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Preparation of silver coated oxide nanomaterials and study of their properties

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Annotation. Nanopowders of aluminum oxide silicon oxide and iron oxide with silver coating were produced by the radiation-chemical method. The dimensions of the nanoparticles were 50 to 80 nm, and the area can be changed from 2-3%, up to 40%. Was carried out the validation of antibacterial properties against E.coli and staphylococcus. Were estimated photocatalytic properties of nanopowders, which showed applications perspective as a photocatalytic agent. Cytotoxic properties were also investigated, which showed the relevance of the use of some the obtained composites for targeted drug delivery.

1. Introduction
Nanopowders of oxide materials with silver coating are a promising compound for application in medico-pharmaceutical sphere due to antimicrobial [1], antitumor [2] and other properties of shell and bioinert nucleus.

Production of composite NPs with silver coating was carried out on the basis of radiation-chemical technology [3]. This method of producing composites is suitable for different oxides. For comparison, aluminum oxide, silicon oxide, and iron oxide composites coated with nanoscale silver were selected because they are of greatest interest for drug delivery and polycomponent action.

The purpose of the present work is to obtain composites with a nanosized silver coating on an oxide basis using radiation-chemical technology and their application in the medico-pharmaceutical sphere.

2. Materials and methods
The method of producing silver-coated oxide-based composites is described earlier in article [3]. NP after irradiation by nanosecond electron beams are divided into 2 parts depending on the time of silver settling on the base: for 15 hours - Al₂O₃Ag15 and SiO₂Ag15, for 96 hours - Al₂O₃Ag96, SiO₂Ag96 and Fe₃O₄Ag96. The solutions were then drained and the resulting powders washed with distilled water (3 times) and dried.

The composition of the obtained NPs and the determination of their structural properties were determined using an electron microscope LEO 982 with the adapter OxfordInstrumentsX-Max.

The antibacterial properties of silver-coated oxide nanomaterials were tested by the volume displacement method against E. coli and staphylococcus strains, which are indicators of environmental contamination.
Sowing of bacterial strains was carried out on meat-peptone agar. Before the microorganisms were seeded, samples of tested NPs were placed on the surface of the nutrient medium: aluminum (Al₂O₃), silver (Ag), silicon oxide (SiO₂), iron oxide (Fe₂O₃), aluminum-based composites, silicon oxide and iron oxide coated with silver (Al₂O₃Ag96, SiO₂Ag96 and Fe₂O₃Ag96, respectively). The microorganisms were then thermostatted and the growth of microorganism colonies around the nanopowder samples was evaluated.

Methyl violet (MV) was used as a contamination simulator to evaluate photocatalytic properties. The MV solution was dispensed into 4 cups with a diameter of 40 mm, 6 ml into each. In each series of experiments, one of the plates was a control sample, and to each of the remaining plates were added 300 μl suspension NP from pre-prepared dilutions of each NP (1 dilution - NP concentration 2 mg/ml, 2 dilution - 4 mg/ml). In the first and second series of experiments we examined Al₂O₃, Ag and Al₂O₃Ag96 with different concentrations, in the third and fourth - SiO₂, Ag and SiO₂Ag96, in the fifth and sixth - Fe₂O₃, Ag and Fe₂O₃Ag96. Thus, in the first, third and fifth series of experiments, the nanoparticles concentration in each dish was 100 μg/ml, and in the second, fourth and sixth, 300 μg/ml.

The optical density of the solution was measured on an Ecros PE-5400UF spectrophotometer to determine the rate of discoloration before irradiation with UV radiation and another 4 times after each irradiation (irradiation time 5 minutes). The error of the method is 0.8%.

The cytotoxic activity of nanomaterials was determined on two cell cultures: dermal FB and HeLa cells (human cervical carcinoma).

MMT test was used to investigate the effects of NP on viability. The cell cultures were placed in 96-well plates of 100 μl. Culturing was carried out for 24 hours. Thereafter, 10 μl NP suspensions at final concentrations of 0.1 mg/ml, 0.5 mg/ml and 1 mg/ml were added to the wells. After culturing the cells in plates for 3 days, an MMT dye of 20 μl was added to each well, after which the plates were placed in a thermostat for 2 hours. Further from holes merged environment and dye, and added 100 μl DMSO after what was carried out the definition of absorption on the automatic spectrophotometric tablet Tecan Infinite M200 PRO scanner at the wavelength of 570 nanometers. The error of the method was estimated using statistical methods.

3. Results and discussions

According to microscopic analysis, the size of nanopowders was established: Al₂O₃Ag15 - 50 nm and Al₂O₃Ag96 - 80 nm, and the proportion of silver coating Al₂O₃Ag15 - 2-3% and Al₂O₃Ag96 - 16 to 40%.

In assessing the antibacterial properties of the NP, it was found that in the first series of experiments for the sample, Al₂O₃ bactericidal or bacteriostatic effects were not recorded, while NP Ag and Al₂O₃Ag96 showed poor activity against E. coli and staphylococcus [3].

In the second series of experiments, samples of SiO₂ and SiO₂Ag96 as well as Al₂O₃ did not show antibacterial properties.

In the third series of NP Ag, Fe₂O₃ were ineffective against the studied bacteria strains, and Fe₂O₃Ag96 showed a bactericidal effect.

Thus, silver-coated aluminum oxide and iron oxide composites have greater antibacterial activity than silver-coated silicon oxide composites.

The results of evaluation of photocatalytic properties are presented in tables 1–3. The dependence of the discoloration of the MV solution on the time of exposure to UV radiation can be described by the linear equation \( y = kx + b \), where the coefficient \( k \) is the rate of photodegradation (discoloration).

It can be seen from table 1 that at the concentration 100 μg/ml, the photodestruction rate of all samples with powders Al₂O₃, Ag and Al₂O₃Ag96 was lower than in the control sample. Therefore, at a given concentration, NPs act as photoprotectors, the composite (Al₂O₃Ag96) exhibiting the least photoprotective properties.
Table 1. Value of coefficient k at different concentrations for samples Al₂O₃, Ag, Al₂O₃Ag₉₆.

| Sample          | At concentration 100 μg/ml | At concentration 300 μg/ml |
|-----------------|---------------------------|---------------------------|
|                 | Absolute value            | Lead to control           | Absolute value | Lead to control |
| Control         | -0.02846                  | 1.00                      | -0.00963       | 1.00            |
| Al₂O₃           | -0.01866                  | 0.66                      | -0.02002       | 2.08            |
| Ag              | -0.01838                  | 0.65                      | -0.02191       | 2.28            |
| Al₂O₃Ag₉₆       | -0.02052                  | 0.72                      | -0.02334       | 2.42            |

At the concentration 300 μg/ml vice versa, the photodestruction rate of all powder samples was greater than in the control sample. Therefore, at the concentration 300 μg/ml, NP showed photocatalytic properties, with the composite (Al₂O₃Ag₉₆) [3] showing the greatest effectiveness.

Table 2. Value of k coefficient at different concentrations for samples SiO₂, Ag, SiO₂Ag₉₆.

| Sample          | At concentration 100 μg/ml | At concentration 300 μg/ml |
|-----------------|---------------------------|---------------------------|
|                 | Absolute value            | Lead to control           | Absolute value | Lead to control |
| Control         | -0.02606                  | 1.00                      | -0.03113       | 1.00            |
| SiO₂Ag₉₆        | -0.02568                  | 0.99                      | -0.02731       | 0.88            |
| SiO₂            | -0.02257                  | 0.87                      | -0.02533       | 0.81            |
| Ag              | -0.02066                  | 0.80                      | -0.02608       | 0.84            |

It can be seen from table 2 that the tested NP SiO₂, Ag and SiO₂Ag₉₆ are photoprotectors at both concentrations, with the weakest photoprotector being the composite.

Table 3. Value of k coefficient at different concentrations for samples Fe₂O₃, Ag, Fe₂O₃Ag₉₆.

| Sample          | At concentration 100 μg/ml | At concentration 100 μg/ml |
|-----------------|---------------------------|---------------------------|
|                 | Absolute value            | Lead to control           | Absolute value | Lead to control |
| Control         | -0.02355                  | 1.00                      | -0.02116       | 1.00            |
| Ag              | -0.02343                  | 0.99                      | -0.02529       | 1.20            |
| Fe₂O₃           | -0.02315                  | 0.98                      | -0.02635       | 1.20            |
| Fe₂O₃Ag₉₆       | -0.02309                  | 0.98                      | -0.02337       | 1.10            |

Analyzing the data of table 3, it was concluded that the powders Fe₂O₃, Ag and Fe₂O₃Ag₉₆ behave similarly to the NP of the first experiment with Al₂O₃, Ag and Al₂O₃Ag₉₆. At the concentration 100 μg/ml all powders exhibit weak photoprotective properties, and at the higher concentration 300 μg/ml, weak photocatalytic properties.

Based on the obtained data, the significant influence of the silver coating on some oxides on their photocatalytic properties was established: for Al₂O₃Ag₉₆ and SiO₂Ag₉₆, the coating stimulated the photodegradation of MV, despite this SiO₂Ag₉₆ proved to be a photoprotector, and Al₂O₃Ag₉₆ as a photocatalyst. However, for a portion of oxides such as Fe₂O₃Ag₉₆, this action has not been detected, they have been inert to MV and behave in a similar manner with or without a coating. Thus, the most suitable composition for water disinfection is Al₂O₃Ag₉₆.
The results of the cytotoxic activity of NP carried out on FB and cell culture HeLa are shown in table 4.

### Table 4. Effect of oxide nanomaterials and silver coated composites on FB and HeLa cells.

| NP, % | Effect on FB | Effect on HeLa |
|-------|--------------|----------------|
|       | 0.1 mg/ml | 0.5 mg/ml | 1 mg/ml | 0.1 mg/ml | 0.5 mg/ml | 1 mg/ml |
| Control | 100  | 100 | 100 | 100 | 100 | 100 |
| Ag     | 82\(^a\) | 68\(^a\) | 66\(^a\) | 82\(^a\) | 34\(^a\) | 39\(^a\) |
| Al\(_2\)O\(_3\) | 93  | 89  | 87  | 83\(^a\) | 83\(^a\) | 88\(^a\) |
| Al\(_2\)O\(_3\)Ag96 | 82\(^a\) | 87\(^a\) | 77\(^a\) | 85\(^a\) | 79\(^a\) | 92  |
| SiO\(_2\) | 106 | 126\(^a\) | 91 | 93 | 86\(^a\) | 92  |
| SiO\(_2\)Ag96 | 100 | 110 | 98 | 87\(^a\) | 69\(^a\) | 45\(^a\) |
| Fe\(_2\)O\(_3\) | 96 | 98 | 114 | 91 | 93 | 97  |
| Fe\(_2\)O\(_3\)Ag96 | 95 | 101 | 98\(^a\) | 92 | 72\(^a\) | 58\(^a\) |

\(^a\)Certain variation from control

Thus, the different effects of the silver coating on oxides on their biological properties were established: composites SiO\(_2\)Ag96 and Fe\(_2\)O\(_3\)Ag96 showed increased toxicity to tumor cells compared to their pure oxides. At the same time, the composites showed low cytotoxicity to FB, similar to their pure oxides.

However, aluminum and the composite based on it (Al\(_2\)O\(_3\)Ag96) do not have similar properties, they approximately equally showed low toxicity to both cell cultures.

Based on the obtained data, composite nanomaterials such as SiO\(_2\)Ag96 and Fe\(_2\)O\(_3\)Ag96 are more promising for use in targeted drug delivery than Al\(_2\)O\(_3\)Ag96 due to multifactorial effects.

### 4. Conclusion

Were produced composite NP of aluminum oxide, silicon oxide and iron oxide coated with silver nanosized layer. The nanoparticles sizes were for Al\(_2\)O\(_3\)Ag15 - 50 nm, for Al\(_2\)O\(_3\)Ag96 - 80 nm, and the share of silver coating Al\(_2\)O\(_3\)Ag15 - 2-3% and Al\(_2\)O\(_3\)Ag96 - 16 to 40%. The advantage of this method of obtaining silver-based composites is the possibility of their controlled (according to the degree of coating) production.

Antibacterial properties of composites have been investigated on E. coli and staphylococcus. Nanoparticles aluminum and silver coated iron oxide showed efficacy against these strains. Composite NPs based on aluminum and iron oxide are promising antibacterial agents. The findings require detail examination.

The photocatalytic properties of the composite NPs were checked. The composite Al\(_2\)O\(_3\)Ag96 showed promise for use as a photocatalyst.

Cytotoxic properties which showed that NP SiO\(_2\)Ag96, Fe\(_2\)O\(_3\)Ag96 didn't show toxic action concerning dermal FB unlike Al\(_2\)O\(_3\)Ag96 are investigated, at the same time all powders showed the inhibiting action on viability of cages of HeLa. Thus, SiO\(_2\)Ag96 and Fe\(_2\)O\(_3\)Ag96 have proven to be potential multimodal agents in the field of targeted drug delivery.

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