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THE DESIGN AND PREPARATION OF CERIUM-DIOXIDE AND ZIRCONIUM(IV)HYDROXIDE-INCORPORATED NANOFIBERS FOR THE DEGRADATION OF CHEMICAL WARFARE AGENTS

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Abstract: *Specifically designed nanofibers enriched with chemically active nanoparticles, capable of destruction of chemical warfare agents (CWA's) and other toxic chemicals are highly desirable for the incorporation in personal protective equipment and decontamination items. In this work, we prepared six types of nanofibrous materials, based on the two types of polymers, polyvinylchloride (PVC) and polyvinylbutyral (PVB). As carriers of active chemistry, nanoparticles of cerium-dioxide (CeO_2) and zirconium(IV)hydroxide ($Zr(OH)_4$) were used. The morphology of the samples obtained and their qualitative chemical composition was investigated by scanning electron microscopy (SEM). The degradation ability of the nanofibrous mats was firstly investigated in an aqueous environment, over wide range of buffered pH conditions, using spectrophotometric method and paraoxon-ethyl as a model compound. A rather slow, but significant degradation of paraoxon-ethyl was observed on nanofibers which contained CeO_2 nanoparticles in neutral conditions. The sulphur mustard (HD) adsorption was investigated in non-aqueous environment using GC-MS method. The samples made of PVC exerted strong adsorption of HD with almost six fold reduction in HD concentration but without any degradation of the test compound. In conclusion, nanofibers obtained showed strong adsorption ability in non-polar solvents, but further modification of CeO_2 and $Zr(OH)_4$ nanoparticles are necessary to enhance their CWA degradation ability.*

Keywords: *protective materials, nanofibers, nanoparticles, degradation, chemical warfare agents.*

1. INTRODUCTION

Engineered materials capable of capture and removal of chemical warfare agents (CWA), toxic industrial chemicals (TICs) and biological agents (bacteria, fungi and viruses) are highly desirable for protective textile applications. The very recent events regarding the highest air pollution in Europe in the past ten years and unprecedented Covid-19 pandemics, more than ever increased the need for the enhancement and/or development and implementation of the new types of the efficient protective materials which can be incorporated in the protective overgarments and masks that serve to maintain the exposure to these agents as low as possible. Therefore, one of the main objectives of our current research activities are design of the lightweight protective composite fabrics, based on the nano-scaled supramolecular entities (particles and fibers) which will meet the following performance requirements:

1. Lightweight and breathability – the resulting material should maintain or increase the overall comfort comparing to materials which are used in the current protective overgarments and masks;
2. Incorporation of active chemistry – the material should incorporate the possibility not only to retain CBW agents but also to destruct (decontaminate and disinfect) the agents in efficient manner and on the reasonable time-scale. This will provide additional protection for the users, reduce the possibility of the cross-contamination and resolve the problems of the secondary waste storage and post-use decontamination and disinfection procedures.
3. Reusability and durability – the resulting nano-engineered material should enable multiple usage and should possess optimal physical and mechanical properties to ensure its durability.

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4. The material should be eco-friendly *i.e.* biodegradable and/or recyclable.

Several research groups described nanofibers made of different kinds of polymers decorated with chemicaly active nanoparticles including titanium-dioxide (TiO_2), cerium-dioxide (CeO_2) and zirconium(IV)-hydroxide ($Zr(OH)_4$) [1-4]. In this work, we prepared six types of nanofibrous materials, based on the two types of polymers, polyvinylchloride (PVC) and polyvinylbutyral (PVB). As carriers of active chemistry, nanoparticles of cerium-dioxide (CeO_2) and zirconium(IV)-hydroxide ($Zr(OH)_4$) were used. The morphology of the samples obtained and their qualitative chemical composition was investigated by scanning electron microscopy (SEM). The degradation ability of the nanofibrous mats was firstly investigated in an aqueous environment, over wide range of buffered pH conditions, using spectrophotometric method and paraoxon-ethyl as model compounds. The sulphur mustard (HD) degradation was investigated in non-aqueous environment using GC-MS methods.

2. MATERIALS AND METHODS

All chemicals were purchased from Sigma Aldrich or Merck, and were used as received.

2.1. Electrospinning

Electrospinning was performed on Linari Starter Kit apparatus, with stationary collector. The 5 mL syringe was used with 0.8 mm needle diameter. The distance between needle tip and collector plate was set to 15 cm, and the feed rate of the syringe was set to 1 mL/h, in all experiments. The voltage applied between needle tip and collector plate was 25 kV.

To obtain PVC nanofibers without nanoparticles (sample 1, **S1**), the 10% PVC solution in dimethylformamide (DMF) /tetrahydrofurane (THF) 3:2 mixture was used. Briefly, 1.5 g of PVC was dissolved in 8.58 mL of DMF and 6.08 mL of THF. The solution was left to stirr over night, aproximately for 12 h, using magnetic stirrer. The 3 mL of the solution were transferred into syringe. The ambient conditions during electrospinning were 21,1 ºC and relative humidity of 44%.

To obtain the PVC nanofibers with CeO_2 nanoparticles (sample 2, **S2**) or ZrO_2 nanoparticles (sample 3, **S3**), the 10 wt% of the nanoparticles was used, calculated in regard to polymer weight. Briefly, 0.3 g of nanoparticles were suspended in 17.6 mL of DMF and 12.16 mL of THF. To de-agglomerate nanoparticles, the suspension was sonicated using Bandelin Sonopuls homogenizer, set to 30 W, and pulse regimen for 2s of ultrasound and pause for 1 s, during 30 minutes. After that, 3 g of polymer was added; the mixture was stirred for 30 minutes and sonicated for 30 minutes under the same conditions. The ambient conditions during electrospinning were 23.2 ºC and relative humidity of 46%.

To obtain PVB nanofibers without nanoparticles (sample 4, S4), the 10wt% of the polymer was used and ethanol as a solvent. Briefly, 3 g of PVB was dissolved in 34.61 mL EtOH, and mixture was stirred using magnetic stirrer for 1 hour. The ambient conditions during electrospinning were 20.2 ºC and relative humidity of 43%.

To obtain the PVB nanofibers with CeO_2 nanoparticles (sample 5, **S5**) or ZrO_2 nanoparticles (sample 6, **S6**), the 10 wt% of the nanoparticles was used, calculated in regard to polymer weight. The samples were prepared according to the same procedure as described for the S2 and S3, and ambient conditions during electrospinning were 22.0 ºC and relative humidity of 43%.

2.2. Characterisation of the nanofibers

The quality, morphology and diameter of nanofibers as well as dispersion of the nanoparticles on their surface were investigated by scanning electron microscopy using JEOL JSM-660 LV microscope. The surface of the samples was covered with layer of gold to assure conductivity. The EDS analysis was done by energy-dispersive spectrometer EDS OXFORDX-Max with Aztec software.

2.3. Degradation of paraoxone

Degradation ability of the samples was investigated in both aqueous media and organic solvent. Series of aqueous buffers were used, including: 0.1 M phosphate buffer pH=7.0, 0.1 M phosphate buffer pH=8.0, 0.1 M Tris.HCl pH 8.5, 0.05 M Glycinate buffer pH 10.5. As a model compound for monitoring the degradation reaction, paraoxon was used. The 1.5 mg/mL paraoxon stock solution was prepared by dissolution of 11.7 μL of the compound in 10 mL of the corresponding media, except for the deionized water and phosphate buffer pH 7.0, where due to low solubility of paraoxon, 2 mL of acetone and 8 mL of water of buffer were used. In all other aqueous media solubility of paraoxon was good.

To investigate degradation ability of the nanofibers toward paraoxon, in polypropylene eppendorf microcuvette around 0.05 g of nanofibers was placed and 1 mL of paraoxon stock solution was added. In specified time intervals an aliquot of 20 µL was drawn from the mixture, and 980 µL deionized water was added. The remaining concentration of paraoxon was determined by measuring absorbance of the solution at 280 nm, by using Cary UV/Vis 50 spectrophotometer.

2.4. Adsorption of the sulfur mustard on the nanofibers

HD stock solutions for the calibration of the GC-MS instrument were made by dissolution of 1 μL of HD in 2 mL of *n*-hexane in the screw-top vial. The series of final calibration standards were made directly into GC-MS vials according to the data given in the Table 1.

Table 1. Concentrations of the HD calibration standards

No.	Vstock [μL]	Vsol [μL]	Cppm	C [μg/mL]	C [μM]
1	5	995	2.5	3.175	20
2	10	990	5	6.35	40
3	12	988	6	7.62	48
4	16	984	8	10.16	64
5	20	980	10	12.7	80

Calibration standards were analyzed on Shimadzu GC-MSQP2020 instrument, and the peak area in the chromatogram and the creation of the calibration curve (peak area vs. concentration) was done in Shimadzu LabSolution software. For the quantification of HD the characteristic and the most intensive mass ion m/z 109 was used. The condition in the chromatograph and mass detector are given in the Table 2.

Table 2. GC-MS conditions

GC Conditions	
Parameter	Value
Starting column temperature	40 °C, 3 min
Temperature program	40-150°C, 10°C/min, 150-280 °C, 25°C/min, 280 °C, 10,8 min
Injector temperature	250 °C
Injection type	Grob type. Splitles t 0,75 min
Colum type	DB-5 ili RTX-5
Column dimensions	30 m x 0,25 mm ID x 0,25 μm
Carrier gas	Helium, 32 cm/sec
MS Conditions	
Parameter	Value
Temperature transfer line	280 °C
Temperature ion source	230 °C
Temperature detector	150 °C
Electron energy	70 eV
Mass range	35-500 *m/z*
Scanning rate	3,15 scan/sec
Library	NIST 05 Mass Spectral Data Base

For the monitoring absorption of HD on the nanofibers, approximately 50 mg of the nanofiber samples cut into smallest possible pieces was placed in the 5 mL screw-top vial, and 1 µL of HD and 2 mL of *n*-hexane was added. At the beginning of the experiment, and afterwards in specified time intervals 20 μL aliquots of the solution were drawn and diluted to 1 mL with acetonitrile directly into GC-MS vial and analyzed under the same conditions as standard HD solutions. The concentration of the unadsorbed HD remaining in the solution is determined from the calibration curve. If the adsorption process is very fast and intensive, so that remaining amount of HD is out of calibration range, than additional specified amount of HD is added in the solution which contain nanofibers, and adsorption is monitored accordingly.

The possible HD degradation products were determined by direct analysis of the solutions above nanofibers without any dilution, and by the silylation of the samples using BSTFA agent.

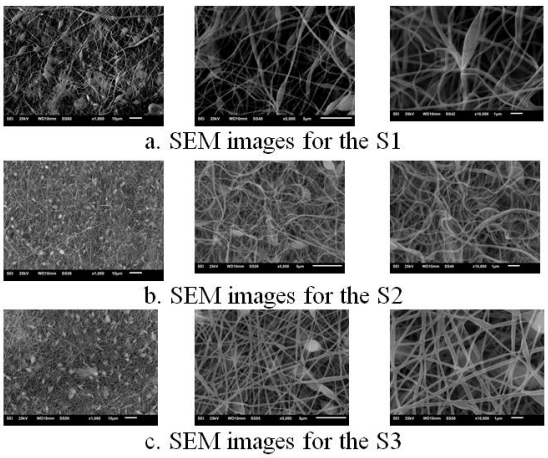
3. RESULTS AND DISCUSSION

3.1. Electrospinning and morphological characterization of nanofibers

Electrospinning of the PVC solution without (**S1**) and with nanoparticles (**S2** and **S3**) was performed at expected manner, with formation of evenly distributed nanofibers in Taylor cone, without visible twisting or breaking, indicating that optimal viscosity of the PVC solution was used as well as optimal syringe feeding rate. Therefore, very homogenous membranes or mats were obtained, given on Figure 1. Electrospinning of the PVB solutions was also satisfactory although viscosity of the solution was slightly lower comparing to PVC, which caused leaking of the solution from the syringe.

Figure 1. Nanofiber membranes obtained by electrospinning.

Morphological characterization of nanofibers was performed by scanning electron microscopy, and semi-quantitative elemental analysis was done by energy-dispersive X-ray analysis. In Figure 2, the images of the samples 1-3 obtained under 1000, 5000 and 10000x magnifications are given.



a. SEM images for the S1

b. SEM images for the S2

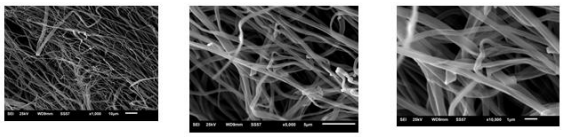
c. SEM images for the S3

Figure 2. The images of the samples 1-3 obtained under 1000, 5000 and 10000x magnifications.

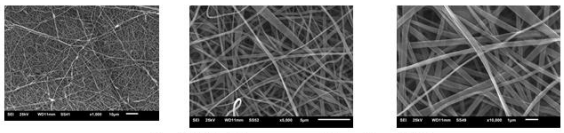
In all three samples it is visible that nanofibers had uneven diameter and morphology, and formation of bead-like structures of micrometer dimensions, indicating that viscosity of the polymer solution was low, and probably the fracture of nanofibers during electrospining occured

resulting in the formation of these bead-like structures, although we stated previously that this process was not visible during electrospinning process. Sample **S2** had the highest density of nanofibers and significantly lower fiber diameter than other two samples. In order to avoid the formation of beads and to obtain more evenly distributed nanofibers in relation to their diameter in the future studies, it is necessary to increase viscosity of the solution somehow, probably by using different solvent or polymer with higher Mw.

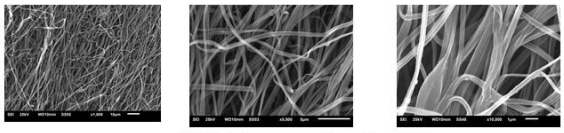
On Figure 3, the images of the samples 4-6 obtained under 1000, 5000 and 10000x magnifications are given.



a. SEM images for the S4



b. SEM images for the S5

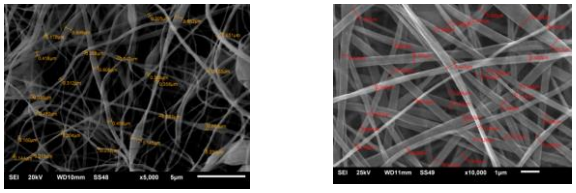


c. SEM images for the S6

Figure 3. The images of the samples 4-6 obtained under 1000, 5000 and 10000x magnifications.

The three samples **S4**-**S6**, exhibited uneven morphology and fiber diameter without beads formation, indicating an optimal viscosity of the PVB solution. This is in accordance with findings of Yener and coauthors [5] which stated that ethanol is the best solvent for PVB solutions electrospinning. Similarly with the results obtained for the samples **S1**-**S2**, it seems that presence of the CeO_2 and $Zr(OH)_4$ nanoparticles reduces average fiber diameter, and this effect is especially evident in case of CeO_2 nanoparticles.

The average fiber diameter was estimated by the measurement in as many fiber points as possible in SEM software and calculation of the average value and standard deviation (Figure 4). Sample 1 had the average fiber diameter of 0.385 ±0.197 nm and sample 5 had 0.349 ±0.108 nm.

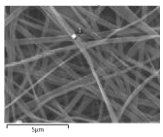
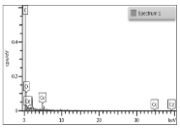
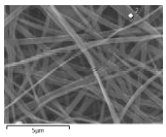
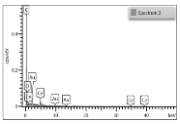
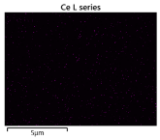
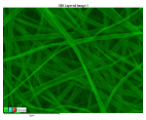
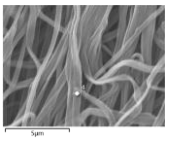
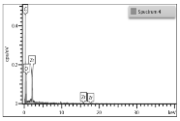
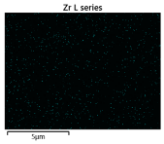
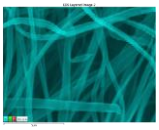


a. Sample 1 б. Sample 1

Figure 4. Estimation of the average fiber diameter for the samples 1 and 5.

Semiquantitative elemental analysis by EDS was performed for the samples 5 and 6 and the results are given in the Table 3. A rather homogeneous and even distribution of cerium or zirconium atoms was observed in both of these samples.

Table 3. EDS analysis for the samples 5 and 6.

Sample	Analysis spot	EDS spectrum	Wt % element
S5			C=70,25%, O=24,09%, Ce=5,63%
S5			C=73,82%, O=20,26%, Ce=5,92%
S5			
S6			C=66,73%, O=27,98%, Zr=5,28%
S6			

3.2. Degradation ability of the nanofibers toward paraoxone

Paraoxone is used as a model compound for the nerve agents, primarily due to its lower toxicity, but another convenience is that it gives yellow *p*-nitrophenoxy anion as hydrolysis and decomposition product, with absorption maximum at 407-412 nm, which may be determined by spectrophotometry. It is also possible to determine paraoxon concentration directly since it has absorption maximum in the UV area around 278 nm.

Various methods for the determination of the decomposition ability of various nanomaterials toward paraoxone can be found and the basic difference between these methods is the type of medium used in the experiment and relative mass ratio of the nanomaterial and the model compound. Some of the studies used aqueous media of different pH and buffer type, while other studies used organic protic solvents (methanol, ethanol and isopropanole) or nonpolar solvents such as heptane. For instance, Zhan and coworkers [6] investigated degradation of paraoxone in the presence of various CeO_2 nanoparticles in different buffers including: ammonia buffer NH_3/NH_4Cl, *N*-methylmorpholine buffer, Tris buffer, 4-(2-hydroxyethyl)-piperazine-1-ethane-sulfonic acid, and sodium-phosphate buffer. Authors did not specified the pH values of the each single buffer, but

stated that the pH range was from 6.0 to 12.0. The mass ratio of nanomaterial and analyte was 100:1. Wang and coauthors [7] investigated degradation of methyl-paraoxone in aqueous environment in 0.45 ethyl-morpholine buffer (pH 10.0) using mass ratio of nanofabers and model compound of 3:1. Another studies monitored degradation of paraoxone in polar organic solvents, and for example the study of Ramashehan et al. [8] which followed degradation of paraoxone in acetone under different starting concentrations of paraoxone (10, 25 and 50 mM), but they did not specified the mass of the nanofibers used in experiments. Another studies used heptane as a solvent.

Taking into account that nanofibers obtained aim to be used for the development of the novel protective materials with self-decontaminating properties, it would be realistic to examine materials obtained with challenge of the real chemical warfare agent in the vapor or aerosol form. However, the experimental setup of this kind would be complicated, expensive and extremely unsafe, so we decided that the degradation ability of the nanoparticles used and nanofibers obtained should be examined in aqueous environment in the following media: mixture of deionized water and acetone (vol. ratio 8:2, pH 5.5), 0.1 M phosphate buffer pH 7.0, 0.1 M phosphate buffer pH 8.0, 0.1 Tris buffer pH 8.5 and 0.05 Glycinate buffer pH 10.5. Preliminary experiments comprised deterimination of the paraoxone stability in buffers used, taking into account its fast degradation under high pH values. A very fast degradation of paraoxone was observed in almost all buffers with and without CeO_2 and $Zr(OH)_4$ nanoparticles. It was concluded that all buffers with basic pH conditions are unsuitable for monitoring of the rate of decomposition reaction, due to very fast reaction both in the presence and in the absence of the nanofibers. However, paraoxon was very stable in the mixture of acetone and deionized water in slightly acidic environment pH 5.5, so the degradation ability of the sample 2 was investigated under these conditions. A rather slow but statistically significant degradation of paraoxone was observed, as showed in Figure 4.

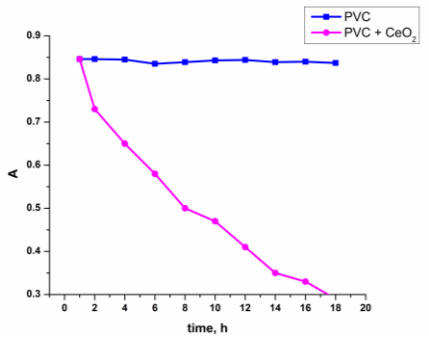


Figure 4. Degradation of paraoxone in the presene of sample 2, in of water/acetone mixture.

3.3. Adsorption of the HD on the nanofibers

Calibration of the instrument for HD was done using series of standard HD solutions and GCMSLabSolution software. The calibration curve and the corresponding HD peak are given on the Figure 5. Calibration curve had a satisfactory correlation coefficient, R^2=0.98. The peak areas of the calibration standard solutions are given in the Table 4.

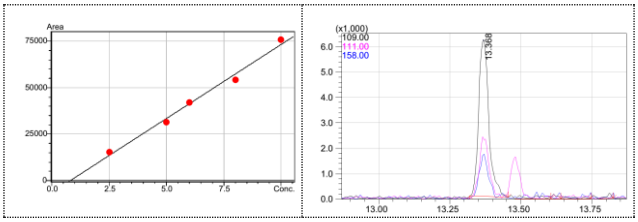


Figure 5. HD calibration curve (left) and characteristic ions in HD chromatogram.

Table 4. HD peak areas for the standard solutions

C, ppm	Peak hight
2,5	631043
5	1291002
6	1763935
8	2135618
10	3249810

In the first set of experiments adsorption of HD was determined on samples **S1**, **S2** and **S3**. In screw-top vials 64 mg of S1, 57 mg of S2 and 62 mg of S3 was placed and HD and *n*-hexane was added. In specified time intervals aliquots of the solution above nanofibers were drawn and the remaining quantity of HD was determined. The areas of HD peaks as well as its estimated concentration are given in the Table 5. It is evident that after 1h of reaction time the HD concentration was extremely low, so additional 2 μL of HD were added which gives the total HD concentration of 30 *ppm*. After that, the remaining HD concentration was determined in 1h intervals and those samples were designated as N1-N4 in the Table 5.

Table 5. HD concentration in solution treated with nanofiber samples S1-S3

Sample	Peak	C, ppm
S1 0h	186445	0.8
S1 1h	189934	0.8
S1 N1	1556584	6.0
S1 N2	1771252	5.9
S1 N3	1639314	5.9
S1 N4	1492626	5.5
S2 0h	250839	1.25
S2 1h	301276	1.00
S2 N1	1874424	7
S2 N2	1430416	5.7
S2 N3	1591757	5.5
S2 N4	1597607	5.5
S3 0h	282945	1.4

S3 1h	374752	1.2
S3 N1	1454896	5.9
S3N2	1587533	5.7
S3 N3	1400440	5.5
S3 N4	1620532	5.5

It is evident in the Table 5 that samples of nanofiber treated with the first, lower HD concentration (10 *ppm*), rapidly adsorb HD from the *n*-hexane, resulting in the final concentration which is out of the range of calibration curve. This means that almost 10-fold reduction in the HD concentration was achieved. After addition of another aliquot (2 μL) of HD, the very fast adsorption still occurred resulting in the 6-fold reduction of HD concentration, yielding the final concentration of HD around 5 ppm. It is evident that further reduction in concentration in the last two hours of monitoring did not occur which is indication that equilibrium was achieved between adsorption/desorption processes, and that probably pure physisorption without HD decomposition took place. This was confirmed by additional GC/MS analysis, since no HD degradation products were found.

4. CONCLUSION

In this work, we described preparation and morphological characterization of different nanofibers made of the two types of polymers, PVC and PVB and without or with chemicaly active nanoparticles CeO_2 and $Zr(OH)_4$. Six types of samples **S1**-**S6** were obtained and morphological characterization of nanofibers was performed by scanning electron microscopy. The samples made of PVC had more uneven morphology and showed pearl-like structure formation. Degradation ability was firstly investigated in aqueous environment, over wide range of pH values. In all basic buffers, paraoxon was unstable, so it was difficult to discern which part of paraoxone was degraded due to basic environment only and which was degraded due to catalyst present. However, paraoxon was stable in acidic environment (pH 5.5) and a rather slow, but statisticaly significant decomposition was observed in the presence of the **S1** in the mixture of water and acetone. Samples **S1**-**S3** showed very fast adsorption of HD in nonpolar organic solvent, as determined by GC-MS methods. In conslusion, the obtained nanofibers showed good adsorption capacity toward HD, but future studies should include or modify nanoparticles with enhanced degradation properties.

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