Textile materials represented in disposable surgical masks pose a serious threat to the environment

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Original scientific paper**

Surgical face masks were introduced over a century ago to protect patients from infections during surgery. Initially designed to filter droplets from the mouth and nasopharynx, their use expanded to the general population during epidemic outbreaks. The COVID-19 pandemic, as the most significant modern health crisis, caused a dramatic rise in the use of personal protective equipment (PPE), particularly disposable surgical masks (DSMs). In Slovenia, DSMs were the most used face masks during the pandemic, with a notable portion (10%) improperly disposed of, leading to environmental contamination. To address these issues, a study was conducted to analyse waste DSMs and their environmental impact. A detailed disassembly and gravimetric analysis were performed, along with infrared spectroscopy of individual mask components. The materials used in DSMs raised concerns about micro/nanoplastic contamination and harmful substances released during leaching and photodegradation. Tests such as artificial weathering and the toxicity characteristic leaching procedure revealed that micro/nanoplastic particles were leached from all five mask components in water. Under natural conditions, DSMs lose up to 30% of their mass within a month, forming micro/nanoplastics through photodegradation. Improper disposal of DSMs thus poses a significant environmental risk due to the release of hazardous particles.

Key words: *disposable surgical masks; micro/nanoplastics; leaching; artificial weathering; environmental pollution*

Izvorni znanstveni rad**

Kirurške maske za lice uvedene su prije više od jednog stoljeća. Izvorno su razvijene za zadržavanje i filtriranje kapljica izbačenih iz usta i ždrijela tijekom operacije kako bi zaštitili pacijente od infekcija. Uz česte epidemije, kirurške maske prešle su u opću upotrebu. Pandemija COVID-19, najveća pandemija u moderno doba, donijela je mnoge izazove na području osobne zaštitne opreme (OZO). Količina upotrebljene OZO se dramatično povećala, posebno jednokratnih kirurških maski (DSM) koje je naširoko koristila opća populacija. Istraživanje je pokazalo da je DSM je bio daleko najčešće korištena vrsta maske za lice u Sloveniji tijekom pandemije. Većina ih je nepropisno zbrinuta, odnosno odložena u okoliš. Utvrđeno je da se u Sloveniji 10% svih korištenih maski nepropisno odlaže. Iz tog razloga je ključno točno analizirati otpad i identificirati sve opasnosti koje predstavlja. Stoga je u radu DSM rastavljena na komponente i provedena je analiza otpada. Provedena je gravimetrijska analiza reprezentativnih DSM komponenti, zajedno s detaljnom infracrvenom spektroskopijom. Zbog različitih komponenti DSM-a postoji potencijal za kontaminaciju okoliša mikro/nanoplastikom i drugim štetnim tvarima koji nastaju otpuštenjem i fotorazgradnjom DSM-a. Za analizu i procjenu fragmentacije mikro/nanoplastike primjenjeno je simulirano vremensko izlaganje te postupak ispiranja s karakteristikama toksičnosti (TCLP). Mikro/nanoplastične čestice ispirane su u vodenom mediju iz svih pet komponenti maske. Izložen prirodnim uvjetima, DSM gubi do 30% svoje mase u samo 1 mjesecu, dok mikro/nanoplastične čestice nastaju procesom fotorazgradnje. Nepravilno obrađeni DSM-ovi predstavljaju potencijalnu opasnost po okoliš zbog ispuštanja mikro/nanočestica.

Ključne riječi: jednokratne kirurške maske; mikro/nanoplastika; ispiranje; umjetno starenje; zagađenje okoliša

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1. Introduction

With the outbreak of COVID-19 and the announcement of a pandemic on March 11, 2020, according to the World Health Organisation (WHO), the global demand for medical PPE has increased significantly [1]. As Czigany and Ronkay note in their article, surgical masks provide protection and an effective way to keep the virus from circulating. They significantly reduce the number of droplets an infected person spreads in their environment. Therefore and consequently, protective masks were one of the most sought-after products in 2020 [2]. SARS-CoV-2 has led to the worldwide consumption of disposable surgical masks (DSM) to prevent human-to-human transmission of the virus. The WHO estimated that 89 million medical masks are needed each month to deal with COVID-19 [1].

At the height of the pandemic, Wuhan alone generated 240 tons of medical waste in a single month [3]. A survey in Slovenia found that in the first year of the pandemic, approximately 344 million protective masks were used, on which Slovenians spent €92.5 million of their personal money. In addition, companies and the government spent much more money to provide sufficient masks in schools, hospitals, industry, etc. [4].

As it was found [2-4] amount of disposable surgical masks (DSMs) consumed increased dramatically, and much of it was improperly disposed of, i.e., it entered the environment. For example, in Slovene, 10% of all used DSMs were disposed of improperly, which means 34,4 million protective masks in one year [4]. For this reason, it is crucial to accurately analyse the waste and identify its hazards. Face masks are made of polymeric materials that degrade over time. Macro plastics break down into smaller fragments, first into micro and later into nanoplastics. Both micro and nanoplastics were the most problematic environmental pollutants even before the pandemic [5-10]. As it was found in our previous study, all five parts of DSM are made of plastic materials: outer, filter and inner layers are made of nonwoven and melt-blown polypropylene or polyethene. Nose wires are made of polypropylene plastic or steel wire coated by polypropylene. Ear loops are made from polyamide, polyurethane or polyethylene terephthalate materials [6].

In this study, DSM was analysed, as it is the most common piece of PPE used widely by the general population. The research included artificial weathering experiments and toxicity-characteristic leaching of textile materials in DSMs to assess the potential release of micro/nanoplastic release during leaching and photodegradation.

2. Method

2.1. Gravimetric analysis

More than 5000 used DSMs of all colours and different manufacturers were collected. That amount had been quartered down to 100 DSMs. A single surgical mask had been divided into five essential components - nose wire, ear loops, outer nonwoven layer, melt blown filter layer and inner nonwoven layer and was dried to constant mass. On a sample of 100 disassembled masks, we performed a gravimetric analysis of the proportion of each component in our sample. The masks were disassembled manually. Each element had been weighted on balance Kern ALT 220-4NM with an accuracy of ±0.001 g.

2.2. Toxicity characteristic leaching procedure (TCLP) and analysis of TCLP products

The Toxicity Characteristic Leaching Procedure (TCLP) - SW-846 Test Method 1311 [11], was performed to determine the leaching of microplastic particles from the sample. A representative sample of DSM was prepared in the following way: all five parts (nose wire, ear loops and outer, filter and inner layer) had been cut on parts with a surface under 1 cm^2. Then the dry matter of the sample was determined according to the standard [12]. The first pristine analysis was done for the whole mask according to this procedure and also for the modified procedure in which distilled water was switched with artificial seawater (ASW) prepared, as written by Kester et al. [13]. Method was modified by switching distilled water with ASW to analyse potential higher leaching of particles when DSM is exposed to see waters. Then unmodified TCLP was performed for all five parts of DSM separately. 6 different samples were analysed. Each was prepared in three parallels – outer layer, filter layer, inner layer, ear loops, and nose wire. This value was used in equation 1 to determine the amount of distilled water needed to perform TCLP of 50 g of our sample. 50 g of the sample has been put in a glass jar with the correct amount of distilled water. Then the jars were put on a shaker HS-501 made by IKA Werk that rotated at 30±2 rpm for 18±2 hours.

$$m_{fluid} = \frac{20 \cdot w_{dry\ matter} \cdot m_{sample}}{100} \qquad (1)$$

Products were first filtered through a colander with a mesh diameter of 5 mm to remove larger parts. Then obtained filtrate was filtered again through polyether sulfone (PESU) filters with an effective pore size of 0.2 μm and diameter of 50 mm, from Sartorius Stedim Biotech GmbH. Microplastics retained on the filter were examined under ZEISS Axiotech 25HD

(+ pole) optical microscope, with an AxioCam MRC (D) high-resolution digital camera, where different parts were observed and measured. Dried microplastics on the filter were also weighed. Filters have been dried to constant mass at 105 °C in a dryer VS50-SC produced by Kambič d.o.o. and weighed before the filtration. After filtration, they were dried again and weighed to determine the mass of microplastics on the filter. Filters have been weighted on balance Kern ALT 220-4NM with an accuracy of ±0.001 g. Obtained microplastic particles were also analysed and measured under the optical microscope. Water obtained in TCLP before and after the filtration process had been tested for simple qualitative properties. With a turbidimeter, Velp Scientifica TB1 turbidity of samples has been measured, and with a conductometer, Metler-Toledo SevenCompact S230 conductivity of samples has been measured. Chemical oxygen demand (COD) has also been determined using tube tests by Macherey-Nagel, heating unit Macherey-Nagel Nanocolor Vario 4 and UV/VIS spectrophotometer Macherey-Nagel Nanocolor UV/VIS.

Water after filtration has also been analysed for particle size distribution (PSD) using Zetasizer Nano ZS® (Malvern Instruments, Ltd., UK) equipped with dynamic light scattering (DLS) technology. Triplicate measurements were carried out using a He-Ne laser at a wavelength of 633 nm and scattering angle of 173 ° at 25 °C and lasted 70 s.

2.3. Photodegradation caused by artificial weathering

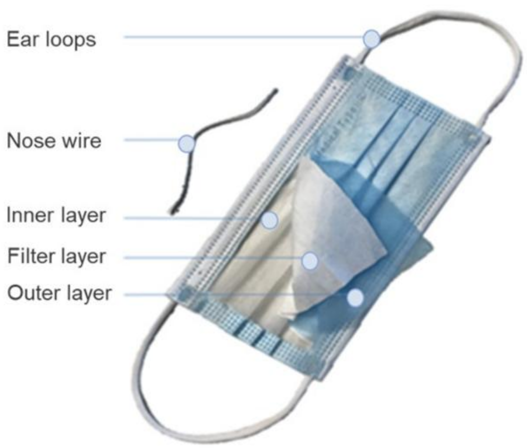
Photodegradation of the mask was performed by artificial weathering using a climate chamber - Xenotest alpha LM high energy (Atlas). It was essentially the same as the standard ISO 4892-2:2013, with minor modifications in cycle composition.

The DSM were manually prepared to fit into the Xenotest holders. The samples were then dried at 90 °C for 1 hour to maintain a constant mass. The samples were then weighed and placed in the Xenotest. One cycle consisted of a 1 min rain period and a 29-min dry period at a relative humidity of 50% and a constant temperature of 38 °C. Irradiance was set to 60 W/m^2, and was provided with a daylight filter. These laboratory conditions are a rapid simulation of the actual natural conditions to which DSM are exposed in nature, thus mimicking natural conditions. A cycle was repeated 25 times, 50 times, 75 times, 100 times, 125 times, 150 times, 175 times and 200 times. Samples were then dried again at 90 °C for 1 h and weighed. Distilled water was used for the simulated rainwater, which was collected and analysed after the simulation. A few drops of the simulated rainwater were examined under an optical microscope ZEISS Axiotech 25HD (+ pole). It was also filtered through a PESU filter with < 0.2 µm mesh size. The filtrate was analysed by DLS to detect any nanoscale particles released from the samples.

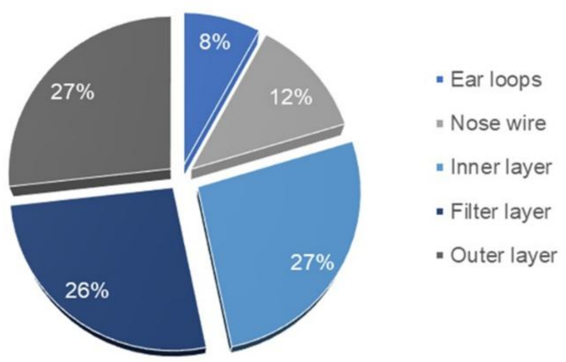
3. Results and Discussion

3.1. Gravimetric analysis

After manually decomposing 100 different DSMs into five components (shown in Fig.1a), we used the basic statistical tools in Microsoft Excel to obtain the results shown in Fig.1b). The average mass of a single mask was 3.1205 g. The maximum mass fraction of the mask represents a 3-layered part, resulting in 79.7%. This percentage is evenly distributed among all 3-layers and most likely contributes significantly to micro/nanoplastic fragmentation. 12.4% of the mass of the DSM represents ear loops, and the lowest percentage of the DSM mass represents nose wire, i.e., 7.9%.



a)



b)

Fig.1 a) Composition of typical DSM, b) Gravimetric analysis of various DSM compositions shown in percentage

3.2. TCLP results analysis

As can be seen from tab.1, qualitative properties of water obtained after TCLP procedures showed the same trend. Particles and chemicals released from DSMs have caused an increase in turbidity, conductivity and COD of distilled water. The values increase for both TCLP procedures is comparable except for conductivity, where ASW ions influence results significantly. A little higher mass of microplastic particles (size between 5 mm and 0.2 μm) was released after the TCLP procedure with distilled water used. This was also the reason why that procedure was used - to evaluate the leaching of microplastic particles by each part of DSM.
Microplastics left in the water after the first filtration true a colander with a mesh having a diameter of 5 mm are shown in the Fig.2a. Microplastics that have been leached during the TCLP procedure and isolated on the filter can be seen in Fig.2b. Fig.2c shows microplastics left in filtrate after second filtration through the PESU filter. Scans of both filtrates shown in Fig.2a and Fig.2c were taken under the optical microscope.
After carrying out TCLP on every part of DSM, it can be seen that most of the microplastic particles are leached from ear loops, followed by the inner, outer and filter layer. The smallest amount of microplastics is caused by nose wires. As a analyse control blank sample has also been done.
Results of released microplastics are also shown in Fig.3a.
After second filtration, PSD analysis was carried out to prove the leaching of nanoscale particles in the filtrate of the whole DSM leachate, presented in Fig.3b. With this analysis, the presence of nanoscale particles released by DSM was confirmed. The particles have an average diameter of 305 nm. Most of the particles (87%) have a diameter of 430 nm, with a standard deviation of 196.1 nm.

3.3. Photodegradation results analysis

Degradation of the DSM 3-layered part after 200 repetitions of 30 minutes cycle of artificial weathering is severe, as is shown in Fig.4a. The whole material is slowly degrading to mezzo and microplastic particles, which are presented in Fig.4b. As part of photodegradation research, artificial rainwater was also collected and scanned under the optical microscope, where microplastic particles were also detected. Fig.4c shows an optical microscope scan of microplastic particles detected in collected artificial rainwater.
Photodegradation analysis of each part of the DSM has also been carried out. As expected, the fastest degradation appears on 3-layered part of DSM. The mass loss after 200 cycles, which is roughly equal to 1 month of exposure in nature, is approximately 24% of its original mass.

Table 1 Simple qualitative properties of the water obtained in TCLP and modified TCLP with ASW before and after filtration

Treatment		**Turbidity** [NTU]	**Conductivity**	**COD** [mg/L O_2]	**microparticles** [mg]
TCLP	Before filtration	15.51	60.42 mS/cm	52.3	7.4
	Filtered	1.86	271.1 μS/cm	53.6	
	Blank	0	35.20 μS/cm	18.0	
TCLP with ASW	Before filtration	16.31	45.43 mS/cm	67.3	7.0
	Filtered	2.05	43.50 mS/cm	63.9	
	Blank	0	31.05 mS/cm	35.8	

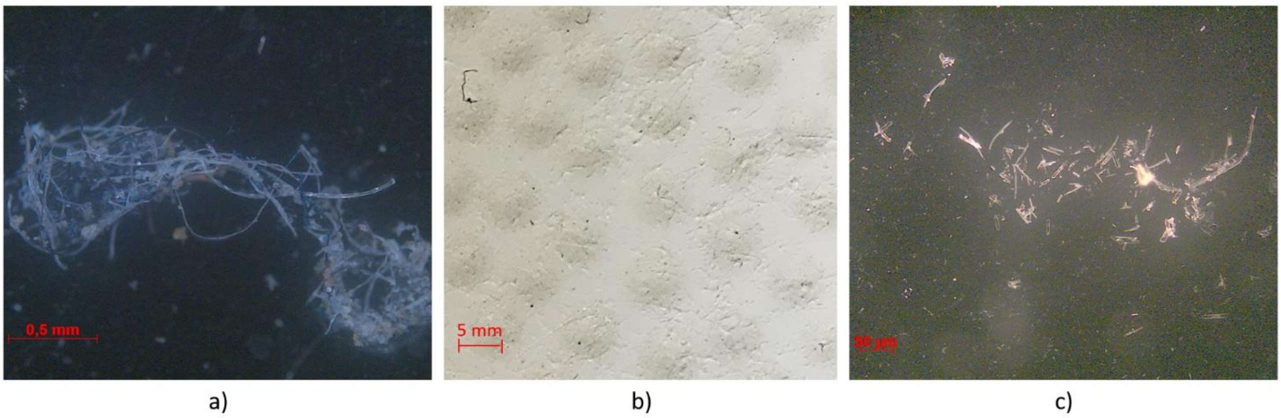


Fig.2 a) Microplastic particles in the first filtrate leached from the whole DSM after the TCLP procedure, b) microplastic particles leached from the whole DSM after TCLP isolated on the PESU filter after the second filtration, c) microplastic particles in second filtrate leached from whole DSM after TCLP procedure

Mass loss of ear loops was about 12% when nose wires are more resistant to photodegradation, as seen in Fig.5a.

To prove the formation of nanoparticles through the process of photodegradation, collected artificial rainwater was analysed by PSD analyse. The obtained results demonstrated the formation of highly inhomogeneous nanoparticles by size. As is also shown in Fig.5b, the majority of formatted nanoparticles are in the region from 400-600 nm.

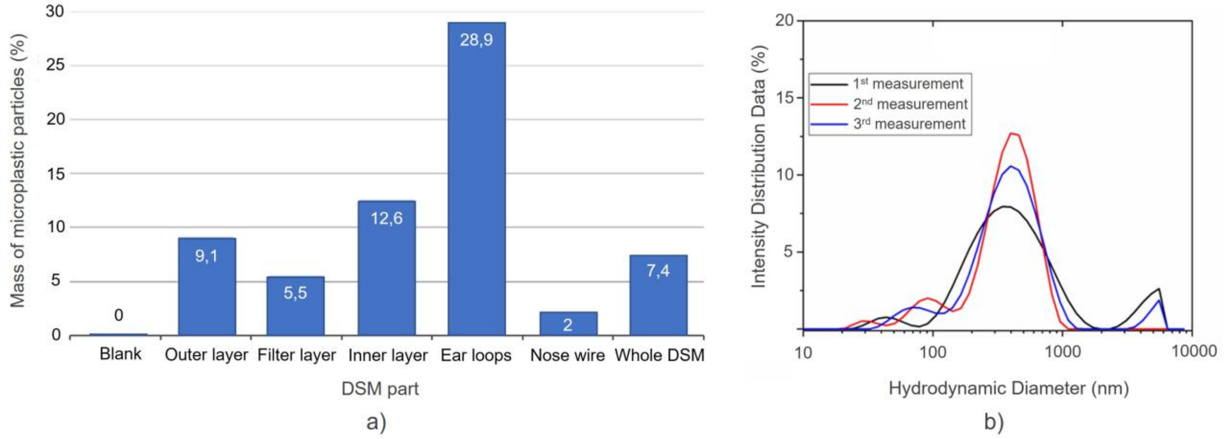


Fig.3 a) Mass of microplastic particles released from each part of DSM after TCLP, b) particle size distribution of second filtrate

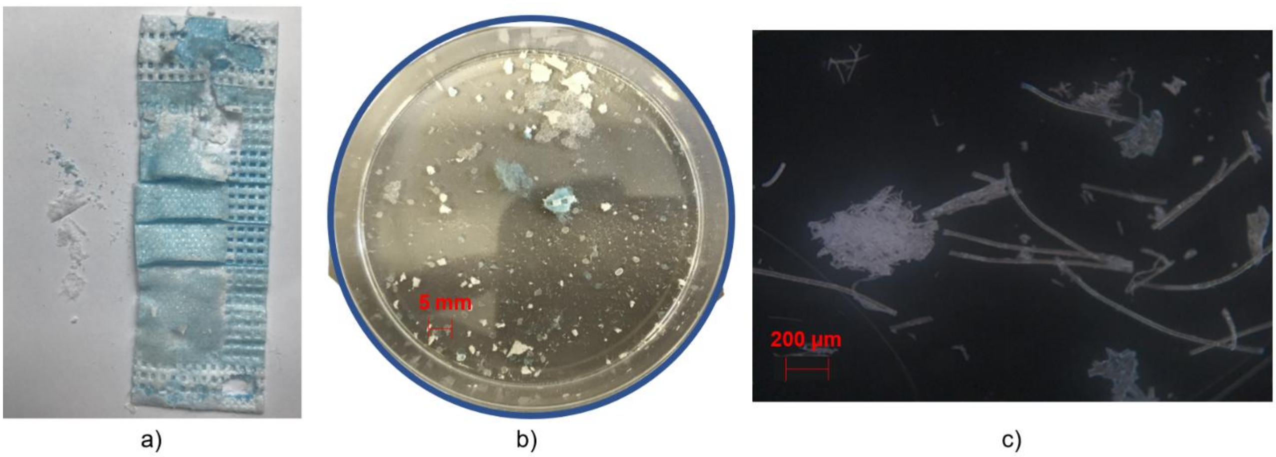


Fig.4 a) Degradation of 3-layered part of DSM, b) isolated mezzo and microplastic particles degrading from 3-layered samples, c) optical microscope scan of microplastic particles isolated from artificial rain water

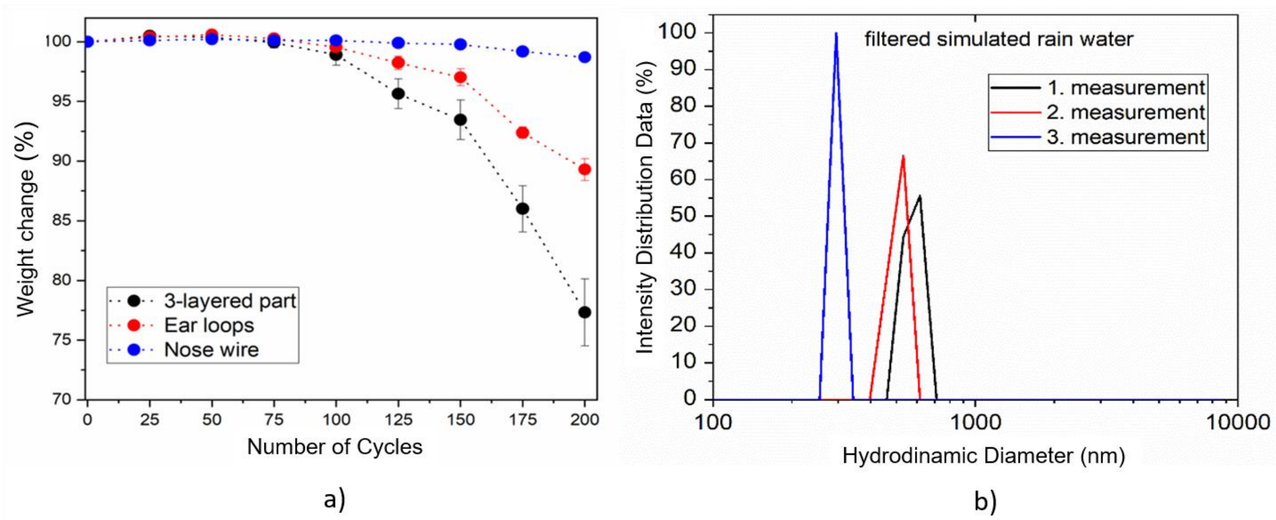


Fig.5 a) Mass loss of DSM parts exposed to artificial weathering from 0 to 200 cycles, b) particle size distribution analysis of filtered simulated rainwater

4. Conclusion

To conclude, disposable surgical masks are present in our everyday life for sometimes now, so it is very important to understand what kind of waste we are producing, after usage. The pandemic of COVID-19 and measures to stem the spread of the disease ordered by the Governments increased the quantities dramatically. Given the volumes that are being generated, it is even more important to understand the wastes that we are dealing with. As we pointed out in the study, it is not very complex type of waste - each mask is made up of only 5 components and is primarily made of polypropylene. However, this should not lead us to forget about the awareness of the hazardous nature of the waste. One of the biggest treats to the environment by this kind of waste is the amount of micro/nanoplastics detected in this study, which are formed in a short time when this waste is exposed to natural conditions such as leaching, moisture, temperature, and UV radiation. So, it is extremely important to aware population about importance of proper disposal of used DSMs and implementing systematic solution in the field of collecting this kind of waste and disposal by waste management companies.

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