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Antibacterial properties of biocides based on silver nanoparticles and organic acids

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Abstract

The paper proposes a method for synthesizing nanocomposites with silver nanoparticles and sorbic acid or 4-hydroxybenzoic acid as components of antibacterial coatings. A synergistic effect was found by combining two biocides (metal ions and acid). The application of the developed synthesis technique made it possible to obtain silver nanoparticles with a particle size distribution of 1–6 nm on halloysite and up to 10 nm on sepiolite. Using thermogravimetric analysis, it was found that the maximum loading of acids into carrier pairs is observed at the carrier:acid ratio of 1:1. According to spectrophotometric data on the release of sorbic acid and 4-hydroxybenzoic acid from the pores of halloysite and sepiolite in an aqueous medium, the release of acids is observed for 150–200 min. The largest diameter of the growth inhibition zones (mm) of *Staphylococcus aureus* (strain 119 (MRSA 45)) is shown by the samples with sorbic acid (13–15 mm).

Key findings

- A broad antibacterial effect was revealed with inhibition of the growth of gram-positive bacteria *Staphylococcus aureus* and gram-negative bacteria *Pseudomonas aeruginosa*.
- Thus, antibacterial drugs based on silver nanoparticles were obtained using organic acids. The materials showed a high degree of release and antibacterial activity.

Accompanying information

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Supplementary information

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Sustainable Development Goals
3 GOOD HEALTH AND WELL-BEING

1. Introduction

The development and rapid spread of new infections, as well as the formation of biofilm, leads to the resistance of bacterial strains to antibiotics and antiseptics. Unfortunately, even the correct selection of the drug does not protect patients from the problem of antibiotic resistance [1–5]. Providing high-quality medical care and developing new antibacterial and wound-healing materials is an important topic in Russian healthcare [5–8]. Metal-containing nanomaterials have been proposed as future antibacterial drugs due to their unique functional properties [3, 9].

The latest publications in the field of nanotechnology [10–15] show that the topic continues to be relevant. Nanomaterials are already used in medicine and are an interesting object for study, because they exhibit high antibacterial activity that can increase with the occurrence of the surface plasmon resonance effect [15, 16]. In modern medicine, nanomaterials can be used to create dressings for closing large and deep wounds, antibacterial coatings, surgical instruments, as well as in targeted delivery of drugs and other active substances in cancer treatment [17–19].

However, it is worth noting that despite these potential advantages only a small number of such drugs have been approved for clinical use [10–13, 20–25].

To implement new bactericidal materials, it is necessary to solve the problems of good reproducibility and simplicity of synthesis for scaling up the process, maintaining good growth suppression and viability of gram-negative and gram-positive bacterial strains, low molecular, cellular and immune toxicity to the host organism, as well as ease and accessibility in use [25].

Previously, it was found that heteropolyacids exhibit synergism with silver nanoparticles as antibacterial agents [1]. Now we want to figure out whether organic acids have the same effect.

In this work, it was necessary to identify which of the organic acids is more suitable for the purposes of the study. The acid that is released more smoothly from the pores of the carrier will work better. If the acid quickly leaves the pores, then the silver ions will be released worse from the carrier. The first day after medical operations is the most critical, since it is then that bacterial colonization can occur. To prevent this from happening, it is necessary to release the acid smoothly.

The novelty of the work lies in the use of relatively safe organic acids in combination with silver nanoparticles to achieve rapid dissolution of silver ions and increase antibacterial activity. The aim of this study is to develop new nanomaterials based on metal nanoparticles together with organic preservatives, evaluate spectrophotometric data on the release of organic acids from the pores of halloysite and sepiolite in an aqueous environment, and analyze the antibacterial activity of the obtained materials.

Silver, as an antibacterial component, is used to combat bacteria resistant to many drugs [26]. For example, silver phosphate-based photocatalysts are already included in components for surface sterilization under the influence of visible light. It is assumed that the antibacterial activity of silver nanoparticles increases with the occurrence of the surface plasmon resonance effect [27]. There is also information on the manifestation of high bacterial activity of electrodeposited calcium phosphate coatings containing silver. Such coatings provide an antibacterial effect against the Staphylococcus aureus strain due to the release of Ag^+ ions as well as metallic AgNPs, which damage bacterial cells. To reduce the toxicity of free AgNPs in relation to eukaryotic cells, it is necessary to use a carrier [10, 16]. Halloysite and sepiolite are proposed as nanocarriers for the delivery of biocides, since they are biocompatible, easily accessible and low-cost. It was found that the use of composites together with sepiolite leads to a noticeable improvement in the properties of silver nanoparticles [28–30]. Earlier, a broad antibacterial effect was revealed with complete inhibition of the growth of Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Pseudomonas aeruginosa* at a concentration of 0.5 g/l and *Acinetobacter baumannii* at a concentration of 0.25 g/l [1].

At this stage of the study, it was revealed that organic acids can be used as a biocide, which, together with AgNP, will enhance the antibacterial effect (for example: methyl ester of para-hydroxybenzoic acid, 4-hydroxybenzoic acid, sorbic acid, dehydroacetic acid, propyl-4-hydroxybenzoate, methyl-4-hydroxybenzoate, etc.) [31–33].

2. Experimental part

The following reactants were used in the work: $AgNO_3$ (s.p., “TD Khimmed”), halloysite ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$), (s.p., Sigma-Aldrich, cat. No. 685445), sepiolite ($Mg_4(OH)_2 \cdot 6H_2O$), (s.p., “Eko-tec”, CAS 63800-37-3), 4-hydroxybenzoic acid (pHBA, $C_8H_8O_3$), (99%), sorbic acid (Sorb, $C_6H_8O_2$), (99%, Sigma-Aldrich, cat. No.: PHR1367), hydrogen peroxide H_2O_2 (37%, AO "ECOS-1"), ethyl alcohol (s.p., JSC "ECOS-1").

Halloysite modification. Halloysite nanotubes were treated with a 40% hydrogen peroxide solution to remove contaminants from the surface and dried at 120 °C for 24 h.

2.1. Silver nanoparticles

The synthesis of silver nanoparticles on the surface of halloysite and sepiolite was carried out as follows. 0.5 g of the carrier (halloysite and sepiolite) was dispersed in 100 ml of ethyl alcohol in an ultrasonic bath. 50 ml of an alcohol solution of $AgNO_3$ (3 mg/ml) was added to the resulting dispersion. The mixture was stirred in an ultrasonic bath for 30 min. The samples were centrifuged, washed with ethyl alcohol and dried at T = 100 °C for 24 h. Drying of silver nitrate adsorbed on halloysite and sepiolite promotes the formation of silver nanoparticles on the surface of the nanotubes [11]. The resulting carriers with silver nanoparticles (Hal-Ag and Sep-Ag) were used for the further loading of organic acids. Heat treatment of the composites containing organic acids leads to maturation of the nanoparticles [12–14].

2.2. Nanomaterials with organic acids

The carrier (Hal-Ag or Sep-Ag, 0.5 g) was dispersed in 100 ml of ethanol using an ultrasonic bath. 0.5 g 4-hydroxybenzoic acid (coded as pHBA) or sorbic acid (coded as Sorb), previously dissolved in 50 ml of ethyl alcohol, was added to the resulting dispersion. The mixture was stirred for 5 h. The samples were centrifuged and washed with distilled water (obtained as a result of a single distillation, aqua distiller DE-10M, OOO Plant "Elektromedoborudovaniye") and dried at T = 60 °C until constant mass. The resulted powder samples (Hal-Ag-pHBA, Hal-Ag-Sorb, Sep-Ag-pHBA, Sep-Ag-Sorb) were subsequently studied.

The morphology of the developed materials was investigated using a JEM-2100 transmission electron microscope (JEOL). The samples applied to a copper grid were analyzed at an accelerating voltage of 200 kV. The particle size was determined using the ImageJ program. The analysis was based on processing 4–5 microphotographs with a count of at least 400 nanoparticles.

The nanomaterials were studied by thermogravimetric analysis (TGA) under nitrogen with an STA 449 F5 Jupiter (Netzsch, Selb, Germany) from 30 to 1000 °C with a preliminary isotherm for 60 min and further heating rate of 10 K/min.

Absorption spectra in the range of 200–600 nm were recorded using a Cary 60 UV-VIS spectrophotometer (Agilent, USA).

Antibacterial activity was estimated by a diameter of growth inhibition zone on a Mueller–Hinton agar after incubation for 24 h at 37 °C.

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3. Result and Discussion

In this way, nanocomposites with silver nanoparticles loaded with sorbic acid or 4-hydroxybenzoic acid as components of antibacterial coatings were obtained. The application of the developed synthesis method made it possible to obtain silver nanoparticles with a narrow particle size distribution on the surface of modified halloysite and sepiolite (Figure 1).

The particle size was determined using the ImageJ program. The analysis is based on processing 5–6 micrographs with a count of at least 400 nanoparticles (Figure 2).

As we can see, the particle size distribution is skewed (in contrast to the expected normal distribution), which may be explained by the Ostwald ripening during the composites drying. Nevertheless, the particle size distribution remains quite narrow, with the majority of the nanoparticles being smaller than 5 nm.

Thermogravimetric analysis (TGA) was also performed (Figure 3). To obtain thermogravimetric curves, the mass loss of a substance during heating to high temperatures is determined. The main mass loss of sorbic acid and 4-hydroxobenzoic acid occurs at 100–484 °C; above 500 °C, the degradation of halloysite occurs. Using TGA, it was found that the maximum load is observed with a 1:1 ratio of halloysite to acid content (mole fraction).

First-derivative weight loss curves for the samples with and without organic acids were almost identical, showing single definite peak for halloysite at circa 500 °C, and two definite peaks at circa 250 °C and 800 °C for sepiolite (most probably, dehydration). The TGA analysis showed that only a few percent of the composite mass is comprised of the loaded acid. In further studies, we will optimize the loading procedure in order to increase the organic acid percentage.

The release was measured by preparing a solution with a concentration of 0.3 mg/l. The spectra were measured every 20 min; the last measurement was performed at 160 min. Spectrophotometric data showed that the entire amount of encapsulated sorbic acid was released during the first 25 min of ultrasound treatment in an aqueous medium (Figure 4). At the initial stage, an explosive release of 90% occurs, the time dependence of which can be described by the Korsmeyer-Peppas model. The release of sorbic acid from the sepiolite occurs with little shielding, judging by the magnitude of the exponent index (0.45 and 0.42).

The spectrophotometric data of 4-hydroxybenzoic acid indicate that its release is slower than that of sorbic acid (Figure 5). During the first 50 min, 70% of the biocide is released.

3.1. Antibacterial activity

Antibacterial activity was estimated by the diameter of the growth suppression zones around 10 mg of a sample on Petri dishes inoculated with methicillin-resistant *Staphylococcus aureus* (strain MRSA 45).

According to the data shown in Table 1, it is evident that the samples containing acids and silver nanoparticles exhibit the best antibacterial activity. If silver nanoparticles and acid are used separately, the antibacterial activity decreases or even disappears. This is evident from the data for sorbic acid. The best activity was demonstrated by the sample with 4-hydroxybenzoic acid.

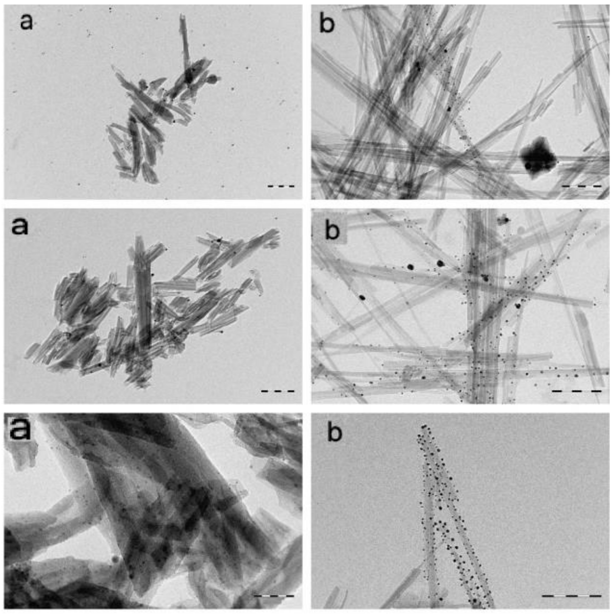

Figure 1 Micrographs of TEM composites based on halloysite (a) and sepiolite (b) with silver nanoparticles. Bars, 200 nm.

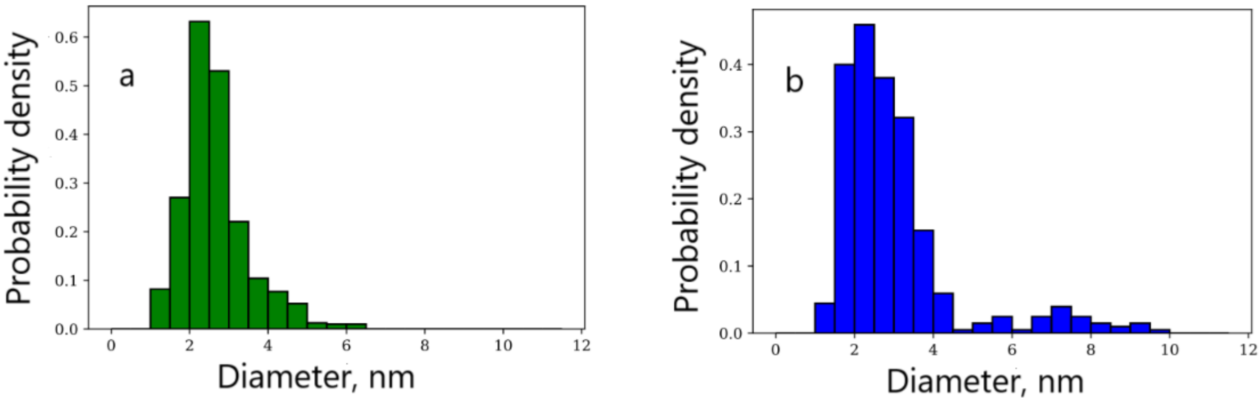

Figure 2 Histogram of silver nanoparticle size distribution according to TEM data: halloysite (a), sepiolite (b).

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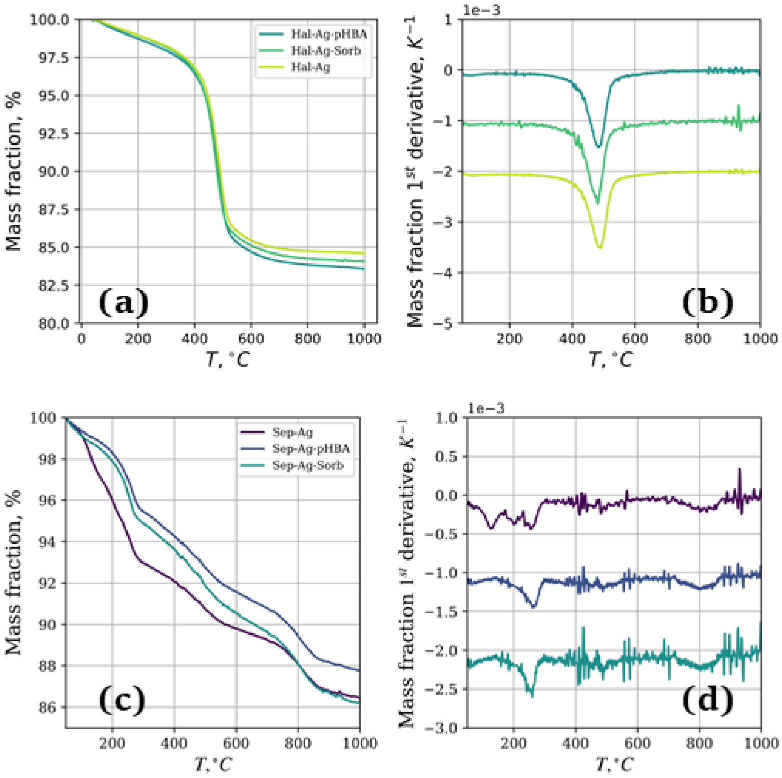

Figure 3 Thermogravimetric analysis (TGA) for samples with sorbic acid and 4-hydroxybenzoic acid, weight loss (a, c) and first derivative of weight loss (b, d) curves.

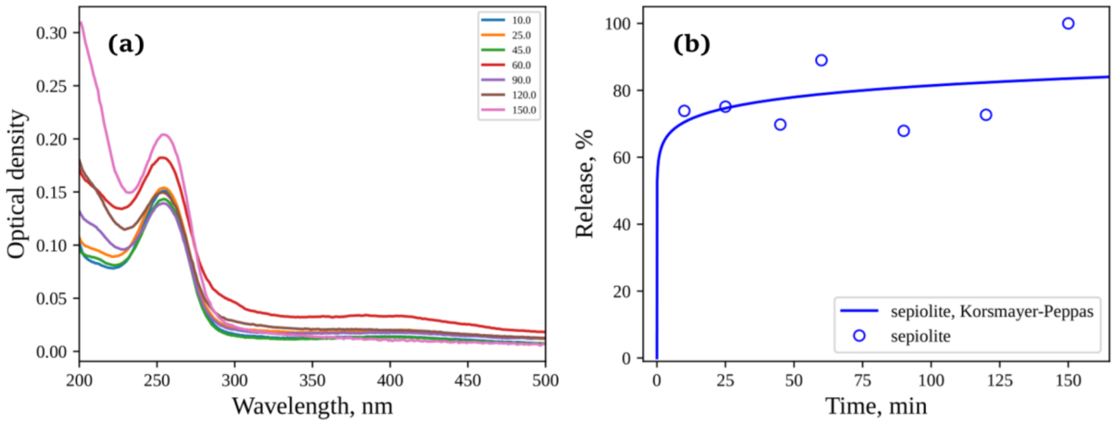

Figure 4 Release of sorbic acid from Sep-Ag-Sorb composite: optical density spectra (time, min is shown in the legend) (a); the sorbic acid release fitted with a Korsmeyer-Peppas model, R^2 = 0.1453 (b).

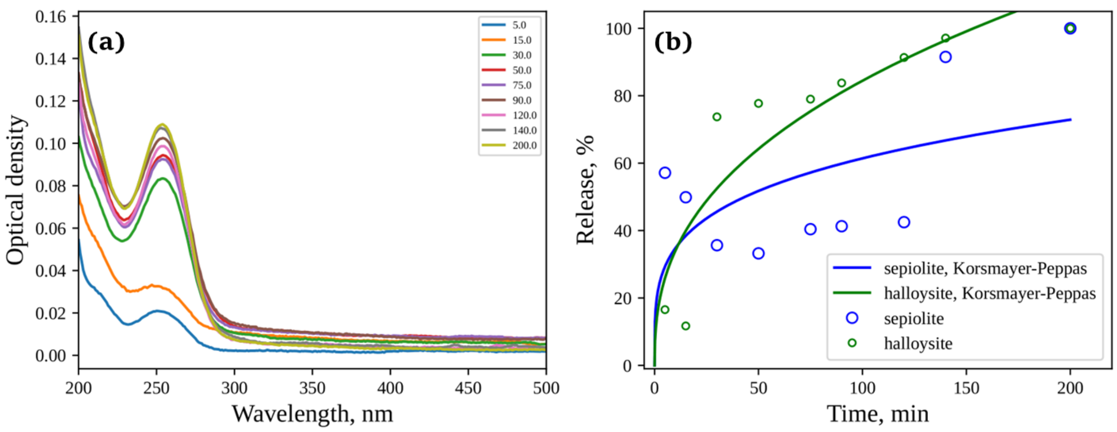

Figure 5 Release of 4-hydroxybenzoic acid from Hal-Ag-pHBA and Sep-Ag-pHBA composites: optical density spectra (time, min is shown in the legend) (a); the acid release fitted with a Korsmeyer-Peppas model, sepiolite - R^2 = 0.2080, halloysite – R^2 = 0.3349 (b).

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Table 1 Antibacterial activity of 4-hydroxybenzoic acid from halloysite and sepiolite and of sorbic acid from halloysite and sepiolite.

Sample	Diameter of the growth inhibition zone, mm (*S. aureus* MRSA 45)
Hal-Ag-PMo	9±2
Sep-Ag-PMo	12±2
4-Hydroxybenzoic acid	11±2
Sorbic acid	0
Hal-Ag-pHBA	14±2
Sep-Ag-pHBA	16±2
Hal-Ag-Sorb	15±2
Sep-Ag-Sorb	13±2

4. Limitations

Upon achieving all the scientific objectives set in this work, it is planned to conduct in vivo experiments, which will give a more detailed idea of the effectiveness of these materials inside a living cell. It is also necessary to understand the possible toxic effects of such antimicrobial materials. In case of successful completion of all stages of scientific work, the antibacterial drug will be transferred to subsequent preclinical studies. As a result of the project, scientific foundations will be developed for the creation of new-generation antibacterial drugs to solve urgent problems of preventive medicine.

5. Conclusions

As a result of the combination of two biocides (metal ions and acid) a synergistic effect was found. When combining silver nanoparticles and organic acids, it was found that the largest diameter of the growth suppression zones (mm) of *Staphylococcus aureus* (strain MRSA45) samples with sorbic acid (13-15 mm) are developed. The full release from the pores of the carriers occurs within 150–200 min.

Supplementary materials

No supplementary materials are available.

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Author contributions

Data curation, visualization, – review & editing: A.N.
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Formal Analysis: A.N., M.R., A.V, C.S.
Methodology, writing – original draft: C.S.
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Conflict of interest

The authors declare no conflict of interest.

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