Digest Journal of Nanomaterials and Biostructures Vol. 8, No. 2, April - June 2013, p. 711 - 719

THE PRELIMINARY COMPARATIVE ANALYSIS OF DIFFERENT ROUTES FOR TiO_2 NANOPARTICLES SYNTHESIS AND THEIR DEPOSITION ON TEXTILES. THE METHYL-ORANGE DEGRADATION AND VX DETOXICATION STUDY

ŽELJKO SENIĆ[a*], SONJA BAUK[a], DANICA SIMIĆ[a],
MAJA VITOROVIĆ-TODOROVIĆ[a], TATJANA MARKOVIĆ[a],
ANTON RADOJKOVIĆ[a], DUŠAN RAJIĆ[b]
[a]*Military Technical Institute, Ratka Resanovića 1, 11132 Belgrade, Serbia*
[b]*Innovation Center, Faculty of Technology and Metalurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*

The world-wide use of pesticides together with the possibility of chemical warfare agent's usage in military actions, terrorist attacks or in accidents, increased the risks of chemical contamination occurrence and consequently stipulated the need for the development of new protective materials and equipment with improved properties. Because of that, today in the world, research are directed toward design of the so-called "smart textiles", which are capable of "self-decontamination", *i.e.* decomposition of toxic chemicals. Therefore, we investigated two methods for the synthesis of TiO_2 nanoparticles and their deposition on the standard military textiles (cotton/polyester 50%). Photocatalytic activity of such obtained textiles was tested by degradation of organic dye methyl orange (MeO) and chemical warfare agent O-ethyl S-(2-diisopropylamino)ethyl methylphosphonothiolate (VX), along with the evaluation of their mechanical properties, tearing strength, tensile strength and air permeability.

(Received December 3, 2012; Accepted April 26, 2013)

Keywords: nano-TiO_2, chemical warfare agents, protective materials, photocatalysis.

1. Introduction

Chemical contamination can be manifested through the use of chemical warfare agents (CWAs) in military actions, in case of accidents and also in terrorist attacks. There are also increased risks of chemical contamination by pesticides, widely used toxic chemicals. The future soldier will be expected to carry more weight, utilize more technologies and withstand more extreme environment conditions. This is why today, in modern armies, there is a need for multifunctional materials and devices. Traditional protective clothes comprise suites and over garments based on permeable materials, usually made of activated carbon liners or based on insulating rubber materials. Although this kind of protective gear affords excellent protection against different kinds of toxic chemicals (especially CWAs), it has some major drawbacks. Some of them are bulk, increased weight and, consequently, the lack of breathability, which induces heat stress in soldiers and other users [1-4]. Moreover, this kind of materials represent only a physical barrier against chemical agents: the toxic chemicals are retained within the material, so further steps of post-use decontamination procedures and adequate disposal are needed. Because of all stated above, there is an increasing need for the development of more effective protective materials for these purposes, which will not only represent a barrier against toxic chemicals, but will also

---

[*] Corresponding author: rajic.pub@gmail.com

perform a decontamination (decomposition) of toxic chemicals. These kinds of products are often called "smart textiles."

One way to achieve self-decontaminating properties of textiles is to employ nanotechnologies, especially metal oxide nanoparticles (MONPs) with photocatalytic activities. This can be achieved in two fundamentally different ways. One way is *de novo* synthesis of nanofibers by the electrospinning process [5]. Electrospinning is a cheap and relatively simple technique of producing nanofibers. It consists of introducing high voltage into a polymer solution through a small syringe, thus obtaining fibers with nanometer radius. Nanofibers of desired properties can be obtained by adding nanoparticles into a polymer solution. For example, with the addition of Al_2O_3, TiO_2 and MgO nanoparticles, fibers with self-decontaminating properties can be obtained. The other way for MONP's employment in textile industry is referred to special ways of woven textile substrates finishing. TiO_2 nanoparticles have proved to be the best for this purpose, because of the easiness of their synthesis, low cost and low toxicity. Since the discovery of TiO_2 nanoparticles, major efforts have been devoted to the development of methods for their synthesis, and numerous, different ways of preparation have been postulated [5]. However, when we take into consideration the application of TiO_2 nanoparticles on textile substrates, it should be kept in mind that the low-temperature methods for the synthesis of crystalline TiO_2 nanoparticles are highly appreciated. Textile substrates are usually dipped into a reaction mixture, without the isolation of nanoparticles; after deposition they are processed at temperatures below 100°C to further induce the crystallization and to remove a solvent. Therefore, the wet chemistry methods such as sol-gel or hydrothermal methods are used to obtain textiles with self-decontaminating properties. We decided to investigate how two different methods of sol-gel TiO_2 anatase nanoparticles preparation, along with different ways of the post treatment of TiO_2 depostited textiles will influence their photocatalytic activity. One method of synthesis is published by Uddin and coworkers [6]. It is performed under inert atmosphere, at room temperature, in isopropanol, with presence of triethylamine as the stabilizer of the solution and small amounts of water. The other method is widely used by different authors [7], and involves hydrolysis of TIP (titanium tetraisopropoxide) precursor in water, in acidic conditions with subsequent heating of the sol formed at 60 °C, during 16 hours. By employment of these two ways for TiO_2 nanoparticles preparation and different subsequent post treatment of the textiles obtained, we produced ten different textile samples, and their photocatalytic activity was tested along with the evaluation of their mechanical properties, tearing strength, tensile strength and air permeability.

2. Experimental section

2.1 Materials

Nerve agent VX of military grade was obtained from The Military Technical Institute (Belgrade, Republic of Serbia and used without further purification. All other reagents were of analytical grade, purchased from Sigma, Fluka or Aldrich.

The textile used in this study was standard military textile, cotton/polyester 50%. Textile was washed first in boiling solution of a detergent (2 g/l) for 30 min, and then it was washed with water and subsequently treated in boiling solution of sodium carbonate (2 g/l). After that, textile samples were rinsed with distilled water and left to dry at room temperature.

2.2 Synthesis of TiO_2 nanoparticles and their deposition on textile substrates

The first method for TiO_2 nanoparticles preparation was as follows: TIP (0.02mol) was added to 2-isopropanol (50 ml) under vigorous stirring and then triethylamine (0.01mol) was added as a stabilizer of the solution and stirred for 2–3 min under an inert environment achieved by argon gas flow. The second solution was then prepared separately as follows: hydrochloric acid (3.0 ml) and water (0.72 ml) were added to 2-isopropanol (50ml) and mixed well by a magnetic stirrer. The two solutions were then mixed together and stirred vigorously for 30 min under Ar gas flow. The formed TiO_2 sol was transparent, quite stable for ten days after the synthesis.

For the TiO_2 nanoparticles deposition, washed textile samples (5 x 5 cm) were immersed into the solution of nanoparticles for 1 min. Then, samples were placed in 70 °C preheated oven to dry. After that, samples were treated in oven at 95 °C for 5 min to complete the formation of TiO_2 nanoparticles. The sample, treated in this way is designated as 'sample **1a**'. The textiles designated as 'sample **1b**' were treated in the same way as sample **1a**, but they are, after the heating in oven, treated in distilled boiling water for 3 h, in order to remove unattached nanoparticles.

The second method of TiO_2 nanoparticles preparation was done as follows: In the mixture of triple distilled or Millipore water (100 ml), nitric acid (1 ml) and acetic acid (10 ml), TIP (0.04 mol) was added dropwise under room temperature and vigorous stirring. Subsequently, the reaction mixture was kept at 60-70 °C during 16 hours. After cooling to room temperature, the textile samples (5 x 5 cm) were immersed in the prepared solution of TiO_2 nanoparticles for 1 minute, and after that, left to dry in oven at 70 °C. Sample treated in this way was designated as 'sample **2a**'. The textiles designated as 'sample **2b**' were treated in the same way as sample **2a**, but they are, after the drying in oven, treated in distilled boiling water for 3 h, in order to remove unattached nanoparticles.

Next, we varied the amounts of TIP employed in reaction mixtures and try to heat the reaction mixture from the first synthesis. So the samples designated as samples **3a** and **3b** were treated with the sol obtained the same way as in the first synthesis, with the exception that double amount of TIP was used (0.04 mol) to obtain the corresponding sol. Correspondingly, sample **3b** were post-treated in distilled boiling water for 3 h. Samples designated as samples **4a** and **4b** were treated with the sol obtained by the first synthetic procedure, but double amounts of TIP were used (0.04) and reaction mixture was subsequently heated at 60 °C, during four hours. Samples **4b** were post-treated in distilled boiling water for 3 h. Samples designated as samples **5a** and **5b**, were treated by the sol obtained according to the second synthetic procedure, with the exception that half of the amount of TIP was used (0.02 mol) to obtain the corresponding sol. Samples **5b** were post-treated in distilled boiling water for 3 h.

2.3 Photocatalytic activity testing

The photocatalytic activity of ten prepared TiO_2-coated textile samples was evaluated by examination of MeO photodegradation under UV light irradiation at room temperature. For each textile sample, experiment was carried out in the closed quartz glass cell filled with 2.5 ml of MeO aqueous solution (10 mg/l). Dimensions of the TiO_2 coated samples used were 1 x 2 cm. After samples were immersed in MeO solution, cells were kept in the dark for 1 h to achieve adsorption equilibrium. The cells were then exposed to UV illumination under 254/366 nm UV light at a distance of ~ 4 cm from the UV lamp (Minuvis, Desaga, Heidelberg, Germany) and thus the photocatalytic reaction was initiated.

The concentration of MeO during the photocatalytic degradation was monitored spectrophotometrically, by the intensity of its absorption peak at 465 nm wavelength. The absorbance of MeO solution was measured at different degradation times, using Perkin-Elmer spectrophotometer (Lambda 17). The percentage of the remaining MeO concentration was calculated from the following equation:

$$\mathrm{MeO}\,\% = 100 \cdot \frac{A_t}{A_0} \tag{1}$$

where A_t is the absorbance after time t under UV irradiation, and A_0 is the MeO initial absorbance before the photocatalytic degradation was initiated.

2.4 Photocatalytic decomposition of VX

One of obtained textile samples was used to study photocatalytic activity of TiO_2-coated textile material for VX degradation. Experimental setup, except for slight differences, was the same as previously described in MeO degradation study. After keeping a one-hour in the dark, closed quartz glass cell containing textile sample immersed in 2 ml of VX aqueous solution (0.1 mg/ml) was exposed to UV irradiation.

The residual VX level was monitored using a bioassay based on acetylcholinesterase (AChE) inhibition. Samples of the VX irradiated solution were taken at specified time intervals and 10^3-fold diluted in distilled water prior to bioassay. Aliquots of the diluted samples were introduced immediately into the AChE inhibition reaction, with additional 100-fold dilution in the cuvette containing potassium phosphate buffer (0.1 M, pH 7.2), AChE (0.02 U/ml) and 5,5′-dithiobis-(2-nitrobenzoic acid) (DTNB, 0.34 mM). The AChE activity measurements were performed essentially according to the method of Ellman [8]. After 15 min of incubation with the residual VX aliquot at 25 ˚C, acetylthiocholine iodide (1 mM final concentration) was added and the increase in absorbance at 412 nm was read for 2 min. Control measurements were performed in parallel, with non-irradiated VX starting solution.

2.5 Mechanical properties of the textile samples

The tearing strengths of untreated and treated textile samples were measured by M008E Digital Elmendorf tearing tester (SDL ATLAS Textile Testing Solutions), according to the EN ISO 13937-1:2000 Standard. Five samples per warp and weft direction were prepared. Consequently, the tearing strength was separately recorded for each sample and the average results were than reported. Tensile strength measurements were performed on a Tinius Olsen H1KS instrument, according to EN ISO 13934-1 Standard. The breaking strength and elongation of warp and weft yarns at fracture were tested in this work. Five samples were used in each test. AIR TRONIC 3240A, Mesdan, air permeability tester was used to obtain the air permeability values of the untreated and TiO_2 treated textile samples, according to EN ISO 9237 Standard. Textile air permeability test were performed five times at 200 Pa pressure for all the samples.

3. Results and discussion

3.1 Synthesis of TiO_2 nanoparticles

The aim of this study was to investigate how different methods of TiO_2 nanoparticles synthesis and their subsequent deposition onto textile surface, will influence the photocatalytic activity. The second method of the synthesis in this study was widely employed by different authors and on different kinds of textiles. The first method is novel, because an organic amine was used in the sol to stabilize the solution of the nanoparticles. Uddin and coworkers [6] employed this method for the deposition of TiO_2 nanoparticles on cellulose fibers. Both methods for the synthesis proved to be reproducible in our laboratories. The first sol synthesized was stable and transparent for 10 days. Second method yielded opaque solution after heating; this can indicate the formation of the nanoparticles of the larger dimensions. Subsequently the reaction mixture from the first synthetic procedure was heated at 60 °C. In this case, heating during four hours produced white precipitate, what is indicative of the formation of larger dimension nanoparticles, or their aggregation. Firstly, we intended to heat this mixture during 16 hours, as with the second synthetic procedure, but since we started to obtain white precipitate, we decided to reduce to heating interval to four hours.

3.2 Photocatalytic activity testing

Photocatalytic MeO degradation experiments were performed in order to evaluate the photocatalytic efficiency of ten different TiO_2-coated fabric samples. The results of MeO removal by tested textile samples under UV irradiation are presented in Figure 1. Obviously, in applied experimental conditions all ten samples possessed noticeable ability to decompose MeO upon UV irradiation. Numerous studies on the destruction rates of various dyes over illuminated TiO_2 indicated that photocatalytic degradation kinetics fitted the Langmuir-Hinshelwood (L-H) kinetics model [9-12], where the reaction rate is proportional to the surface coverage, θ, according to the expression:

$$r = -\mathrm{d}C/\mathrm{d}t = k_r\theta = \frac{k_r KC}{(1+KC)} \tag{2}$$

where k_r is the reaction rate constant, K is the adsorption coefficient of the reactant and C is the reactant concentration. When the MeO concentration is small, the equation can be simplified to an apparent first-order equation:

$$\ln\left(\frac{C_0}{C}\right) = k_r Kt = k_{\mathrm{app}}t \tag{3}$$

where C_0 is the initial MeO concentration (equal to the concentration at the adsorption equilibrium) and k_{app} is the apparent first-order rate constant.

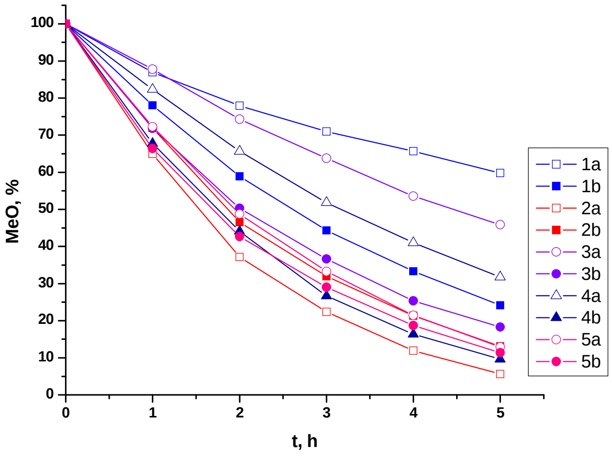

Fig. 1. Photodecomposition kinetics of MeO in aqueous solution as a function of UV irradiation time with ten different TiO$_2$-coated textile samples

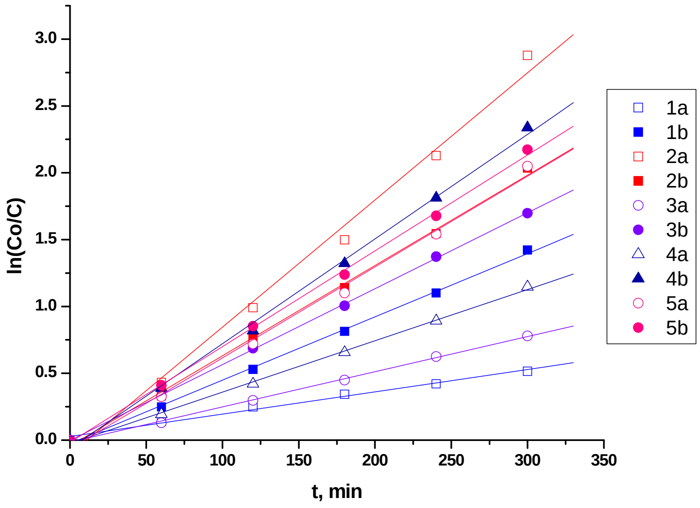

Fig. 2. First order kinetic plots for the decomposition of MeO in the presence of tested TiO$_2$-coated textile samples

The plots of ln C_0/C versus time for tested TiO_2-coated fabric samples in Figure 2 represent a straight lines. The results show that the photocatalytic decolourization of MeO dye, under the experimental conditions, follow first-order reaction kinetics. The slopes of linear regressions are equal to the apparent first-order rate constants, k_{app}. Values of the k_{app} corresponding to tested fabric samples, together with conditions applied, are shown in Table 1 and permit a direct comparison of the photocatalytic efficiency of different TiO_2-containing materials.

The textile sample designated as **1a**, obtained by the treatment with sol from the first synthetic procedure, had the lowest photocatalytic activity. On the other hand, sample **1b**, which was treated in the same way as **1a**, but subsequently treated in boiling water, exerted substantially better photocatalytic activity. This was the surprise, considering the fact that treatment in boiling water is usually conducted in order to remove TiO_2 nanoparticals which are not firmly bound to textile. Both samples (**1a** and **1b**) are treated in the oven at 95 °C, for 5 min. According to Uddin and coauthors [6] this step is necessary for the complete formation of TiO_2 from the precursor (TIP), and to induce their crystallization. Considering the photocatalytic activity results, obtained by this study, this treatment is not sufficient to obtain photocatalytically active TiO_2 nanoparticles. Subsequent treatment with the boiling water completes the formation of the TiO_2 nanoparticles and induces their crystallization, since only nanosized, crystalline TiO_2 performs photodegradation of organic substances. Samples **2a** and **2b** showed considerably higher photocatalytic activity. In this case, sample treated in the boiling water (**2b**) exerted lower activity. These samples are treated with sol obtained by direct hydrolysis of TIP in acidic water, and heated at 60 °C during 16 hours, TiO_2 nanoparticles are already formed in the resulting sol, and as such are deposited onto textile substrate. Consequently, treatment of the textile in the boiling water, only removes TiO_2 nanoparticles which are not firmly bound to the textile substrate. Samples **3a** and **3b** are obtained in the same way as samples **1a** and **1b**, except the double amount of TIP was used in the reaction mixture. In this case, the increase in the amount of TIP used to obtain the resulting sol does not improve substantially photocatalytic activity of the textile substrates.

What we further wanted to examine are the effects of the thermal treatment of reaction mixture obtained by the first synthetic procedure. We supposed that the thermal treatment at 60 °C will improve the formation of the TiO_2 nanoparticles. In this way sample **4a** and **4b** are obtained. This improved the photocatalytic activity of the samples obtained, but still, the sample treated in boiling water exerted better photocatalytic activity. Samples **5a** and **5b** are obtained in the same way as sample **2a** and **2b**, with the exception that half of the amount of TIP was used in the reaction mixture to obtain the corresponding sol. In this case, photocatalytic activity is not significantly lower than that of samples **2a** and **2b**. The differences between boiled and not boiled samples can be observed. We can conclude that the second synthetic procedure, the direct hydrolysis in acidic water is superior to the first one, in isopropanol as solvent, for the TiO_2 nanoparticles synthesis. Based on the results of MeO degradation, it is highly probable that formation of TiO_2 nanoparticles is not completed in the isopropanol as the solvent, and subsequent treatment of the samples in the boiling water contributes to the formation and crystallization of TiO_2 nanoparticles.

Table 1. Synthetic conditions and Kapp values for the tested samples

Sample	solvent	TIP rel. amount	T (°C), time (h)	Post treatment	k_{app}
1a	*i*-PrOH	0.5	r.t.	no	1.67
1b	*i*-PrOH	0.5	r.t.	yes	4.74
2a	H_2O	1	60, 16	no	9.52
2b	H_2O	1	60, 16	yes	6.76
3a	*i*-PrOH	1	r.t.	no	2.63
3b	*i*-PrOH	1	r.t.	yes	5.68
4a	*i*-PrOH	1	60, 4	no	3.84
4b	*i*-PrOH	1	60, 4	yes	7.84
5a	H_2O	0.5	60, 16	no	6.79
5b	H_2O	0.5	60, 16	yes	7.17

3.3 Photocatalytic decomposition of VX

The textile sample designated as **2a** was chosen for VX photodecomposition testing. Residual VX levels in UV-irradiated and non-irradiated (control) samples, calculated in relation to the initial VX amount in respective (irradiated or control) VX aqueous solutions, are shown in **Figure 3**. From the inspection of the resulted plot, it could be concluded that photocatalytic potency of sample **2a** toward VX degradation was obviously much lower than in MeO degradation testing. This could be a consequence of the slow VX adsorption rate, originated as a result of the low VX concentration in starting solution, but some other consideration concerning the nature of model compound and analytical technique used in VX photocatalytic degradation study should be taken into account.

Organophosphorus compounds (OPs) possess different biological activities and potencies as AChE inhibitors, depending on their structural differences. On the other hand, the photocatalytic degradation of OPs is a very complex process in which the disappearance of the starting compound is only the first step in a long sequence of transformations. That treatment may produce a variety of organic intermediates, which can be even more toxic than the parent compound, as in the case of conversion of phosphorothionates, which are characterized by the presence of the thiono moiety (P=S), to the corresponding oxons (P=O analogs), which are considerably more potent AChE inhibitors [13,14].

Among other chemical warfare agents, VX is the most difficult for destruction and, in some cases, the generated products possess toxicity which could be lower, but also equal to that of VX. Furthermore, some impurities in VX stockpiles likes O,S-diethyl methylphosphonothioate and S-2-(diisopropylamino)ethyl methylphosphonothioate are very toxic [15]. Efficient destruction method must decrease toxicity of the VX starting material, that is, it must result in degradation of VX, its toxic impurities and eventual toxic by-products.

All of the above highlight the importance of toxicity monitoring during the degradation of OPs in evaluation of process efficiency. Bioassays based on AChE inhibition provide information on the toxicity whereas they respond specifically to the presence of AChE inhibiting and therefore neurotoxic compounds, which should be of primary concern in OPs removal. It was therefore the objective of this work to evaluate the progress of toxicity during photocatalytic treatment by measuring the inhibitory properties of irradiated samples on the target enzyme AChE in order to achieve degradation efficiency of the starting compound correlated with anti-AChE behaviour of photodegraded samples. This analytical procedure implies that the amount of detected VX is, actually, cumulative concentration of all present AChE inhibiting compounds, expressed in equivalents of VX which is used for calibration. From this point of view, it is important to note that the anti-AChE behaviour of photodegraded samples persistently decreased with the irradiation time, but reached only about 70 % of the initial VX amount in non-irradiated starting solution. Although this result could be mainly attributed to the initial reaction conditions related to the low VX concentration, it is likely that better degradation efficiency could be also achieved through the optimization of the other reaction parameters.

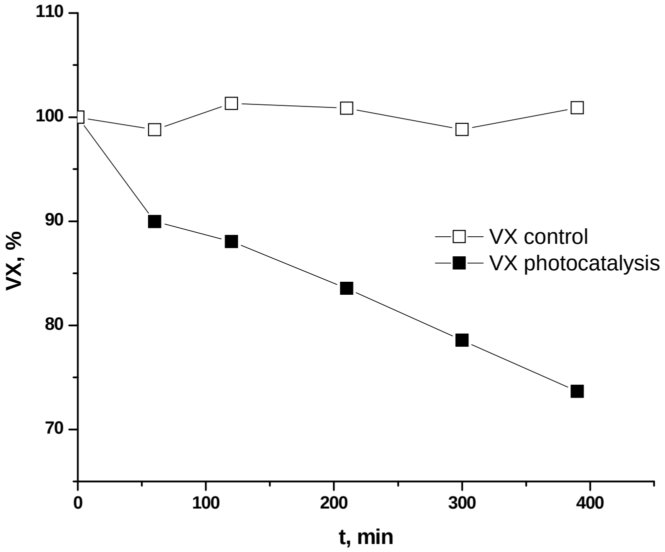

Fig. 3. VX photodecomposition in the presence of TiO_2-coated textile sample 2a as a function of UV irradiation time

3.4 Mechanical properties of the textile samples

We further examined the effects of the treatment of the textile samples on mechanical properties: tearing strength, tensile strength and elongation at fracture as well as air permeability (**Table 2)**. Treatment of the textiles considerably diminishes their mechanical properties. This effect is more pronounced with the sample **1a**, since these samples are treated at 95° C in the oven, while sample **2a** is not subjected to this kind of the treatment. Deposition of TiO_2 nanoparticles on the textile substrates does not decrease substantially the air permeability of the tested samples.

Table 2. Mechanical properties of the tested textile samples

Sample		Tearing strength [N]	Tensile strength [N]	Elongation [%]	Air permeability [L/min]
untreated	warp	49.21	1494.60	21.36	33,7
	weft	35.97	804.60	17.27	
1a	warp	27.07	890.70	28.60	30,1
	weft	19.99	715.30	24.03	
2a	warp	31.18	1015.60	24.21	30,5
	weft	22.31	734.21	21.17	

4. Conclusion

We have applied two different methods for the synthesis of TiO_2 nanoparticles and subsequent application on the textile substrates. The second method, hydrolysis of TIP in acidic water, proved to be superior over the first method, performed in isopropanol in the presence of the small amounts of water and triethylamine as the stabilizer of the obtained sol. Textile samples, treated with sol obtained from the second method, showed far better photocatalytic properties then samples treated with sol obtained by the first synthetic procedure. We believe that is highly probable that in the first synthesis, the formation of TiO_2 nanocrystals is not completed, nor is it completed by treatment of the textile samples at 95 ºC. Probably subsequent treatment in boiling water contributes to the final formation of the TiO_2 nanocrystals and their attachment on to textile surface. This could be the main reason of lower photocatalytic activity of the sample **1**, **3** and **4**. We have also tested textile sample **2a** for VX photodecomposition testing. Detection of VX by enzymatic AChE method, allowed us to monitor residual toxicity of the solution. Photocatalytic potency of sample **2a** toward VX degradation was much lower than in MeO degradation testing. Although this result could be mainly attributed to the initial reaction conditions related to the low VX concentration, it is likely that better degradation efficiency could be also achieved through the optimization of the other reaction parameters.

Acknowledgements

Ministry of Education and Science of the Republic of Serbia support this work, Grant No TR34034 (2011-2014).

References

[1] Ž. Senić, M. Jevremović, R. Karkalić, Proceedings, 2nd Scientific expert conference on defensive technologies, , **1**(2), IX-25 (2007).
[2] R. Karkalić, Ž. Senić, P. Proceedings, 2nd Scientific expert conference on defensive technologies, , **1**(2), IX-28. (2007)
[3] R. Karkalić, S. Radaković, Ž. Senić, N. Lazarević, D. Jovanović, Proceedings, 3rd Scientific expert conference on defensive technologies 2009, Belgrade, 2009.
[4] M. Vitorović-Todorović, Novi glasnik, No 2, 2007.
[5] X. Chen, S. S. Mao, Chem. Rev., **107**, 2891, (2007).
[6] M. J. Uddin, F. Cesano, F. Bonino, S. Bordiga, G. Spoto, D. Scarano, A. Zecchina, J. Photochem. Photobiol. Chem. A, **189**, 286 (2007).
[7] K. Qi, X. Chen, Y. Liu, J. H. Xin, C.L. Mak, W.A. Daoud, J. Mater. Chem., **17**, 3504 (2007).
[8] G.L. Ellman, D.K. Courtney, V.J. Andres, and R.M. Featherstone, Biochem. Pharmacol. **7**, 88 (1961).
[9] N. Guettaï, H. Ait Amar, Desalination, **185**, 439 (2005).
[10] J. M. Herrmann, Catal. Today, **24**, 157 (1995).
[11] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J. M. Herrmann, Applied Catalysis B: Environmental, **39**, 75 (2002).
[12] R. W. Matthews, J. Catalysis, **111**, 264 (1988).
[13] D. Krstić, M. Čolović, M.B. Kralj, P. Trebše, K. Krinulović, and V. Vasić, Russian Journal of Physical Chemistry A, **82**, 663 (2008).
[14] M. Bavcon Kralj, P. Trebše, M. Franko, Trends in Analytical Chemistry, **26**, (2007).
[15] Alexandre V. Vorontsov, Yi-Chuan Chen, Panagiotis G. Smirniotis, Journal of Hazardous Materials **B113**, 89 (2004).