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Poly (Vinyl Alcohol) and Poly (Vinyl Alcohol) /Zinc Oxide Composite Nanofibre Webs: Quality Control with Conductometer

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Abstract. In the market a wide variety of products are find that contains/releases metal nanoparticles, therefore topical become researches on it impacts on the environment and human health. In the textile industry important step is the development of testing methodology to monitor the quantity of nanoparticles that get into the environment from nanoparticles containing textile materials. In the study analyzed the method based on the use of conductometer for textiles testing with nano-size metal oxides content to determine the persistence of nanoparticles/ions in the water after textile soaking/washing. Compared results acquired in the experiments with nanofibre webs manufactured by electrospinning from pure polyvinyl alcohol (PVA) and PVA/ZnO composite. The nanofibre webs were soaked in distilled water and obtained samples of water tested with conductometer. The results of the experiments confirm that measurements taken with the conductometer are fairly stable and repeatable; the equipment is suitable for measurements in distilled water for nanoparticles/ions detection. The measurements of the solution's specific electric conductance allows to pinpoint the nanoparticles/ions concentration, but for this purpose, must be created the database that contains the resources needed for the calculations and methodology for sample preparation.

Keywords: conductometer, nanofibre webs, poly(vinyl alcohol), textile testing, zinc oxide.

I. INTRODUCTION

Metals are the oldest of mankind known toxic substances. Lead gained four thousand years ago, but in 370 BC Hippocrates described the lead colic of mining workers. Teofrast described arsenic and mercury in 4 century BC (approximately 372-287 BC). However, many toxic properties of the metals ascertained only today. From 105 periodic system's elements about 80 are metals, but pronounced toxic characteristics have not less than 30 metals or their compounds [1].

Environmental quality may vary according to different geographical, geological, biological and other reasons. These are natural changes that can be quite significant, such as composition of water from the river during flood can be ten and even more times different from the quality indicators of the water in the summer period. Human activity can affect the quality of the environment significantly more than natural processes. Anthropogenic influences disrupt the natural cycle and impact ecosystems.

The industrial activity of the people can greatly shorten the time of metal existence in ores of the Earth crust, creating new combinations and change the distribution of metals in the nature. As such example of impact of human activity can give two hundred time increase of lead amount in the Greenland ice in the 20th century, compared with its natural levels about 800 years before our era [1]. So the quantity of metals in the environment depends on both natural processes and human industrial activity.

More and more different compounds get into the environment. Currently it is known about 10 million different chemicals, a large part of which does not exist in the nature. About 11 000 chemical compounds are produced in quantities exceeding 500 kg/year, moreover, amount of industrially produced substances are supplemented each year with 1000-3000 new substances [2].

Comparing by different types of water pollution heavy metals are the second main source of contamination after pathogenic micro-organisms [2]. Particularly dangerous pollutants of aquatic environment are lead, mercury, copper, zinc, cadmium, chromium and nickel [2].

In Latvia is carried out monitoring of diffusion of heavy metals in moss and soil. Concentration of heavy metals in mosses suggests that the background level is relatively low. The highest concentrations are found in the Riga region (copper, lead, nickel, cobalt, iron) and near Rezekne (nickel, zinc) [3].

Researching the metal content in the forest soil, detected additional sources of contamination, such as in the soil around the cement factory of Broceni found high levels of the contamination of lead, chromium, zinc and cadmium, but in the soil at

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chemical pharmaceutical companies of Olaine – high level of the copper [3].

Heavy metals are found in sediments at the bottom of the Baltic Sea. In addition, greater concentrations of the cadmium, lead, copper and zinc found in port areas of Riga, Liepaja and Ventspils [4], [5].

Main peculiarity of effect from most part of the toxic metals is that, penetrating in the environment, they enter in the human and animal food chains. Thus the heavy metals contaminate food-stuffs [6].

Any material effect on living organisms depends not only on the nature of the exposure (toxicity), but also on the quantity of the substance that gets into the body. Not rare is the situation when taking substances in small quantities, it is showing positive effect on the body, but increased quantities exposed it negative. A typical example of such substances are metal ions, which in microscopic amounts are required for normal operation of enzymes and therefore it is an important ingredient of the multivitamins, but in increased quantities entering in the nature, the same substances works acutely toxic [7].

Exposure to a living organism depends not only on the nature of the substance, but also on the body's age and gender, duration of the exposure and a relapse of the dose, access manner of the substance in the body, the transformation of the substance in the environment and in the body [2].

Mostly exposures of the substances to human are analyzed using obtained information from laboratory experiments with the animals. However, ascribing the results of such experiments to people is as safe as any other extrapolation of substance exposure assessment between species [7].

Nowadays has changed the concept of metal toxicity thresholds. Earlier metal toxicology deals mainly with acute or open metal exposure effects such as lead colic or mercury compounds affected bloody diarrhea. Listed effects of metals exposure must be known and understood in our days too, however, due to strict environmental standards, they now occur less frequently. Now required to find out more subtle chronic or long-term effects that cause-and-effect relationship is not obvious and can be subclinical. For this purpose required to obtain comprehensive information about the doses received and the quantity of metals in the tissues, deeper investigating metal metabolism, especially in tissue and cellular level, as well as found out the metal toxicity affecting factors, such as diet or protein complex formation, which increases or reduces the toxic effect [8].

Most metals effects many organs, their toxicity is determined by the metal ion effects on specific biochemical processes and/or cell membranes or organelles. To assess the effects of metal must be known the concentration in the environment and exposure time. These values have an impact on dose - the quantity of the metal existing in the cells or organs that determines the toxicological effect. More accessible tissue for dose measurement is blood, urine and hair – sometimes it is called indicator tissue [8].

Toxicological studies show that, compared with the larger size particles, the same chemical composition nanolevel particles cause different toxicological effects on organisms that are most likely related with the large surface area of nanoparticles [9]; [10]. The study [11], which analyses the copper microparticles', nanoparticles' and ionic effects on mice, found that the particle size can greatly affect the toxicity of the substance - the smaller particles, the stronger effect. In referred study used the copper microparticles (17 µm) copper nanoparticles (23.5 nm) and copper ions (0.072 nm). The results of the experiment found that the lethal dose of copper ions (LD_{50}) is 110-118 mg/kg, which belongs to class 3 (moderately toxic) at Hodge and Sterner Scale. The lethal dose of copper nanoparticles is 413 mg/kg, which also applies to class 3, but the lethal dose of copper microparticles is 5610 mg/kg - class 5 (non-toxic).

Toxicological studies of various metal oxides' (zinc oxide, titanium dioxide and aluminium oxide) nanoparticles and larger size particles in aqueous suspension show that ZnO is the most dangerous for the zebra fish embryos and larvae in the early stages of development - the development is delayed, reduced the number of surviving embryos and induced damages of tissue, whereas neither titanium dioxide nor aluminium oxide does not produce toxic effects on zebrafish embryos and larvae [12].

Zinc oxide, titanium dioxide and copper oxide impact studies [13] to freshwater invertebrates (*bacteria Vibrio fischeri, crustacean Daphnia magna and Thamnocephalus platyurus*) show that zinc oxide and copper oxide is highly toxic compounds, but the titanium dioxide is non-toxic for these freshwater invertebrates, although significantly affects the *Daphnia magna* reproduction system [14].

Verifying effects of various metal oxides (TiO_2, ZnO, Fe_3O_4, Al_2O_3 and CrO_3) nanoparticles (size 30-45 nm) on mammalian cells, found that zinc oxide causes significant mitochondrial changes in cells and necrosis. Mitochondrial function results confirm that ZnO displays higher toxicity than other metal oxide nanoparticles. Fe_3O_4, Al_2O_3 and TiO_2 does not produce any effect on the cells, while the metal oxides concentration reaches 200 µg/ml, whereas ZnO toxic effect in mammalian cells is presented already at a concentration of 50 µg/ml [15]. However, analyzing the zinc oxide toxicity to aquatic organisms [16], ascertained that it is important in the freshwater environment (pH 7.6), as the ZnO dissolves in such an environment. The study discusses the nanoparticles of zinc oxide (30 nm), uncrushed ZnO and zinc chloride effects on freshwater algae (*Pseudokirchneriella subcapitata*). As concluded in

the study, particle size don't have an effect on the toxicity of zinc oxide because the ZnO toxicity is associated not with particle size, but with its solubility in the freshwater environment.

Comparing titanium dioxide, silicon dioxide and zinc oxide toxicity on aquatic microorganisms (Bacillus subtilis, Escherichia coli), concluded that the least toxicity produced silicon dioxide, then titanium dioxide, but the largest zinc oxide. This study found that even light significantly affects bacterial development, but even in the darkness was observed inhibition of bacterial growth [17].

II. MATERIALS AND METHODS

In the article analyzed 9 samples of nanfibre webs - 3 samples of pure poly(vinyl alcohol) (PVA), 3 samples of composite fibres of PVA and zinc oxide (ZnO) nanoparticles with 1 wt.% nanoparticle composition and 3 samples of PVA/ZnO composite fibres with 3 wt.% ZnO nanoparticles content. Considering that the resulting nanowebs area density differs significantly (8-21 g/m^2), for obtaining samples important are their weight rather than size. Each nanoweb sample weight is 0.024 g.

Raw materials used in the experiment: PVA (Mowiol 28-99; purity > 99%; MW ~ 145,000; producer Sigma-Aldrich Co, LLC.); ZnO nanoparticles powder (producer Nanjing High Technology Nano material Co., Ltd.; 99.5% purity; D= 20 nm), distilled water (producer SIA "Statoil Fuel & Retail Latvia; the date of manufacture 30.09.2015.; specific electric conductance 2 µS/cm at temperature 22°C).

Spinning solution acquisition technology: 10 wt.% PVA dissolved in distilled water at 80˚C, stirred with a magnetic stirrer (BioSan MSH-300) for 2 h at a speed 1000 rpm. Before adding ZnO nanoparticles to PVA solution they were dried at 60˚C for 3 h and grinded in mortar to minimize clumping. Then ZnO nanoparticles powder gradually added to PVA solution and sonicated with ultrasonic homogenizer (Hielscher UP200H) for 4 h.

Electrospinning made using the laboratory type Elmarco needle-free (free liquid surface) electrospinning equipment Nanospider LAB 200 with rotating cylindrical electrode. Electrospinnng process parameters: electrode rotation speed 4 rpm, distance between the electrodes 150 mm, the applied spinning voltage was 60 kV. For the supporting surface used non-woven polypropylene material (PP spunbond non-woven; area density 30 g/m^2). Electrospinning was realized without support material feeding speed, with intervals of 30 seconds, in total 5 min.

Nanofibre samples after electrospinning were heat treated in drying and heating chamber (Binder EU 280) for 15 min at 140°C.

After heat treatment nanofibre webs separated from the supporting material and soaked in distilled water. For each sample used 60 ml distilled water. Nanofibre webs were stored in distilled water at temperature 22˚C for 72 h. The conductivity measurements were made with a time intervals of 24; 48 and 72 h.

Liquid samples were tested with conductometer "Extech EC100". Its electrical conductance range: 0 ÷ 1999 µS/cm; resolution 0.1 µS/cm. Temperature range: 0 ÷ 50 ° C; resolution 0.1 ° C.

III. RESULTS AND DISCUSSION

In Table 1 summarized data are direct measurement results of the experiment. Obtained data shows that, by inserting in distilled water sample without ZnO nanoparticles, the specific electric conductance does not vary. In addition, the same results show all of the parallel samples.

Table 1
Experimental results

ZnO, wt.%	Sample	Specific electric conductance, µS/cm		
		After 24h	After 48h	After 72h
0%	1.	2	2	2
	2.	2	2	2
	3.	2	2	2
	Average	2	2	2
1%	1.	8	15	24
	2.	9	16	22
	3.	8	17	25
	Average	8,3	16	23,7
3%	1.	12	20	30
	2.	12	21	28
	3.	10	18	24
	Average	11,3	19,7	27,3

Even after 72 h, during which nanofibre samples were in distilled water, water have not changed the specific electric conductance. This means that pure poly(vinyl alcohol) samples does not affect the specific electric conductance of distilled water. Taking into account previous studies [18], the results of this experiment are more appreciated. Otherwise it would be necessary to implement the adjustment of the results, subtracting from the specific electric conductance of the water measurement results of PVA/ZnO composite nanofibre indication that match the measurements of pure PVA nanofibre.

Fig. 1 demonstrates average value changes of the experiment results during time. Inserting the sample with ZnO nanoparticles composition in distilled water after 24 h already observed increase of the specific electric conductance of the water, which evenly augment also after 48 and 72 h.

In Fig. 1 visible differences between the 1 wt.% and 3 wt.% ZnO composition in nanowebs structure –

a higher specific electric conductance of distilled water has sample with 3 wt.% ZnO composition.

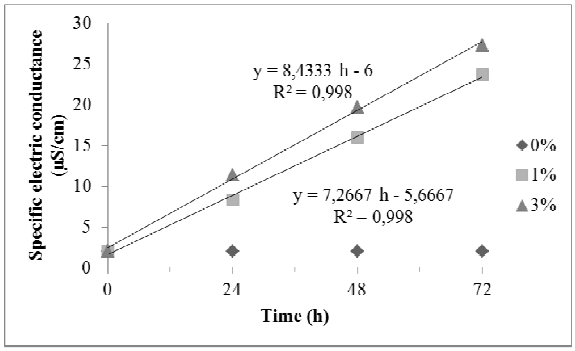

Fig. 1. Changes of the average specific electric conductance after 24, 48 and 72 h of distilled water with nanowebs placed in it.

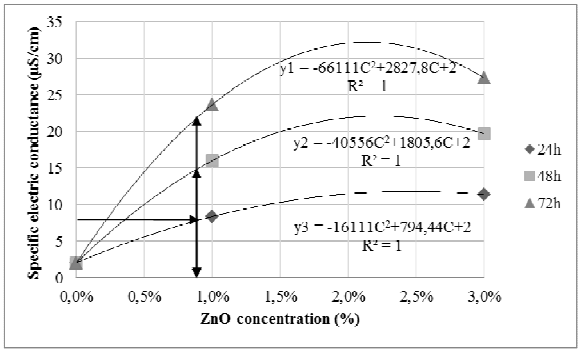

Fig. 2. Influence of the concentration on the results of the specific electric conductance (C-concentration).

The chart in Fig. 2 and incorporated equations can be used not only to determine the percentage of ZnO nanoparticles composition in the nanoweb sample presented in the water, but also to forecast the changes of the specific electric conductance of the water in the longer term. For example, by measuring the specific electric conductance after 24 h and placing a measurement result in the corresponding equations, can be find out specific electric conductance of the same water after 48 and 72 h.

Data summarized in Table 1 are direct indications of measurements, they are raw data. To obtain the specific electric conductance that describes a particular liquid, from the measurement indications must be subtracted initial specific electric conductance of the water - in this case it is 2µS/cm (Table 2). This is necessary because it is not always possible to get distilled water with the same specific electric conductance.

Statistical characteristics of the experimental results were calculated: arithmetic mean, variance, amplitude, standard deviation, average standard error and average relative standard error (Table 2). The average relative standard error with confidence level 0.95 changes from 4.1% to 7.1%, which is satisfactory. Although in this case a maximum matching of the parallel samples' results are not required, however, for a certain extent it describes the measurement stability.

Compared with the samples without ZnO nanoparticles composition having saved the initial distilled water's specific electric conductance, the nanowebs composite samples with 1wt.% and 3 wt.% ZnO nanoparticles after 24 h soaking water specific electric conductance has increased on average 6.3 and 9.3 units (Table 2). Prolonging soaking time to 48 h, the specific electric conductance of the water increases even more, up to 14 and 17.7µS/cm, but after 72 h it reaches accordingly 21.7 and 25.3 µS/cm.

Table 2
Summary of adjusted measurements and statistical data

ZnO, wt.%	Sample	Adjusted specific electric conductance, µS/cm		
		24h	48h	72h
0,0%	1.	0	0	0
0,0%	2.	0	0	0
0,0%	3.	0	0	0
Average, µS/cm		0	0	0
Difference, µS/cm		0	0	0
Relative Standarderror, %		**0%**	**0%**	**0%**
1,0%	1.	6	13	22
1,0%	2.	7	14	20
1,0%	3.	6	15	23
Average		6,3	14,0	21,7
Difference, µS/cm		1	2	3
Relative Standarderror, %		**5,3%**	**4,1%**	**4,1%**
3,0%	1.	10	18	28
3,0%	2.	10	19	26
3,0%	3.	8	16	22
Average		9,3	17,7	25,3
Difference, µS/cm		2	3	6
Relative Standarderror, %		**7,1%**	**5,0%**	**7,0%**

To determine the concentration of ZnO nanoparticles and/or ions existing in water, which become detached from the nanoweb sample, in Table2 summarized results of the specific electric conductance must be compared with measurements obtained by adding to distilled water the same size ZnO nanoparticles without nanoweb. Inserting data from Table 2 in the previously calculated equation [19] can be ascertained the percentage of nanoparticles/ions of specific size presented in the water after nanoweb sample soaking and/or washing.

IV. CONCLUSIONS

Analysis of the experimental results demonstrates that the conductometer can be applied to metal oxides

nanoparticles'/ions' concentration determination in distilled water. After soaking in water pure PVA and PVA/ZnO composite nanoweb samples concluded that the specific electric conductance of water is different – the samples without ZnO nanoparticles remain the original specific electric conductance of distilled water, while samples with 1wt.% and 3wt.% composition of ZnO nanoparticles after 24 h soaking specific electric conductance of water has increased to average 6.3 and 9.3 units. The prolonged soaking up to 48 and 72 h causes increase of the specific electric conductance of the water even more, with the exception of pure PVA nanoweb's soaking water, which specific electric conductance remains at the same level during the whole experiment. This proves that the PVA/ZnO composite samples affect the specific electric conductance of distilled water, which can be used to create a testing methodology for textile with metal oxides nanoparticles content, but for this purpose must be created the database that contains the resources needed for the calculations and methodology for sample preparation.

However creating a methodology, it would be necessary to increase the number of parallel measurements to obtain more precise results. The accuracy of the results could also improve higher resolution conductometer.

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