This observation indicated that the suggested methods do not provide long-term protection for the textile and that the synthesized materials can only be used for a limited time, for example, as removable photocatalytic filters in air purifiers. Such an application is very attractive due to the low cost of the functionalized textile materials.

To increase the UV stability of the textiles, the “2 bath” impregnation method was modified, i.e., a lower concentration of TiO₂ in the suspension and a higher pH value were applied to decrease self-degradation (**samples 13–15**). The activities of these samples are also presented in Fig. 3.

3.3. Tensile strength of prepared materials

Table 2 shows the data on the mechanical properties of the initial and treated textiles before and after UV irradiation for 7 or 30 days for the most stable synthesized materials. The mechanical properties were not measured for the samples with low photocatalytic activity (**samples 1–3** and **10–12**).

The non-treated, cotton/polyether blend CP3 demonstrates a very high degree of self-destruction under UV irradiation. SiO₂ deposition leads to a decrease in its degradation rate. This observation once again underlines the importance of the protective layer. Unlike the mixed polyester textile, the rates of self-degradation of the cotton textiles F and C were much lower, especially of textile C. The reason for such a difference is that the value of the flannel sur-

Table 2
Tensile strengths and extents of degradation after UV irradiation for 7 or 30 days.

Sample	Initial tensile strength (N)	Tensile strength after ^a (N)	
		7 days	30 days
F	340	330 (–2.9%)	230 (–32.4%)
F + SiO ₂ + TiO ₂ (sample 13)	350	200 (–42.9%)	70 (–80%)
C	1080	1070 (–0.9%)	1040 (–3.7%)
C + SiO ₂ + TiO ₂ (sample 14)	1200	870 (–27.5%)	150 (–87.5%)
CP3	920	720 (–21.7%)	500 (–45.7%)
CP3 + SiO ₂	760	720 (–5.3%)	610 (–19.7%)
CP3 + SiO ₂ + TiO ₂ (sample 15)	750	460 (–38.7%)	90 (–88.0%)

^a The data in round brackets are the degradation extent relative to the initial tensile strength.

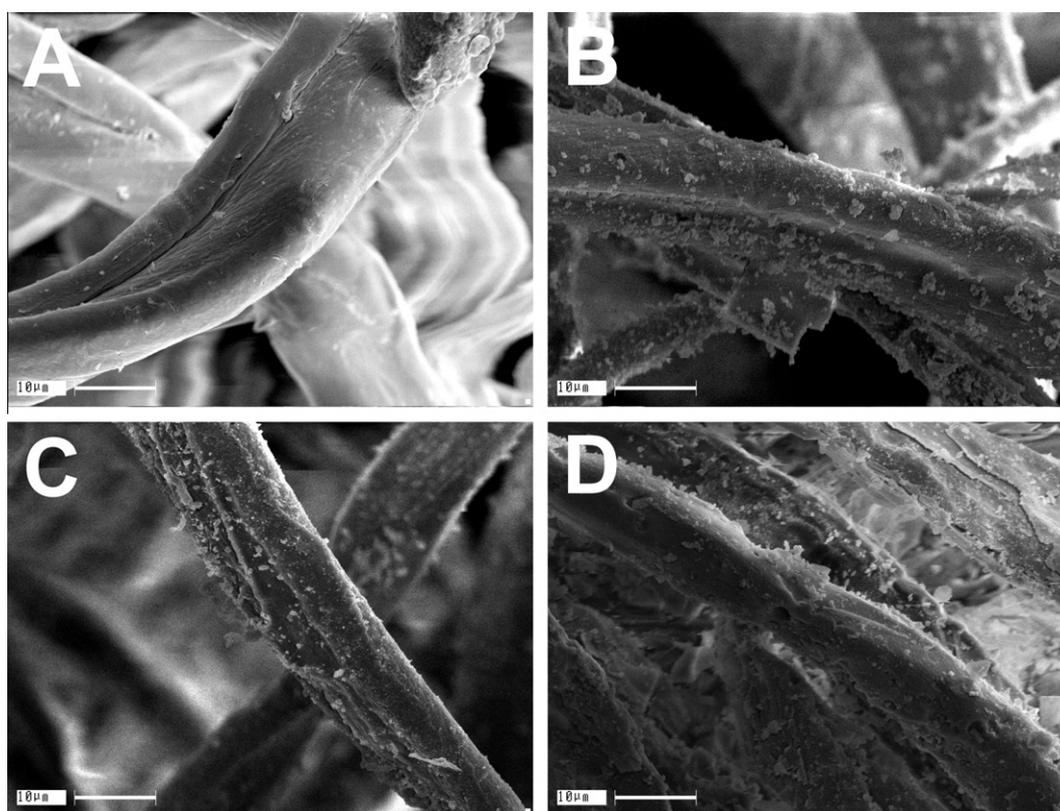


Fig. 5. SEM photographs of flannel textile (A) and **sample 13** non-irradiated (B) and irradiated for 7 days (C) and 30 days (D).

face density is higher than that of the cotton/polyester blends (table 1, SI).

The degradation of the textiles with the TiO₂ photocatalyst incorporated was higher compared with the non-modified textiles. Such modified textiles were not completely degraded even after continuous UV irradiation over one month. The decrease in tensile strength for one of the most active prepared materials after UV irradiation for a month was 80%. Further development of the “2 bath” method is required to decrease the photodegradation of the textiles. In particular, we think that using TiO₂ sol instead of commercially available TiO₂ in the second bath will provide more stable materials.

To illustrate the changes in morphology of the materials under UV irradiation, the SEM technique was employed. SEM photos of the flannel textile and flannel-based **sample 13** are presented in Fig. 5. Fig. 5A corresponds to the net material, whereas B illustrates the SiO₂ and TiO₂ deposition, which leads to the formation of agglomerates on the surface of the textile fibers with sizes less

than 3 μm. Fig. 5C and D presents SEM photographs of **sample 13** irradiated for 7 or 30 days, as indicated. The degradation of the fiber in contact with the photocatalyst particles could be easily observed, as well as the decrease in the smoothness of the fiber's surface in Fig. 5C and D.

4. Conclusion

The data presented in this work demonstrate that the functionalized textile materials possess high photocatalytic activity, but their stability under the UV irradiation should be a subject of further improvement. In particular, the following are noted:

- (1) Cotton textiles and cotton/polyester blends were impregnated with a photocatalyst (TiO₂) and a binding agent (SiO₂ or Al₂O₃) to produce photocatalytically active, functionalized textile material using either the “1 bath” or “2 bath” procedure. In the “1 bath” method, the impregnating

solution contained both TiO₂ and a binder, whereas in the “2 bath” method, impregnation with TiO₂ or binder solution was performed separately after intermediate drying of the textile.

- (2) The “2 bath” method, with commercially available SiO₂ water sol and TiO₂ Hombifine N, is a good method to prepare highly photocatalytically active textile materials with good TiO₂ fixation, which has activity that is comparable to the activity of commercially available TiO₂, but the TiO₂ content is in the range of 3–6 wt.%.
- (3) Self-degradation of the functionalized textiles was observed, and H₂O, CO and CO₂ were detected as the gaseous degradation products.
- (4) The mechanical properties of the functionalized textiles were investigated at different UV irradiation times. The decrease in the tensile strength of one of the most active prepared materials after UV irradiation for a month was 80%. This material was prepared using the flannel textile by the “2 bath” procedure with 10% SiO₂ in the first bath and 2% TiO₂ in the second bath.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2012.12.003>.

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