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PREPARATION AND CHARACTERIZATION OF SELENIUM NANOPARTICLES ON TREATED TEXTILE FABRIC

PERDUM Elena[1], POPESCU Alina[1], CHIRILA Laura[1], LITE Cristina[1], DINCA Laurentiu[1], RADULESCU Razvan[1], LUPESCU Cezar[1]

[1] National Institute for Textile and Leather Bucharest, Lucretiu Patrascanu Street 16, 030508, Bucharest, Romania

Corresponding author: Perdum Elena, E-mail: elena.perdum@incdtp.ro

Abstract: *Infectious diseases are a serious threat to global health. In today's tightly connected world, a disease can be transported from any remote village to any major city on any continent very rapidly. By accumulating contaminants from air, clothes can become a transport vector and source of 'secondary exposure'. Thus, the development of new and efficient antimicrobial textiles to kill or slow the spread of microorganism is a focus point in textile research and gained much interest in recent years. These antimicrobial textiles are used in various applications ranging from households to commercial, including air filters, food packaging, health care, hygiene, medical, sportswear, storage, ventilation and water purification systems. There is a considerable interest for incorporating metal nanoparticles in textiles in order to obtain functional properties. Selenium nanoparticles are emerging as an effective antimicrobial agent for textiles. In this study, we investigated the properties of SeNPs prepared by a green method of synthesis. Formation and size distribution of SeNPs was confirmed by dynamic light scattering (DLS) analysis and scanning electron microscopy (SEM). Chemically stabilized SeNPs dispersions were subsequently used to treat cotton fabrics by padding. DLS analysis and Zeta potential measurements confirmed the synthesis of spherical, well-dispersed SeNPs and SEM analysis showed the successful deposition of SeNPs on cotton fabrics.*

Key words: *selenium, antimicrobial, textiles, nanoparticles, SEM microscopy*

1. INTRODUCTION

Textiles are indispensable objects and shape our daily life. In the last 30 years, textile industrial companies in Europe have been producing textiles that are used in many fields of application: in the field of agriculture, they are nets to protect crops against insects or climatic aggressions, textile screens for thermal insulation and solar filtration; in furnishing/decoration field: cover sofas, household linen (sheets, blankets, bedding protection), bathroom linen, furniture, curtains, and many others; in the building and construction sector, there are textiles and fabrics for solar protection, facade cladding, stretch roofs for football stadiums, interior and exterior blinds, etc.; in the industrial sector, textiles are used as fiberglass, used for electrical insulation and hot air filtration, truck covers, etc.; in the medical/health sector, textiles are used for implants, dressings, medical devices and masks; in transport, seats, airbags are made of textile, as well as helicopter blade tips, aircraft, and rocket nose sections for the aerospace industry [1,2].

Textile structures possess the ability to retain moisture, enabling bacteria spreading, which causes a range of unwanted effects, not only on the textile itself, but also on the user. Over the last few years, coronavirus pandemic generated an increase of public health awareness of the pathogenic effects regarding personal hygiene and associated health risks, thus intenstive research has been performed in order to minimize microbes'growth (bacteria, viruses and fungi) on textiles [3].

In the last decades there was a tremendous progress in textile functionalization by chemical or physical modifications, providing functions as antimicrobial [4], insect-repellent [5], water-repellent [6], odour-control [7], flame-retardant [8], etc. Nanotechnology can enhance fabrics properties. Among the nanomaterials used, metal nanoparticles are the most popular and versatile. Inorganic nanoparticles such as SeO_2, TiO_2, Cu_2O, CuO, ZnO, SiO_2 and Al_2O_3 are most commonly used because they are thermo-stable at high temperatures. Silver nanoparticles have become one of the most explored nanotechnology-derived nanostructures and have been intensively investigated for their unique physicochemical properties in terms of toxicity, surface plasmon resonance and electrical resistance [9]. The same unique properties that led to their widespread applications raise questions about potential environmental and health effects of exposure during the manufacture and usage. Thus, exposure to silver nanoparticles by inhalation, skin and parenteral exposure can led to oxidative stress, DNA damage, and inflammation [10]. Selenium is a naturally occurring metalloid, essential to human health and plays a substantial role in the functioning of the human organism. It is incorporated into selenoproteins, thus supporting antioxidant defense systems [11]. Several chemical and physical procedures for selenium nanoparticles formation have been discovered, however, the employment of different chemical compounds and physical approaches can result in hazardous agents that restrict the therapeutic potential of selenium nanoparticles in industry. As a result, significant efforts and research have been dedicated towards the green synthesis of selenium nanoparticles, which is eco-friendly and non-toxic [12,13].

In this research, selenium nanoparticles were synthetized by a green method, different types of nanoparticles dispersions were formulated and applied on cotton fabrics. Dynamic light scattering (DLS) analysis was used to confirm the formation of nanoparticles, and characterization of treated fabrics was performed by scanning electron microscopy (SEM).

2. EXPERIMENT

2.1 Materials

The fabrics used in this research were 100% cotton (shirt fabric). Sodium biselenite ($NaHSeO_3$), ascorbic acid, polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) were purchased from Sigma-Aldrich and are of analytical grade. Itobinder AG, polyacrylic binder was purchased from LJ Specialities, UK.

2.2 Methods

Selenium nanoparticles (SeNPs) were synthesized from sodium biselenite as a precursor (in various concentration of 50 and 100 mM) by a green method [12]. Reducing agent of sodium biselenite to selenium nanoparticles was ascorbic acid, prepared in various concentration of 100 mM and 200 mM and added to dispersions at the same molar ratio of 2:1 for both dispersions (acid ascorbic: sodium biselenite). We used stabilizing agent PVP and PVA in concentration of 60 g/L for 50 mM sodium biselenite solution (Table 1).

Table 1. *Recipes of the nanoparticle dispersions*

Dispersion number	$NaHSeO_3$ (mM)	Ascorbic acid (mM)	Concentration of stabilizing agent (g/L)	Stabilizing agent
1	50	100	60	**PVP**
2	100	200	120	**PVA**

Treatment of textile materials with nanoparticles dispersions was performed by padding on laboratory dyeing machine RedKrome REDP – Ugolini, as following: 50 mL NPs dispersion + 30 g/L Itobinder, drying at 100ºC for 2 minutes and condensing at 150ºC for 1 minute.

The surface morphology of the selenium nanoparticles coated fabric was investigated by scanning electron microscope (SEM Quanta 200, FEI, Holland) equipped with energy-dispersive X-ray analysis (EDX) system.

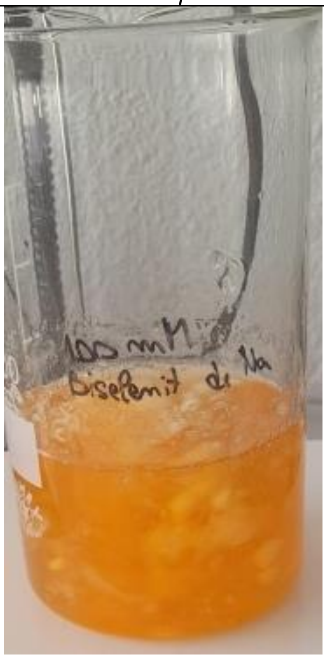
Particle size was determined by dynamic light scattering technique (DLS) by measuring the random changes in the intensity of light scattered from dispersions. The samples were analysed using Zetasizer Nano ZS equipment (Malvern).

2.3. Reduction of selenium precursor to selenium nanoparticles

The formation of selenium nanoparticles was observed by changing the color of biselenite precursor solution from colorless to orange and to dark orange when adding ascorbic acid (Table 2).

As a reductive agent, ascorbic acid acts as an electron donor and provides the reduction of orange colored precursor sodium biselenite to dark orange color selenium nanoparticles.

Table 2. *Reduction of sodium biselenite to selenium nanoparticles by ascorbic acid*

	
Sodium biselenite and PVA on magnetic stirring	Sodium biselenite, PVA and ascorbic acid as a reductant

2.4. Dynamic light scattering (DLS) analysis and Zeta potential measurements.

Dynamic light scattering is a suitable technique for the determination of the size distribution profile of particles in a dispersion. DLS was performed to confirm the formation of selenium nanoparticles and revealed a gaussian size distribution of nanoparticles for both dispersions.

All the samples were measured 3 times, without further preparation at 25°C, using disposable folded capillary cells (DTS 1070).

Pdl represents the polydispersity of the sample and values <0.2 are preferred. Pdl values obtained are below 0.2 for both dispersions, suggesting that the samples are quite polydisperse. The Zeta potential is an indicator of sample stability.

Dispersion 2 was stabilized with polyvinylic alcohol and revealed promising results, with an average size of the nanoparticles determined by DLS of around 170 nm, and a zeta potential of -0.382 mV, compared with dispersion 1, stabilized with polyvinylpyrrolidone that determined the agglomeration of particles, revealing an particles average size of approximately 5000 nm and a zeta potential of 0.402 mV (Figure 1 and 2)

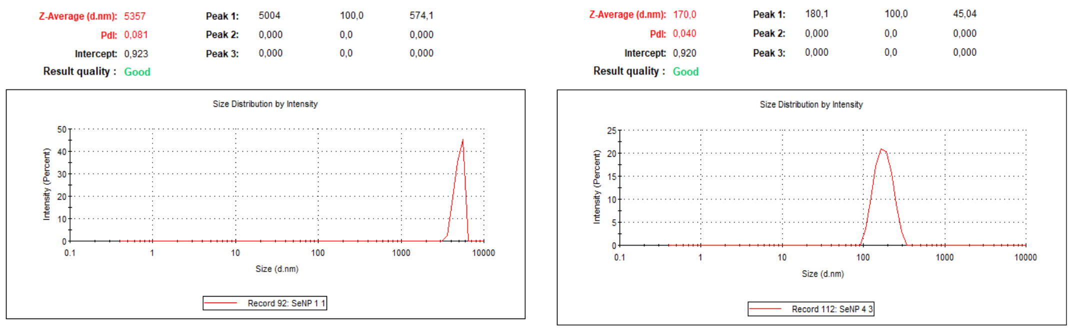


Figure 1. *Size distribution by Intensity of dispersion 1 (left) and dispersion 2 (right)*

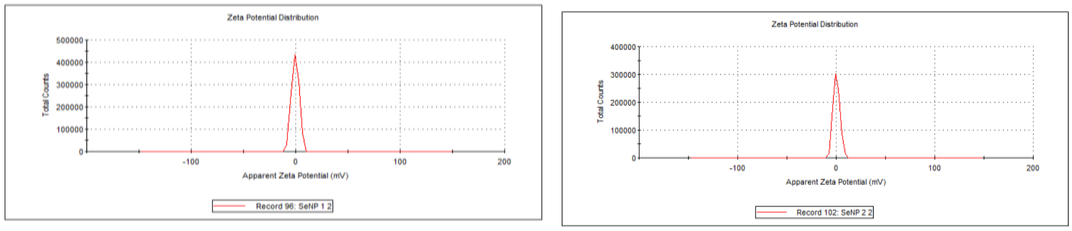
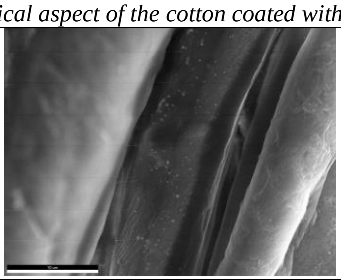
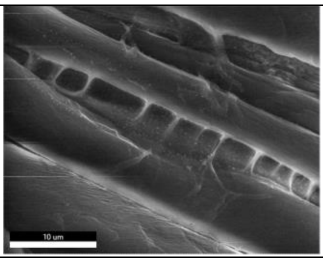


Figure 2. *Zeta Potential distribution of dispersion 1 (left) and dispersion 2 (right)*

2.5. SEM/EDX analysis of the fabric coated with SeNPs dispersions

Table 3: *Morphological aspect of the cotton coated with SeNPs*

		
Untreated fabric	**Fabric treated with dispersion 1**	**Fabric treated with dispersion 2**

The cotton fabric treated with selenium nanoparticles is covered with relatively uniform dispersed nanoparticles (Table 3), the smallest ones ranging from 118.2nm to 181.5nm. Itobinder AG is a self cross linking aqueous acrylic emulsion. It was used to increase the adherence of nanoparticles dispersions on the cotton surface. It is possible that some of the carboxyl groups of the binder interact with selenium particles and other functional groups existing in dispersion. Also, during drying, the binder forms a network which immobilizes the nanoparticles, assuring a stronger fixation of the nanoparticles on the fabric.

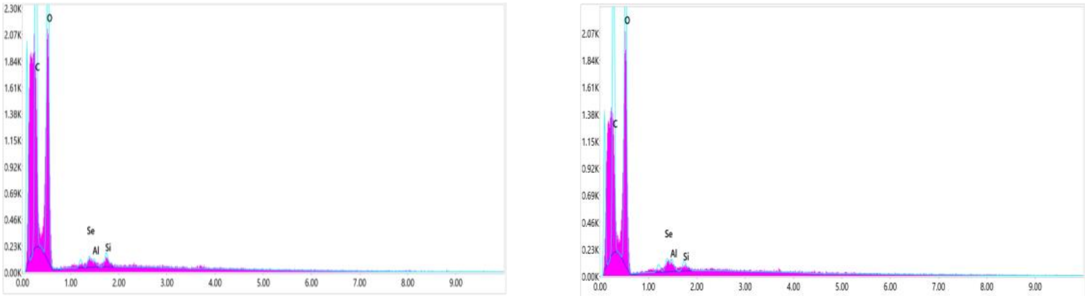


Fig. 3. *EDX spectra of the fabrics coated with SeNPs dispersion 1 (left) and dispersion 2 (right)*

Table 4: *EDX quantification of the Se% wt on the cotton fabrics*

Dispersion 1				Dispersion 2			
Element	**Weight %**	**Atomic %**	**Error %**	**Element**	**Weight %**	**Atomic %**	**Error %**
C K	50.53	58.21	9.5	C K	45.89	53.78	9.76
O K	47.51	41.09	10.28	O K	51.52	45.31	10.13
AlK	0.37	0.19	19.61	AlK	0.69	0.36	13.73
iK	0.72	0.36	9.55	SiK	0.66	0.33	11.35
SeL	0.87	0.15	13.18	SeL	1.24	0.22	12.35

A greater amount of selenium nanoparticles (1.24%) is evidentiated by EDX quantification equipped with Smart Quant software on dispersion 2 (Figure 3 and Table 4), due to a better stabilization capability of PVA compared to PVP, and a better fixation of selenium nanoparticles on fabrics.

4. CONCLUSIONS

Cotton fabrics were treated with dispersions of selenium nanoparticles, synthesized by a green chemistry route. The size and morphology of selenium particles investigated by DLS demonstrated that PVA assures a better stabilization of the dispersion showing that majority of the particles were approximately 170 nm compared to PVP, that determined the agglomeration of particles. SEM-EDX analysis confirmed the presence of selenium nanoparticles on cotton fabrics, in a greater amount on fabric stabilized with PVA. Research will continue with investigation of antimicrobial properties of treated fabrics.

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REFERENCES

[1] Skills4Smart TCLF Industries 2030, *Enhancing the modernisation and competitiveness of the European Union's Textile*, Clothing, Leather, and Footwear (TCLF) sectors.

[2] A.C.Q. Silva, A.J.D. Silvestre, C. Freire, C. Vilela, "*Modification of textiles for functional applications*", Fundamentals of Natural Fibres and Textiles, Woodhead Publishing, 2021, pages 303-365, ISBN 9780128214831, https://doi.org/10.1016/B978-0-12-821483-1.00010-3.

[3] A. Ibrahim, J-É. Laquerre, P. Forcier, V. Deregnaucourt, J. Decaens and O. Vermeersch, *Antimicrobial Agents for Textiles: Types, Mechanisms and Analysis Standards*, Textiles for Functional Applications, ch. 2, IntechOpen, 2021, https://doi.org/10.5772/intechopen.98397.

[4] M.C. Lite, E.C. Tanasescu, L.O. Secareanu, I.M. Sandulache, E. Perdum, G.O. Iordache, "*Silver nanoparticles application for textile conservation*", Annals of the University of Oradea, Fascicles of textiles, leatherwork, vol. 24, no. 2, 2023.

[5] A. Agnihotri, S. Wazed Ali, A. Das, R. Alagirusamy, "*Insect-repellent textiles using green and sustainable approaches*", Textile Institute Book Series, 2019, pp. 307-325, https://doi.org/10.1016/B978-0-08-102491-1.00011-3.

[6] T. Textor, B. Mahltig, "*A sol–gel based surface treatment for preparation of water repellent antistatic textiles*", Applied Surface Science, Volume 256, Issue 6, 2010, pp. 1668-167, DOI:10.1016/j.apsusc.2009.09.091.

[7] R. Rathinamoorthy, G. Thilagavathi, "*Effect of Antimicrobial Finish on Odor Control Properties of Apparel Fabric*", Journal of Textile & Apparel Technology & Management, 2014, Vol 9, Issue 1, p1.

[8] A.R. Horrocks, B.K. Kandola, P.J. Davies, S. Zhang, S.A. Padbury, "*Developments in flame retardant textiles – a review"*, Polymer Degradation and Stability, vol. 88, 2005, pp. 3-12, https://doi.org/10.1016/j.polymdegradstab.2003.10.024.

[9] A. Syafiuddin, M.R. Salim, A. Beng Hong Kueh, T. Hadibarata, H. Nur, "*A review of silver nanoparticles: Research trends, global consumption, synthesis, properties, and future challenges*", J. Chin. Chem. Soc. 2017, 64:732–756, doi: 10.1002/jccs.201700067.

[10] V. De Matteis "*Exposure to inorganic nanoparticles: Routes of entry, immune response, biodistribution and in vitro/in vivo toxicity evaluation*" Toxics. 2017;5:29. doi: 10.3390/toxics5040029.

[11] G. Genchi, G. Lauria, A. Catalano, M.S. Sinicropi, A. Carocci, "*Biological Activity of Selenium and Its Impact on Human Health",* Int J Mol Sci. 2023 Jan 30;24(3):2633. doi: 10.3390/ijms24032633.

[12] T.A. Elmaaty; K. Sayed-Ahmed; H. Elsisi, S.M. Ramadan, H. Sorour, M. Magdi, S.A. Abdeldayem, "*Novel Antiviral and Antibacterial Durable Polyester Fabrics Printed with Selenium Nanoparticles (SeNPs)*", Polymers 2022, 14, 955.

[13] K.K. Karthik, B.V. Cheriyan, S. Rajeshkumar, M. Gopalakrishnan, "*A review on selenium nanoparticles and their biomedical applications*", Biomedical Technology, vol. 6, 2024, pp. 61-74, DOI 10.1016/j.bmt.2023.12.001.