

TOXIC EFFECT OF NANOTEXTILES AS WASTE OF RESPIRATORS AND FACE MASKS

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INTRODUCTION

Nonwovens are formations of textile fibres, fillaments or yarns which are interconnected by techniques other than weaving, knitting, bobbin-making, plaiting and turfing. However, the production and handling of nanofibres cannot completely eliminate their release into the environment or the working environment. This can occur in four ways, namely during the manufacturing process of the nanofibres that make up the textiles, during the processing of the materials containing the nanofibres (which also results in release to the working environment and exposure of workers), during the use of the nanofibres (as the fibres are mechanically stressed and thus further released to the environment) or during the disposal of the textiles already used, when the nonwovens are discarded freely into the environment and its components, water and soil, where the undesirable effect of adsorbed pollutants trapped during use or absorbed into the layers of the nonwovens may be manifested, which may lead to a change in toxicological properties [1]. Three types of materials were selected to be tested in the tests carried out. These are personal protective equipment used for respiratory protection, which were widely used during the spread of the Covid-19 viral disease. Specifically, they are unlaminated PP-PVDF (polyvinylidene fluoride laminated on one side with a polypropylene layer), laminated PP-PVDF-PP, which is similar to the first material mentioned, but this time laminated on both sides, and the last material is a specific type of Nanovia mask (all of them are shown in Figure 1), respectively. The ecotoxicity of these three materials was tested on two different organisms - mustard seeds in a range of concentrations of aqueous leachates, following the OECD methodology, and perch leaves, also in a range of concentrations of aqueous leachates, following the standard EN ISO 20079 (2001) Water quality - Determination of toxic effects of water and wastewater constituents on perch (*Lemna minor* L.) - Perch growth inhibition test. [2] The basis of the experimental part is the production of polymer nanofibres - these can be prepared in several different ways, some of which can only be discussed in the laboratory for the time being. Others, however, have already been improved to such a level that they can be used in large-scale production - for example, electrospinning or nanospider™. Other methods include centrifugal force spinning (Force Spinning) or the Melt - Blown method, which is based on the melt blowing principle. The requirements for product properties and production speed are then a decisive factor in the production of the technology. However, the most widely-used production method is undoubtedly electrospinning, the essence of which is the use of the effect of an electrostatic field on a charged viscoelastic liquid (usually a polymer solution), whereby thin filaments of different lengths are formed when given conditions are met [3,4].

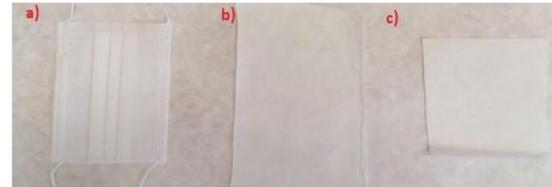


Figure 1 Photographs of materials before preparation of aqueous leachates (from the left Nanovia facemask, unlaminated PP-PVDF, laminated PP-PVDF-PP)

2. EXPERIMENTAL PART

The first test was to test *Sinapis alba* L. seeds using a concentration range of aqueous leachates of all selected materials to observe the effect of increasing concentrations on the resulting root length compared to the control. The procedure is based on the methodology of the Ministry of Environment for the determination of ecotoxicity of wastes. The basis of this test is to pipette a specified amount of solution (2.5 mL) at different concentrations (10, 20, 50, 100, 200, 500 and 1000 mL/L) and to place 20 seeds (4 rows of 5 seeds = 20 seeds) on a soaked filter paper. First, Petri dishes and filter papers are prepared, then the solution is pipetted, always 2.5 mL, (the 1st concentration is always for the blank solution) and a number of seeds (20 in this case) are sown. Finally, the petri dishes are placed in an unlit place where the temperature is constant at $(20 \pm 1)^\circ \text{C}$. After 72 hours, a root growth reading is taken and the values obtained are entered into the formula. The percentage of root inhibition can then be calculated. The second test carried out was a semichronic toxicity test on lesser perch, a monocotyledonous plant that often covers the surface of standing water [6]. The test procedure is based on the standard EN ISO 20079 (2001) Water quality - Determination of toxic effects of water and wastewater constituents on perch (*Lemna minor* L.) - Perch growth inhibition test and lasts for 7 days, during which the perch grows in a nutrient solution to which different concentrations of the substances whose ecotoxicity is to be determined are added. The result of this semi-chronic toxicity test is the effect of the substance on the growth rate, which varies based on how the number of leaves changes with different concentrations of the test substance. The concentrations of the filtrates of each material were then adjusted so that the resulting concentrations of the aqueous leachates were 200; 500 and 1000 mL/L (100 g/L), all concentrations being prepared in parallel determinations A and B. However, prior to the actual deployment of the perch, the pH of all filtrates had to be adjusted so that the pH was between 5 and 6. Once the filtrates were adjusted and prepared, four two-leaf and four three-leaf perch colonies were carefully transferred into these beakers. In total, there were therefore 20 leaves. Tweezers, a spoon and possibly a glass rod were used for the transfer. Once the perch had been moved into all the beakers, the entire tray was covered with clear food-grade foil and placed in a culture chamber for 168 hours. [5]

2.1 Documentation of the process

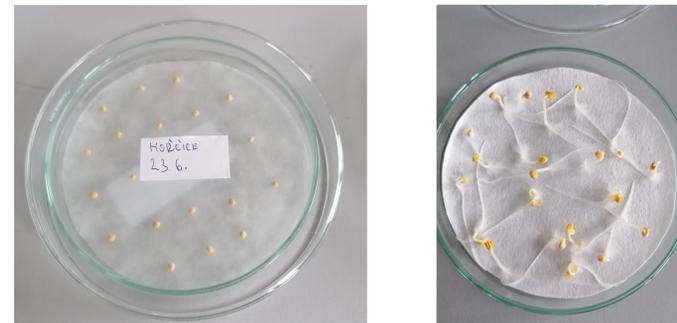


Figure 2 Seeds of *Sinapis alba* L. before the test (left) and after the test (right)



Figure 3 Perch in the beakers

Figure 4 All concentrations of parallel determinations prepared on the tray covered with food-grade foil ready to be placed in a culture chamber

3. RESULTS

Table 1 Resulting inhibition of mustard seeds for a concentration range of aqueous leachates of all materials

Leachates concentration [mL/L]	Nanovia		PP-PVDF-PP		PP-PVDF	
	IC [%]	Leachates concentration [mL/L]	IC [%]	Leachates concentration [mL/L]	IC [%]	Leachates concentration [mL/L]
10	8.48	10	22.51	10	6.92	
20	-4.56	20	8.19	20	1.91	
50	-9.96	50	13.78	50	2.89	
100	-1.62	100	3.19	100	-16.72	
200	-5.74	200	20.26	200	7.41	
500	5.74	500	23.31	500	0.15	
1000	25.55	1000	-2.01	1000	-3.09	

Table 2 Inhibition of periwinkle growth after 168 hours for all materials in parallel determination

Material	Leachates concentration [mL/L]	Number of leaves for parallel determination (A/B)	Average number of leaves	Inhibition [%]
Nanovia	0	28/34/44	35.3	0.0
	200	30/32	31.0	23.0
	500	31/34	32.5	14.6
	1000	32/36	34.0	6.8
PP-PVDF-PP	200	38/32	35.0	1.7
	500	41/40	40.5	-24.0
	1000	40/39	39.5	-19.6
PP-PVDF	0	51/51/55/51	52.0	0
	200	74/58	66.0	-24.8
	500	70/56	63.0	-19.7
1000	55/54	54.5	-4.4	

CONCLUSIONS

Based on the ecotoxicity tests performed on mustard seeds and the aquatic perch plant, it was shown that the test substances (Nanovia drape, laminated PP-PVDF and unlaminated PP-PVDF) do not meet the limit values for being toxic to the selected organisms. However, in no case can the effects of the test materials on the selected organisms be completely excluded. Testing a concentration range of aqueous leachate materials on seeds gave good results, with none of the materials tested acting as an overly large inhibitor or stimulant on mustard seeds. The maximum inhibition achieved was around 25.0 %, while the highest stimulation was 15.0 %. This was the first test on the basis of the results of which it can be stated that aqueous leachates from the materials tested are not ecotoxic, whether the leachate is dilute or maximally concentrated. The semichronic toxicity test on lesser perch was aimed at monitoring inhibition (or stimulation) of leaf growth per unit. The results were as follows - the inhibition of leaf growth of the Eurasian watermilfoil occurred essentially only in the Nanovia sample, with the highest inhibition (23 %) occurring when using a 200 mL/L aqueous leachate concentration. From this value, $IC_{20} = 276.5$ mL/L was subsequently calculated. Which means that at this concentration just 20 % of the test specimens will be inhibited (IC_{50} and IC_{80} could not be determined because such inhibition values were not achieved). The other inhibitions were then only lower (14.6 and 6.8 % for Nanovia, 1.7 % for PP-PVDF-PP). Across the other samples, there was always stimulation, with the highest stimulation achieved in the PP-PVDF sample, when it was close to -25.0 %. The summary of all the experiments performed can be made relatively simply, since in none of the cases were the threshold values reached to make it possible to label the tested materials Nanovia, laminated PP-PVDF-PP and unlaminated PP-PVDF as ecotoxic. At the same time, however, the results show that interactions between organisms and materials are there - both positive and negative. Further tests will be carried out in the future in order to specify and explain this interaction; at present, even the literature outputs do not agree on explanations in all cases.

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ACKNOWLEDGEMENTS

THE PUBLICATION WAS WRITTEN WITHIN THE STUDENT GRANT COMPETITION "RELEASE OF NANO AND MICROPLASTICS FROM NANOTEXTILES AND DETERMINATION OF THEIR EFFECT ON THE ENVIRONMENT 2" — PROJECT NUMBER SP2022/119.