Biophysical analysis of silver nanoparticles prepared by green synthesis and their use for 3D printing of antibacterial material for health care.

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2019

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***Abstract*—The resistance of microorganisms to antibiotics is growing steadily. The development of new antibacterial agents is highly topical. Metal nanoparticles have shown significant antibacterial activity similar to the plant/animal materials used in traditional medicine. The study focuses on the synthesis of silver nanoparticles (AgNPs) modified with biomolecules from used plant extracts (*T. serpyllum, S. officinalis, T. pratense*). The obtained nanoparticles were studied in detail by physicochemical methods. In addition, they were deposited on acrylonitrile butadiene styrene (ABS). We created unique antibacterial material using 3D printing. 20–40% inhibition of S. aureus and E. coli was observed in the evaluation of their efficacy.**

Chemical properties: ABTS – a decrease of 40–80 % after 15 min of quenching radicals, DPPH – a decrease of 15–55 % after 15 min of quenching radicals, total phenols (extract): 1200–1800 mg/mL of GA equivalent. The SEM analysis showed that the particles were mostly polyhedron in shape and had a size of 50 nm. The SPR method determined the particle size at intervals of 20–60 nm and zeta potential in the range of -20 to -5 mV.

[illegible]

Analysis of Ag(I) was performed in acetate buffer (0.2 M, pH 5.0) (carbon working electrode, Ag/AgCl 3M KCl reference electrode, platinum auxiliary electrode) according to the method previously published [9]. To increase the sensitivity of the method, accumulation potential at 400 mV for 240 s was performed. Scanning was done from 0–800 mV. The Ag(I) signal was recorded at a potential of 120 s.

The concentration dependence was linear with LOD = 1 nM, LOQ = 7 nM. AgNPs were mineralized by the following procedure: 200 μL HNO_3 (65%) was added to the crushed printed material (1 mg). After 1 h, the mixture was decomposed by microwave decomposition (300 W, 3 min).

The mixture was then neutralized with 200 μL of NaOH. The sample (10 μL) was analysed by the optimized procedure described above. The amount of silver analysed in AgNPs was 40–65% of the amount deposited.

B. Modification of 3D filament

The possibilities of using 3D printing in chemical laboratories and for biotechnology applications have been intensively developed over the last ten years [10, 11]. 3D filament (fiber, ABS – acrylonitrile-butadiene-styrene, ⌀1.7 mm, white) of the required length (at least 40 cm for wheelshaped printing; r = 14 mm, force = 2 mm) was tensioned between two chemical stands. The purified silver nanoparticles were dispersed in 18 MΩ of water and acetone (Fig. 3 C) (1:1, c = 3 mg/mL). Silver nanoparticles in this form were applied to the fiber by means of a brush. The brush was cleaned between the use of different silver nanoparticles with a stream of flowing water, followed by 70% ethanol, washed with distilled water and dried. AgNPs were applied to the surface of a 3D filament of the ABS type, on which small notches were created for better attachment of AgNPs. AgNPs were dispersed in the mixture of acetone and water (1:1) at a concentration of 3 mg/mL before application. A 1 mL of such dispersion was applied to a 40 cm fiber (Fig. 3D). Between each printing of the material, the 3D printer jet was removed and cleaned with acetone. The Teflon tube was also cleaned with acetone. After the dispersion dried at the string, the string was printed (Fig. 3 E). In other procedures, PLA (polylactic acid) and PET-G (glycol-modified polyethylene terephthalate) filaments testing will be performed. Another direction of our work will be to use other printing methods that use lower temperatures.

Figures:

Fig. 1 **(A)** A simplified representation of the spread of the infection. A patient is the source of infection, there is fecal contamination of medical equipment, clothing along with the hands of healthcare professionals and visitors. The infectious agent is deposited on door handles, toilets, furniture, beds, keyboards, etc. **(B)** Predicted probable targeting of antibiotics to a prokaryotic cell. The effect is directed to DNA/RNA synthesis, cell wall, cell membrane, protein synthesis and folate metabolism. The resistance of bacterial

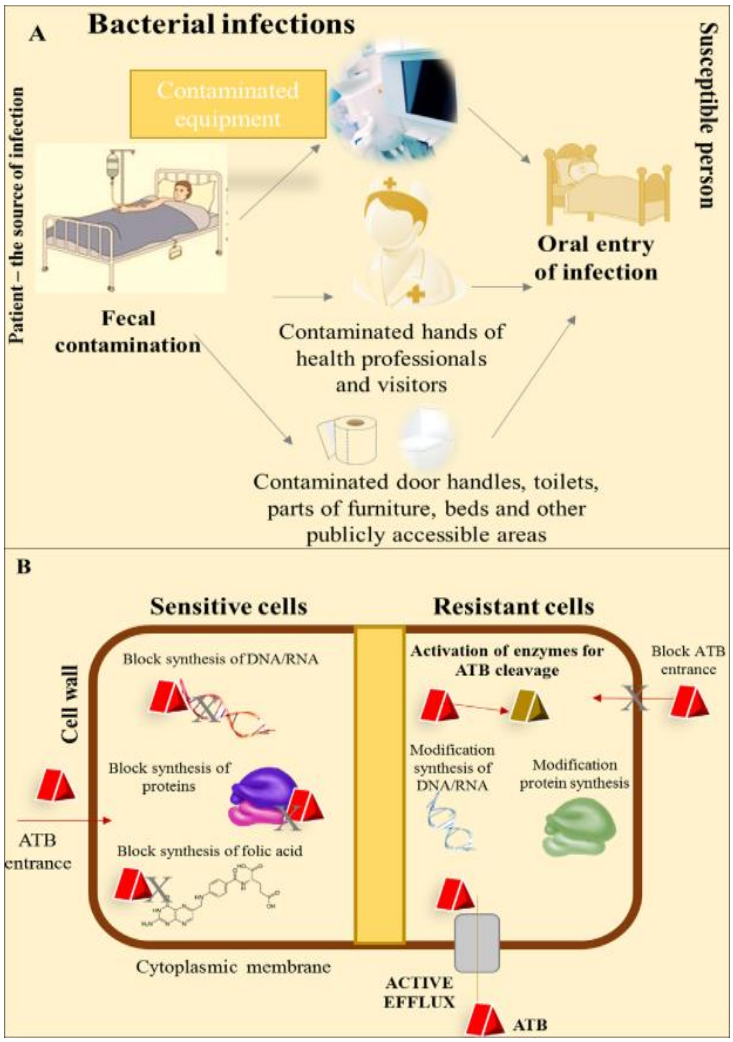

Fig. 2 (**A**) A frequency of occurrence of records on nanoparticles. 275,618 records from Web of Science based on the following keywords “nanoparticle, nanoparticle application, nanoparticle synthesis“ were evaluated. Individual records are expressed as the ratio of the number of searched records on the topic to the total searched records. (**B**) Typical VIS spectra of generated AgNPsT, AgNPsS, AgNPsJ.

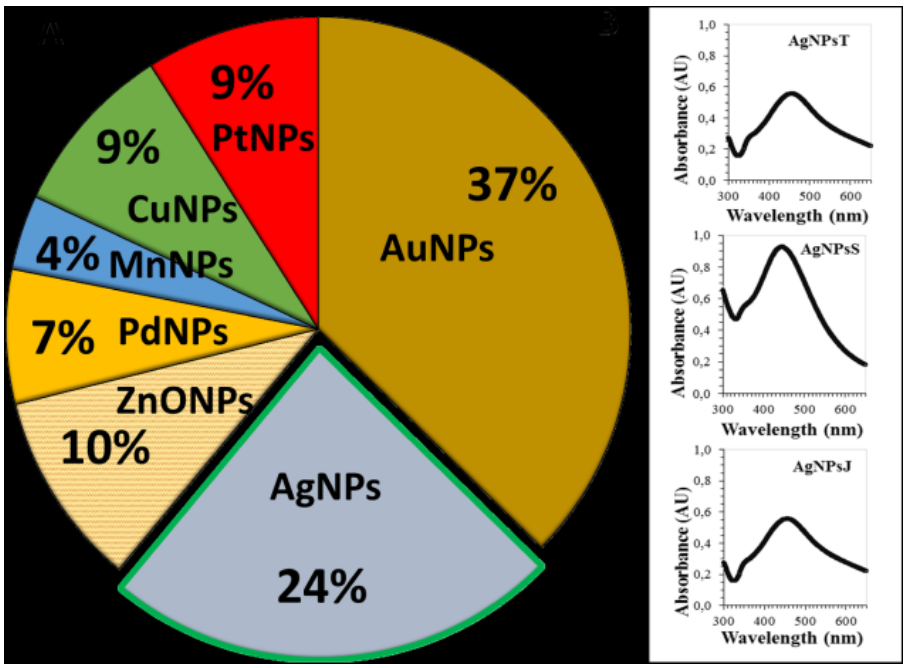

Fig. 3 (**A**) Typical appearance of *T. serpyllum*, *T. pratense*, *S. officinalis* extracts with addition of 0.1 M $AgNO_3$ for 60 min, 80 ° C, 560 rpm. (**B**) Visual appearance of precipitated (methanol 1 : 1) and dried AgNPsT, AgNPsS, AgNPsJ (24 h, 60 ° C). (**C**) Purified AgNPsT, AgNPsS, AgNPsJ dispersed in ultrapure water by ultrasound (3 mg/mL). (**D**) Visual appearance of ABS material after application of prepared AgNPsT, AgNPsS, AgNPsJ. (**E**) 3D printing-prepared platform with AgNPsT, AgNPsS, AgNPsJ (3 mg/mL). The extruder was heated to 240 ° C and the plate temperature was 80 ° C, the jet 0.5 mm.

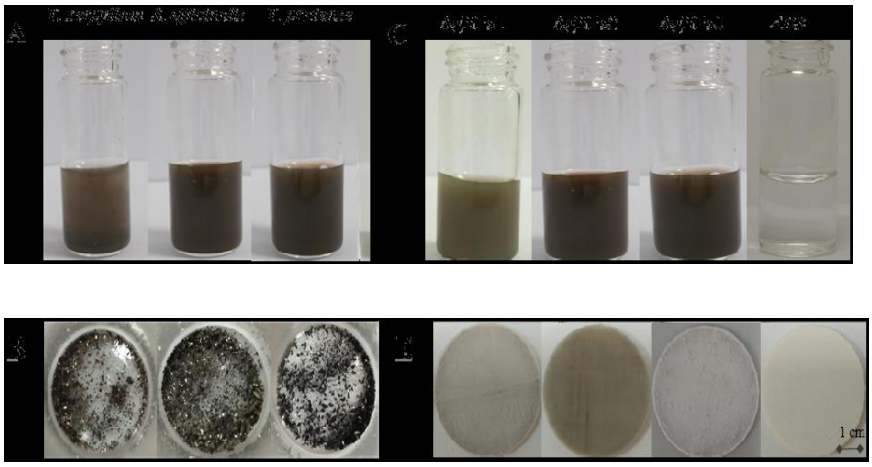

TABLE I. CHARACTERISTICS OF SYNTHESIZED SILVER NANOPARTICLES

Nanoparticles	Parameters of prepared NPs		
	Average yield (%)	*Equivalent of phenol (%)*	*Maximum UV-VIS signal*
AgNPsT	65	0.304	420
AgNPsS	77	1.387	440
AgNPsJ	67	1.336	430

[a] Plant extracts: T - thyme, S - sage, J - cover

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The work was carried out with the support of the H2020 CA COST Action CA15114, INTER-COST LTC18002.