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GOLD NANOPARTICLES STABILIZED WITH AMINOPOLYCARBOXYLIC ACIDS

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This study presents the synthesis, morphological characterization, and preliminary antimicrobial evaluation of novel colloidal gold nanoparticle (AuNP) systems stabilized with aminopolycarboxylic acids: ethylenediaminetetraacetic acid (EDTA) and ethylenediaminedisuccinic acid (EDDS). These complexing agents act not only as chelators but also as simultaneous reducing and stabilizing agents in the formation of AuNPs, offering a green and environmentally friendly approach to nanomaterial fabrication. The synthesis was carried out under mild aqueous conditions without external protective additives, enabling the production of stable colloidal systems with minimal side products. The resulting nanoparticles were characterized by UV-Vis spectroscopy, FTIR spectroscopy, and scanning electron microscopy (SEM). Characteristic surface plasmon resonance (SPR) bands were observed in the 530–550 nm range, with their intensity and spectral position sensitive to pH, ligand nature, and stabilization time. The most stable and monodisperse systems were obtained at pH≈9, with spherical nanoparticles ranging in size from 8 to 20 nm. Particular emphasis was placed on evaluating the biological activity of the synthesized dispersions. Antimicrobial screening was performed against Gram-positive (*Bacillus subtilis*) and Gram-negative (*Escherichia coli*) bacterial strains. The results demonstrated moderate to high bactericidal activity, especially in EDTA-stabilized samples, likely due to enhanced surface stabilization and potential ligand involvement in membrane interactions.

Keywords: gold nanoparticles, complexes, aminopolycarboxylic acids, nanosystems, morphology, dispersion, antimicrobial activity.

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Introduction

In recent decades, the development of nanotechnology has reached its peak. Of particular interest to researchers are nanosystems of a given composition with predicted properties. When used in chemistry, medicine, biotechnology, the size of nanoparticles or nanosystems is of great importance, since it depends on the permeability, activity, solubility and toxicity of nanoparticles [1]. The peculiarity of such nanoparticles is that they easily form complex

compounds with organic ligands, which have new properties compared to macrocompounds. Thus, nanoparticles can bind with complexones, nucleic acids, proteins, integrate into membranes, penetrate into cellular organelles, changing the functions of biostructures [2]. A number of authors have shown that the biological activity of metal nanoparticles is determined not only by their size, but also by their shape: dendritic and spindle-shaped nanoparticles have higher cytotoxicity than spherical particles [3]. Thus,

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metal nanoparticles have biological activity, the severity of which depends on their size, shape, surface structure, state of aggregation, chemical composition, solubility and a number of other factors [4]. Among the various forms of nanomaterials, solutions of metal nanoparticles are of interest. Their advantage lies in a relatively narrow distribution by size (up to 12 nm) and shape (mainly spherical) and a long period of preservation of biological activity. Therefore, the use of stable metal nanoparticles in aqueous solutions is promising in various fields of biology, veterinary science and medicine. In this regard, an urgent task is to search for new methods of forming monodisperse systems with a controlled size of nanoparticles.

Among the nanoparticles under study, special attention is paid to nanoparticles of noble metals, in particular gold, for the creation of new functional materials: optical and nanoelectronic devices, chemical and biological sensors, and catalysts. Non-aggregated gold nanoparticles (AuNPs) are used in detection systems [5], for targeted drug delivery, including photothermal therapy [6,7], and for the destruction of malignant cells [8].

One of the key aspects of the study of gold nanoparticles is their stability in solutions, which is achieved with the help of various stabilizers. In this context, aminopolycarboxylic acids (complexons, APA), such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), ethylenediaminediacetic acid (EDDS) play an important role. These compounds form strong complexes with metal ions, preventing the aggregation of nanoparticles and ensuring their long-term stability in aqueous environments. The use of complexes as stabilizers and modifiers of gold nanoparticles opens up new opportunities for the creation of functional nanomaterials with specified properties.

In studies [9,10], gold nanoparticles were synthesized from HAuCl_4 using EDTA as a reducing agent and it was shown that the size of the obtained AuNPs is determined by the reactivity of the Au(III) ionic forms and the charge of the EDTA molecule at different pH. By changing the pH of the reaction medium, it is possible to regulate both the size of Au nanoparticles (from 25 to 100 nm) and their shape (nanowires, spherical particles). Bonggotgetsakul et al. [11] obtained a monolayer of gold nanoparticles of average size 20 nm on the surface of a polymer membrane using EDTA solutions (pH 6) as a reducing agent. At the same time, increasing the concentration of EDTA and the temperature of the solution contributed to the decrease in the size of AuNPs. Mogilireddy et al. [12] fabricated gold nanoparticles

coated with Gd chelate with diethylenetriaminepentaacetic acid (Au@GdL) by replacing Au citrate with a GdDTPA complex. The average size of Au@GdL was 12 nm and they can be used as contrast agents in MRI diagnostics.

Thus, the use of aminopolycarboxylic acids as reducing agents in chemical condensation allows not only to stabilize the system, but also to control the particle size [13,14].

The aim of this work is the synthesis of gold(III) complexes with ethylenediaminetetraacetate and its structural analogue ethylenediaminedisuccinate, their transformation into a dispersed state and the synthesis of dispersed nanosystems by complexometric reduction. This synthesis does not require the selection of a separate stabilizer, since complexones have a diphilic structure, i.e. are surface-active substances and perform the function of the latter. When gold interacts with complexones, along with the reduction processes, complex particles will be formed, which act as dispersion stabilizers. The use of complexones as a reducing agent in chemical condensation allows not only to stabilize systems, but also to control the size of particles depending on the pH of the solution. It should be noted that Au(III) complexes with EDDS have practically not been studied.

Experimental

Materials and synthesis

For the synthesis of Au(III) complexes, solutions of tetrachloroauric acid (HAuCl_4) and sodium salts of aminodicarboxylic acids (Na_2EDTA , $\text{Na}_2\text{H}_2\text{EDDS}$) were used as starting reagents. The synthesis was carried out in aqueous solutions at a concentration of the starting components of 0.05 M and a ratio of $\text{HAuCl}_4:\text{Na}_2\text{EDTA}/\text{Na}_2\text{H}_2\text{EDDS}=1:1$, pH=7–8. The choice of such a low concentration is due to the reduction processes that occur at high concentrations and pH of solutions. The complexes were precipitated from the solution with acetone and/or alcohol, filtered and dried in a vacuum desiccator over calcium chloride in a dark place. Unlike previously studied systems [15], the nature of the solvent used for precipitation does not affect the shape of the particles. The $\text{Na}[\text{AuEDTA}]$ powder had a pink-violet color. EDDS-based complexes were dark gray in color and precipitated immediately upon decantation of the solutions.

To 0.5 ml (0.1 M) of HAuCl_4 solution, 0.2 ml (0.025 M/0.05 M) of disodium salt of ethylenethiaminetetraacetate/disodium salt of ethylenediaminedisuccinate, respectively, were added. It should be noted that $\text{Na}_2\text{H}_2\text{EDDS}$ has a higher reducing power, so the synthesis was carried out at lower concentrations. The solution was brought to

5 ml, after which the pH was adjusted with 0.1 M NaOH solution on MS without heating. Boiling water was poured into the resulting system and placed on a heated stirrer, temperature 80°C for 2 hours. Disperse systems containing gold nanoparticles were synthesized at pH=3; 7–7.5; 9, and 11. The solution obtained after mixing the components had a pink color, but during heating the color of the solution changed. After pouring the solution into boiling water, a color change was observed. For pH=3, the solution became blue-violet; for pH=7.5; 9; and 11, it turned pink. During heating, the colors of the solutions became more saturated, and after 90 min they did not change.

Previously [9], it was established that in an alkaline medium in the presence of tetrachloroaurate and EDTA, EDTA decarbonylation occurs and formaldehyde is formed, which, depending on the pH, interferes with the reduction process and promotes synthesis. As for another reduction mechanism, the zwitterionic structure that complexones have has an excess charge that can transfer to the metal ion.

Methods

The IR spectra of the complexes were recorded on a Spectrum BX II FT-IR spectrophotometer (Rerkin-Elmer) in the range from 400 to 4000 cm^{-1} in the solid state in KBr tablets.

Electronic absorption spectra (UV-VIS spectra) were recorded on a UV/VIS Shimadzu UV-3600 spectrophotometer in the quartz cuvettes with $l=1$ cm (measurement range of 10000–50000 cm^{-1} ; relative error in the measurement of absorbance was ± 0.05).

Micrographs of complex samples were recorded on a Tescan Mira 3 LMU scanning electron microscope (SEM).

The antibacterial properties of powdered Au(III) nanoparticles were evaluated on a solid nutrient medium (nutrient agar) by the disk diffusion method. The preparation of the nutrient agar medium was

carried out according to the following method: the nutrient agar solution was boiled until completely dissolved, followed by sterilization by autoclaving. After cooling to 45°C, the nutrient medium was poured into sterilized Petri dishes and left to solidify. Microorganisms were cultivated in an incubator for 24 h at a temperature of 37°C in a sterile liquid nutrient medium (meat-peptone broth). To obtain a suspension of microorganisms, the inoculant was washed with sterile saline and standardized to 0.5 units according to the McFarland standard. As test cultures, the strain of gram-positive spore-forming rod-shaped bacterium *Bacillus subtilis* UKM B-5006^T and the strain of gram-negative rod-shaped bacterium *Escherichia coli* UKM B-906 were used. Bacterial and fungal cultures were inoculated into sterile Petri dishes. Filter paper discs moistened with distilled water and a sample of the powder of the studied compounds were placed on the inoculated surface. The nutrient medium with the sample was incubated at a temperature of 37°C for three days, monitoring changes daily. The diameter of the zone of inhibition (mm) was measured with a caliper and taken as a measure of antibacterial activity.

Results and discussion

To confirm the formation of Au(III) complexes with aminopolycarboxylic acids and to establish the method of coordination of the functional groups of the ligands to the metal ion, IR spectra were recorded (Table 1).

In all IR spectra of Au complexes with diamine complexones, a broad band with a frequency of approximately 3400 cm^{-1} is observed, which corresponds to the stretching vibrations of outer-sphere water molecules. The absence of absorption bands at 1710/1724 cm^{-1} , which correspond to protonated carboxyl groups of complexones, indicates that all carboxy groups participate in complexation. In

Table 1

Basic vibrational frequencies (cm^{-1}) and their assignments in the IR spectra of Au(III) complexes with aminopolycarboxylic acids

Band assignment	AuEDTA	Na ₂ EDTA	Na ₂ EDDS	AuEDDS
$\nu(\text{H}_2\text{O})_{\text{inter}}$	3450	3408	3447	3420
$\nu(\text{C-H})$	2950, 2875	2997	3038	2950, 2820
$\nu(\text{COOH})$	–	1710	1724	–
$\nu_{\text{as}}(\text{COO}^-)$	1570	1640	1633, 1608, 1567	1590
$\nu_{\text{s}}(\text{COO}^-)$	1410, 1385	1436	1400–1450	1410, 1330
$\nu(\text{CN})$	1130	1095	1100	1108
$\nu(\text{CC})$	925, 860	920, 860	930, 886	932, 870
$\nu(\text{M-O})$	530, 555	–	–	550, 585, 620
$\nu(\text{M-N})$	454	–	–	468

the spectra of the complexonates, bands were recorded in the regions of $1410\text{--}1340\text{ cm}^{-1}$ and $1640\text{--}1560\text{ cm}^{-1}$, related to asymmetric and symmetric stretching vibrations of the carboxyl groups, respectively, which are significantly shifted to the low-frequency region relative to pure ligands, indicating the formation of a bond between metal ions and dissociated COO groups. The difference in the position of the $\nu_{\text{s}}\text{COO}^-$ and $\nu_{\text{as}}\text{COO}^-$ bands in the complexes ($\Delta\nu \approx 180\text{ cm}^{-1}$) indicates their monodentate coordination. The presence of multiplet bands at $530\text{--}620\text{ cm}^{-1}$, related to the stretching vibrations of the M–O bond, in the low-frequency region of the IR spectra also indicates the coordination of the central atom with the carboxyl groups of the complexons.

The spectra of the AuEDTA and AuEDDS complexes contain an absorption band at 454 and 468 cm^{-1} , corresponding to the stretching vibrations of the M–N bond. The formation of a bond between the metal and the amino groups of the acids is also indicated by the presence in the IR spectra of a band of stretching vibrations of the C–H bond in the region of $2950\text{--}2820\text{ cm}^{-1}$. This band is one of the criteria for the formation of the M–N coordination bond in complexonates. The betaine structure of EDTA/EDDS corresponds to $\nu(\text{CH}) = 2997/3038\text{ cm}^{-1}$, respectively, and in the complexes a decrease in the frequency $\nu(\text{CH})$ of approximately by $80\text{--}120\text{ cm}^{-1}$ is observed as a result of the induction effect $\text{R}-\text{C}-\text{N} \rightarrow \text{M}$. The metal–nitrogen coordination bond is formed, and the betaine hydrogen atom is split off.

Taking into account the structure of EDTA and EDDS, it can be assumed that the AuEDTA complex will have a monomeric structure, and the AuEDDS complex will have a dimeric structure, in which the binuclear structure is formed by the coordination ratio of the acid atom of the β -carboxyl group of EDDS with the adjacent metal atom.

The simplest and most accessible method that allows establishing the presence of noble metal nanoparticles in the system is the method of electronic absorption spectroscopy. The presence of nanosized particles allows registering the band of surface plasmon resonance (SPR) in the absorption spectra, which is a collective oscillation of particles smaller than the wavelength of radiation. Probably, the dissociation of aminopolycarboxylic acids when changing pH is accompanied by a change in the refractive index of the dispersion medium, which will cause a shift of the maximum of the SPR band. It is for this reason that the position of the band SPR, and the change in its position over time, allows us to draw conclusions about the stability of the system and intermolecular interactions in it. The shape and position of the PPR

band are significantly influenced by the characteristics of individual particles and the dielectric constant of the dispersion medium. Therefore, electronic absorption spectra in the UV-visible region were recorded for all the studied solutions (Figs. 1 and 2). The SPR band was observed in all spectra, but the position of the maximum and the width of the band differed, which is evidence of different dispersity.

As can be seen from Figs. 1 and 2, regardless of the aminopolycarboxylic acid, at $\text{pH}=3$ the solutions have a blue color with $\lambda_{\text{max}} = 542\text{ nm}$ and 534 nm for AuEDDS and AuEDTA, respectively. In this case, the intensity of the band is low, and the half-width of the line (40 nm) indicates the polydispersity of the systems and the large particle size ($\approx 40\text{ nm}$) [9].

With increasing pH ($7.5\text{--}11$), a hypsochromic shift of the PPR band occurs for both systems with $\lambda_{\text{max}} = 516_{\text{AuEDDS}}$ and 522_{AuEDTA} nm, which is accompanied by a change in the color of the solutions from blue to pink. The intensity of the bands increases,

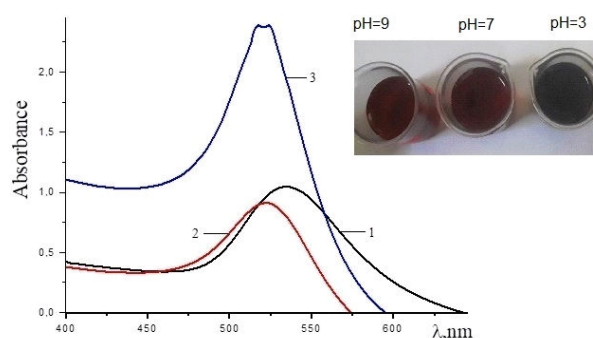


Fig. 1. UV-visible absorption spectra of AuNPs obtained by EDTA reduction of HAuCl_4 at pH 3 (1); 7.5 (2); and 9 (3). Inset shows the color change of Au–EDTA/EDDS solutions at different pH

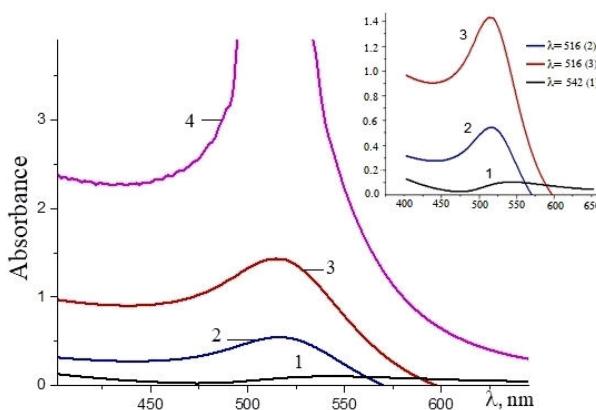


Fig. 2. UV-visible absorption spectra of AuNPs obtained by EDDS reduction of HAuCl_4 at pH 3 (1); 7 (2); 9 (3); and 11 (4)

and the half-width of the bands decreases by half, which, based on literature data, allows us to assume the presence of nanoparticles with a size of 20–30 nm in the system [9,10]. In the case of the Au-EDTA system at pH=9, a splitting of the maximum into two components ($\lambda=518$ and 524 nm) is observed, which may indicate the same ratio in the system of nanoparticles of two sizes. Since the positions of the maxima of the split band are quite close, it can be expected that during the maturation of the nanosystem their sizes will equalize (possibly due to intermolecular interactions).

The aggregative stability of the systems under study over time was estimated. To this end, repeated spectra of solutions of dispersed gold systems from APA were recorded after 7 days (Fig. 3a,b, Table 2). In the case of ethylenediaminedisuccinate, compared with the original system at pH=3, the intensity of the PPR band decreases, and its half-width increases, which is due to the aggregation of particles of the colloidal solution. In a weakly alkaline (pH=7.5) or alkaline (pH=9) solution, the λ_{\max} shift almost does not occur, which indicates a high dispersion of the system, in which particles of the same size prevail and the habituation of the dispersed system. The width of the line indicates a uniform distribution of the dispersed phase in the dispersion medium.

In the Au-EDTA system at pH=3, there is a shift of the maximum to the long-wave region by 3 nm and a slight increase in the intensity of the band, but at the same time the half-width of the line increases slightly, i.e. the system is not stable enough. At pH 7.5, the intensity of the band increases by 40%, the position of λ_{\max} and the half-width practically

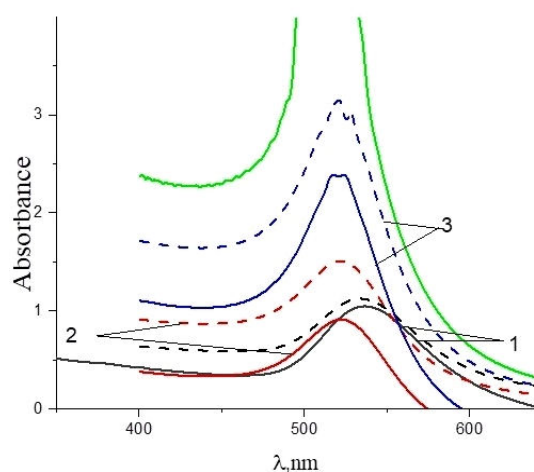
do not change. The increase in intensity may (Fig. 3a, curve 2) indicate the recrystallization of small particles and the alignment of the particle size of the system as a whole, which causes an increase in the stability of the dispersed system. With increasing pH, a noticeable increase in the intensity of the band and a clear maximum were observed (Fig. 3a, curve 3), which may indicate the presence of predominantly close-sized particles in the system.

In the Au-EDDS system at pH=3, a non-obvious maximum of the PPR band is barely noticeable (Fig. 3b, curve 1); however, after a week, the intensity of the maximum is much lower, and a partial precipitate of metallic gold has precipitated from the solution. With an increase in pH to 7.5, an increase in the intensity of the band and a shift of the maximum to the short-wave region are observed, which indirectly indicates the presence of smaller particles in the system. A rather wide half-width of the line indicates the polydispersity of the system (Fig. 3b, curve 2). A significantly narrower half-width of the line and a higher intensity at pH>8 (Fig. 3b, curve 3) indicate the presence of small particles in the system and

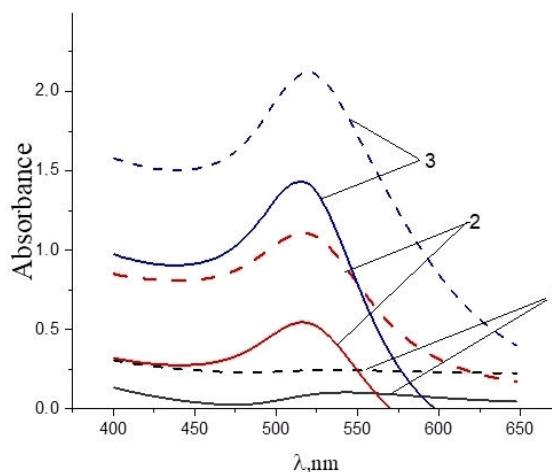
Table 2

Position of the SPR band in the electronic spectra of Au(III) complexes with aminopolycarboxylic acids

pH	λ_{\max} , nm			
	AuNPs-EDDS		AuNPs-EDTA	
	in 1 hour	in 7 days	in 1 hour	in 7 days
3	542	537	534	537
7.5	516	517	522	521
9	516	519	518, 524	521



a



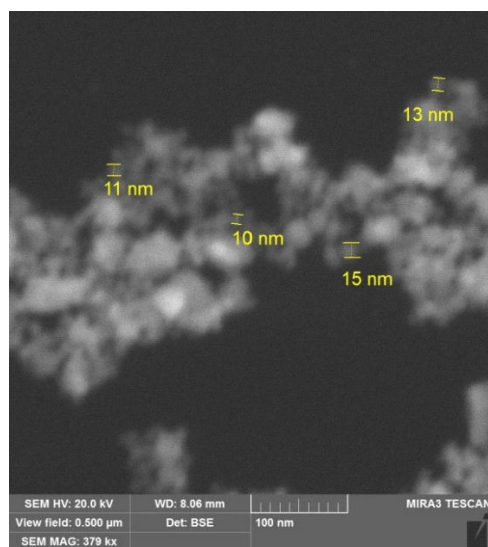
b

Fig. 3. Change in the position of the SPR band in the AuNPs-EDTA (a) and AuNPs-EDDS (b) systems after 1 hour (solid line) and 7 days (dashed line) depending on the pH: 1 – pH=3; 2 – pH=7.5; and 3 – pH=9

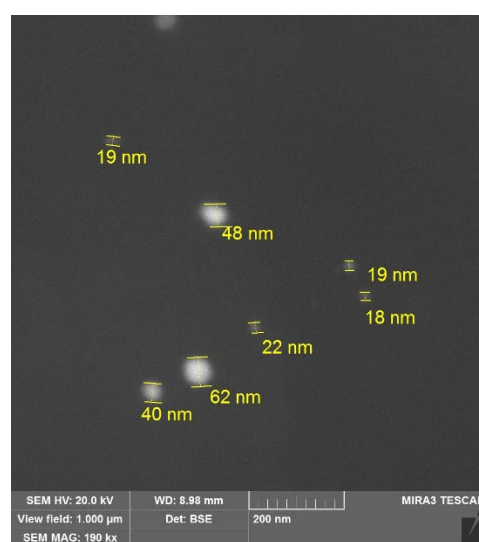
their uniform distribution in the dispersion medium.

The morphology and dispersion of the obtained AuNPs–EDTA/EDDS nanosystems and gold nanoparticles stabilized with aminopolycarboxylic acids were studied using scanning electron microscopy (Fig. 4). The obtained particles of the dispersed phase, as well as solid nanoparticles AuNPs have a spherical shape with an average particle size in the range of 8–60 nm. The size of the particles of the dispersed phase depends on the pH of the solution. In an acidic solution (pH=3), the recovery process occurs more slowly for both studied systems. The process is accompanied by the formation of polydisperse systems

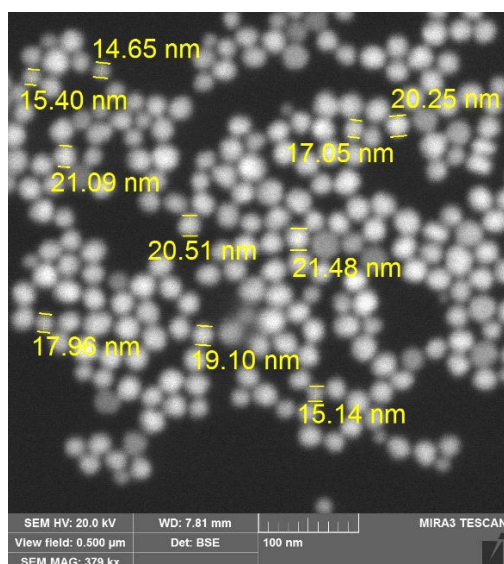
with noticeable agglomeration and an average size of 8–30 nm (Fig. 4a), which is in good agreement with the half-width of the PPR bands (Fig. 3, curve 1). Such systems are unstable due to the absence of complex particles in them, which can act as stabilizers of dispersed systems. Complex formation in the studied systems begins at pH>3.5. As the pH increases to 7, the particle size increases, but agglomeration processes are less noticeable (Fig. 4b). At pH=9 for systems based on Au–EDDS, the particle size does not exceed 9 nm (Fig. 4c); for the Au–EDTA system, the particle size is 15–20 nm (Fig. 4d). The morphology of the particles is spherical, agglomeration processes are



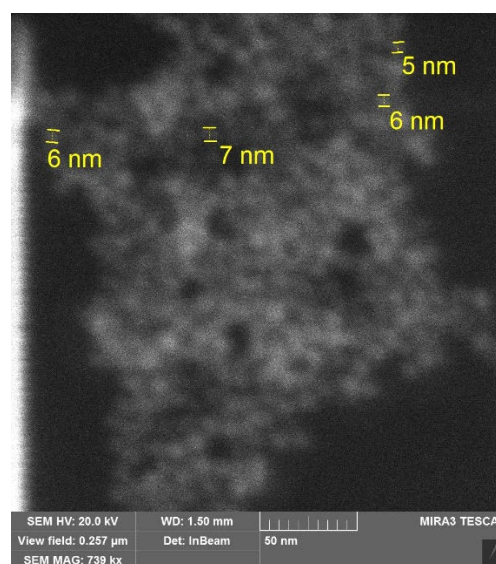
a



b



c



d

Fig. 4. SEM micrographs of the systems $\text{HAuCl}_4\text{:Na}_2\text{H}_2\text{EDTA}$ (a and b) and $\text{HAuCl}_4\text{:Na}_2\text{H}_2\text{EDDS}$ (c and d). Micrographs were recorded 24 hours after synthesis. Scale bars 100 nm (a and c); 200 nm (b); and 50 nm (d)

absent, the systems are resistant to temperature changes for a long time and do not require additional stabilization.

It is now known that gold nanoparticles exhibit biological activity [8]. Therefore, in this work, a study of the biological activity of AuNPs–EDTA/EDDS nanocomplexes was conducted (Table 3). It turned out that all the studied compounds showed inhibitory effect on the growth of *B. subtilis* and *E. coli* bacteria, but their activity was different. The most sensitive to both strains of bacteria was the AuNPs–EDTA complex with an inhibition zone of 3–7 mm (*B. subtilis*) and approximately 5 mm (*E. coli*). At the same time, the highest inhibitory effect was registered for AuEDTA on the *E. coli* culture, as indicated by well-defined transparent zones, where bacterial growth was completely absent.

The growth of the gram-negative bacterium *E. coli* was also inhibited by the AuNPs–EDDS complex (zones of inhibition being 0.5–3 mm). However, its effect on the gram-positive microorganisms *B. subtilis* was less pronounced (zones of inhibition being 0–3 mm) and the zones overgrown with culture




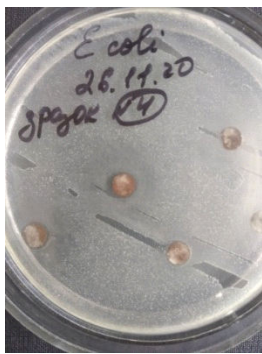
over time.

Thus, summarizing the testing of Au(III) complexonates against two bacterial strains, we can conclude that both complexes show antimicrobial activity (Fig. 5). However, the AuEDTA complexonate has a greater effect on cultures (especially on *B. Subtilis*), which contributed to a significant increase in inhibitory zones compared to the AuNPs–EDDS complexonate.

Probably, the lower antimicrobial effect of gold ethylenediamine disuccinate is associated with the high biological activity of ethylenediamine-N,N-disuccinic acid, which contains fragments of aspartic and succinic acids in its molecule, known as adaptogens. In a living organism, wine not only performs the function of delivering trace elements, but also carries a biologically active load. Under the action of enzymes of a living organism, the organic part of the complex breaks down into essential amino acids (arginine, leucine, isoleucine, valine, histidine, asparagine, and alanine), which are components of the metabolic chain.

Table 3

Effect of Au(III) complexing agents on *B. subtilis* and *E. coli* bacteria and size of the inhibition zone

System	Photograph and size of the inhibition zone (mm)	
	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>
AuNPs–EDTA		
	3–7	4–5
AuNPs–EDDS		
	0–3	0.5–3

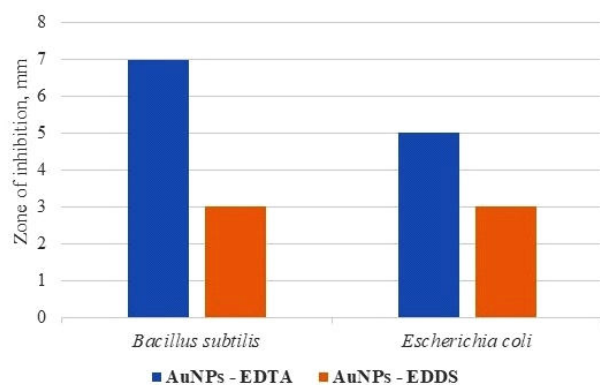


Fig. 5. Diagram comparing the antimicrobial activity of Au(III) complexes with aminopolycarboxylic acids against bacterial strains

Conclusions

Au(III) complexes with aminopolycarboxylic acids, EDTA and EDDS, was synthesized. The method of coordination of the central atom with the functional groups of the ligands was established. It was shown that the metal ion is bound to the dissociated carboxyl groups and the nitrogen atom of the amino group of the ligands. The AuEDTA complex probably has a monomeric structure, and the AuEDDS complex is a dimer, in which the binuclear structure is formed by the binding of the oxygen of the β -carboxylic group of EDDS to the neighboring metal atom.

The method of complexometric reduction was used to obtain nanodispersed systems of Au(III) with disodium salts of ethylenediaminetetraacetate and ethylenediaminedisuccinate. It was shown that the synthesized dispersed systems are aggregatively stable for a long period of time and have a uniform distribution of the dispersed phase in the dispersion medium. Regardless of the complexon, the synthesized nanoparticles have a spherical morphology and a dispersion in the range of 7–20 nm, depending on the reducing acid. The high stability of dispersed gold systems is due to the presence of complex particles in the system, which act as stabilizers of the synthesized systems.

The biological activity of AuNPs–EDTA/EDDS nanocomplexes was studied and it was shown that all the studied systems showed inhibitory effect on the growth of bacterial strains *Bacillus subtilis* and *Escherichia coli*. The highest inhibitory effect was registered for AuNPs–EDTA on *E. coli* culture.

Overall, this work highlights the potential of aminopolycarboxylic acids as versatile agents for the one-pot synthesis of functionalized AuNPs. The obtained findings lay the foundation for future development of biocompatible nanomaterials with

promising applications in medicine, antimicrobial systems, and chemical sensing.

Acknowledgments

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REFERENCES

1. Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations / Jeevanandam J., Barhoum A., Chan Y.S., Dufresne A., Danquah M.K. // *Beilstein J. Nanotechnol.* – 2018. – Vol.9. – No. 1. – P.1050-1074.
2. Novel effects of nanoparticulate delivery of zinc on growth, productivity, and zinc biofortification in maize (*Zea mays* L.) / Subbaiah L.V., Prasad T.N.V.K.V., Krishna T.G., Sudhakar P., Reddy B.R., Pradeep T. // *J. Agric. Food Chem.* – 2016. – Vol.64. – No. 19. – P.3778-3788.
3. Effect of lattice constant of zinc oxide on antibacterial characteristics / Yamamoto O., Komatsu M., Sawai J., Nakagawa Z.E. // *J. Mater. Sci. Mater. Med.* – 2004. – Vol.15. – P.847-851.
4. Bactericidal effect of iron oxide nanoparticles on *Staphylococcus aureus* / Tran N., Mir A., Mallik D., Sinha A., Nayar S., Webster T.J. // *Int. J. Nanomedicine.* – 2010. – Vol.5. – P.277-283.
5. Ray P.C., Yu H., Fu P.P. Nanogold-based sensing of environmental toxins: excitement and challenges // *J. Environ. Sci. Health C Environ. Carcinog. Ecotoxicol. Rev.* – 2011. – Vol.29. – No. 1. – P.52-89.
6. Size- and shape-dependent antibacterial studies of silver nanoparticles synthesized by wet chemical routes / Raza M.A., Kanwal Z., Rauf A., Sabri A.N., Riaz S., Naseem S. // *Nanomaterials.* – 2016. – Vol.6. – No. 4. – Art. No. 74.
7. Correction to: application of gold nanoparticles for improvement of analytical characteristics of conductometric enzyme biosensors / Soldatkin O.O., Soldatkina O.V., Piliponskiy I.I., Rieznichenko L.S., Gruzina T.G., Dybkova S.M., Soldatkin A.P. // *Appl. Nanosci.* – 2022. – Vol.12. – No. 4. – P.1005.
8. Dykman L., Khlebtsov N. Gold nanoparticles in biomedical applications: recent advances and perspectives // *Chem. Soc. Rev.* – 2012. – Vol.41. – No. 6. – P.2256-2282.
9. On the synthesis of Au nanoparticles using EDTA as a reducing agent / Dozol H., Meriguet G., Ancian B., Cabuil V., Xu H., Wang D., Abou-Hassan A. // *J. Phys. Chem. C.* – 2013. – Vol.117. – No. 40. – P.20958-20966.

10. *Diamai S., Negi D.P.* EDTA-capped gold nanoparticles as a colorimetric probe for aluminium // *Mater. Res. Express.* – 2016. – Vol.3. – No. 11. – Art. No. 115002.

11. *Bonggotgetsakul Y.Y.N., Catrall R.W., Kolev S.D.* The preparation of a gold nanoparticle monolayer on the surface of a polymer inclusion membrane using EDTA as the reducing agent // *J. Membr. Sci.* – 2011. – Vol.379. – No. 1-2. – P.322-329.

12. *Thermodynamic stability and kinetic inertness of a Gd-DTPA bisamide complex grafted onto gold nanoparticles / Mogilireddy V., Dechamps-Olivier I., Alric C., Lauren G., Laurent S., Vander Elst L., Chuburu F.* // *Contrast Media Mol. Imaging.* – 2015. – Vol.10. – No. 3. – P.179-187.

13. *Asemave K.* Greener chelators for recovery of metals and other applications // *Org. Med. Chem. Int. J.* – 2018. – Vol.6. – No. 4. – P.92-102.

14. *Facile synthesis of gold trisubstituted nanocrystals with controllable sizes and dihedral angles / Huo D., Ding H., Zhou S., Li J., Tao J., Ma Y., Xia Y.* // *Nanoscale.* – 2018. – Vol.10. – No. 23. – P.11034-11042.

15. *Synthesis and properties of new nanosystems of argentum / Berezhnyska O., Semeniv V., Sikorska K., Kamenska T., Khrokalo L., Trunova O.* // *Ukr. Chem. J.* – 2021. – Vol.87. – No. 2. – P.95-106.

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НАНОЧАСТИНКИ ЗОЛОТА, СТАБІЛІЗОВАНІ АМІНОПОЛІКАРБОНОВИМИ КИСЛОТАМИ

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У даній роботі надано результати синтезу, морфологічного аналізу та вивчення антимікробних властивостей нових колоїдних систем наночастинок золота, отриманих з використанням амінополікарбонowych кислот: етилендіамінтетраоцтової (EDTA) та етилендіаміндісукцинової (EDDS) кислот. Обґрунтовано застосування комплексонів не лише як хелатуючих агентів, а й як відновників і стабілізаторів у процесі формування наночастинок, що дозволяє реалізувати екологічно безпечний («зелений») підхід до синтезу наноматеріалів. Синтез наночастинок проводили за м'яких умов у водному середовищі без залучення додаткових захисних агентів, що дозволяє зменшити кількість побічних продуктів та отримати стабільні колоїдні системи. Сформовані наночастинок були охарактеризовані методами УФ-видимої спектроскопії, ІЧ-Фур'є спектроскопії та скануючої електронної мікроскопії. У спектрах поглинання для зразків з EDTA та EDDS зафіксовані характерні смуги поверхневого плазмонного резонансу (ППР) у діапазоні 530–550 нм, інтенсивність і положення яких чутливі до рН середовища, природи ліганду та часу стабілізації. Найбільш стабільні та однорідні системи формувалися при рН≈9, де домінують сферичні наночастинок діаметром 8–20 нм. Здійснено попередню оцінювання антимікробної активності синтезованих колоїдних систем відносно грампозитивних (*Bacillus subtilis*) та грамнегативних (*Escherichia coli*) штамів. Виявлено помітну бактерицидну активність, особливо у зразків, стабілізованих EDTA, що ймовірно зумовлено кращою стабілізацією активної поверхні наночастинок і можливою участю ліганду в мембранній взаємодії.

Ключові слова: наночастинок золота, комплекси, амінополікарбонowych кислоти, наносистеми, морфологія, дисперсність, антимікробна активність.

GOLD NANOPARTICLES STABILIZED WITH AMINOPOLYCARBOXYLIC ACIDS

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This study presents the synthesis, morphological characterization, and preliminary antimicrobial evaluation of novel colloidal gold nanoparticle (AuNP) systems stabilized with aminopolycarboxylic acids: ethylenediaminetetraacetic acid (EDTA) and ethylenediaminedisuccinic acid (EDDS). These complexing agents act not only as chelators but also as simultaneous reducing and stabilizing agents in the formation of AuNPs, offering a green and environmentally friendly approach to nanomaterial fabrication. The synthesis was carried out under mild aqueous conditions without external protective additives, enabling the production of stable colloidal systems with minimal side products. The resulting nanoparticles were characterized by UV-Vis spectroscopy, FTIR spectroscopy, and scanning electron microscopy (SEM). Characteristic surface plasmon resonance (SPR) bands were observed in the 530–550 nm range, with their intensity and spectral position sensitive to pH, ligand nature, and stabilization time. The most stable and monodisperse systems were obtained at pH≈9, with spherical nanoparticles ranging in size from 8 to 20 nm. Particular emphasis was placed on evaluating the biological activity of the synthesized dispersions. Antimicrobial screening was performed against Gram-positive (*Bacillus subtilis*) and Gram-negative (*Escherichia coli*) bacterial strains. The results demonstrated moderate to high bactericidal activity, especially in EDTA-stabilized samples, likely due to enhanced surface stabilization and potential ligand involvement in membrane interactions.

Keywords: gold nanoparticles; complexes; aminopolycarboxylic acids; nanosystems; morphology; dispersion; antimicrobial activity.

REFERENCES

1. Jeevanandam J, Barhoum A, Chan YS, Dufresne A, Danquah MK. Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. *Beilstein J Nanotechnol*. 2018; 9: 1050-1074. doi: 10.3762/bjnano.9.98.
2. Subbaiah LV, Prasad TNVKV, Krishna TG, Sudhakar P, Reddy BR, Pradeep T. Novel effects of nanoparticulate delivery of zinc on growth, productivity, and zinc biofortification in maize (*Zea mays* L.). *J Agric Food Chem*. 2016; 64(19): 3778-3788. doi: 10.1021/acs.jafc.6b00838.
3. Yamamoto O, Komatsu M, Sawai J, Nakagawa ZE. Effect of lattice constant of zinc oxide on antibacterial characteristics. *J Mater Sci Mater Med*. 2004; 15(8): 847-851. doi: 10.1023/B:JMSM.0000036271.35440.36.
4. Tran N, Mir A, Mallik D, Sinha A, Nayar S, Webster TJ. Bactericidal effect of iron oxide nanoparticles on *Staphylococcus aureus*. *Int J Nanomedicine*. 2010; 5: 277-283. doi: 10.2147/IJN.S9220.
5. Ray PC, Yu H, Fu PP. Nanogold-based sensing of environmental toxins: excitement and challenges. *J Environ Sci Health C Environ Carcinog Ecotoxicol Rev*. 2011; 29(1): 52-89. doi: 10.1080/10590501.2011.551315.
6. Raza MA, Kanwal Z, Rauf A, Sabri AN, Riaz S, Naseem S. Size- and shape-dependent antibacterial studies of silver nanoparticles synthesized by wet chemical routes. *Nanomaterials*. 2016; 6(4): 74. doi: 10.3390/nano6040074.
7. Soldatkin OO, Soldatkina, OV, Piliponskiy II, Rieznicenko LS, Gruzina TG, Dybkova SM, et al. Correction to: Application of gold nanoparticles for improvement of analytical characteristics of conductometric enzyme biosensors. *Appl Nanosci*. 2022; 12(4): 1005. doi: 10.1007/s13204-021-01981-7.
8. Dykman L, Khlebtsov N. Gold nanoparticles in biomedical applications: recent advances and perspectives. *Chem Soc Rev*. 2012; 41(6): 2256-2282. doi: 10.1039/C1CS15166E.
9. Dozol H, Meriguet G, Ancian B, Cabuil V, Xu H, Wang D, et al. On the synthesis of Au nanoparticles using EDTA as a reducing agent. *J Phys Chem C*. 2013; 117(40): 20958-20966. doi: 10.1021/jp4067789.
10. Diamai S, Negi DP. EDTA-capped gold nanoparticles as a colorimetric probe for aluminium. *Mater Res Express*. 2016; 3(11): 115002. doi: 10.1088/2053-1591/3/11/115002.
11. Bonggotgetsakul YYN, Cattrall RW, Kolev SD. The preparation of a gold nanoparticle monolayer on the surface of a polymer inclusion membrane using EDTA as the reducing agent. *J Membr Sci*. 2011; 379(1-2): 322-329. doi: 10.1016/j.memsci.2011.06.003.
12. Mogilireddy V, Dechamps-Olivier I, Alric C, Lauren G, Laurent S, Vander Elst L, et al. Thermodynamic stability and kinetic inertness of a Gd-DTPA bisamide complex grafted onto gold nanoparticles. *Contrast Media Mol Imaging*. 2015; 10(3): 179-187. doi: 10.1002/cmmi.1616.
13. Asemave K. Greener chelators for recovery of metals and other applications. *Org Med Chem Int J*. 2018; 6(4): 92-102. doi: 10.19080/OMCIJ.2018.06.555694.
14. Huo D, Ding H, Zhou S, Li J, Tao J, Ma Y, et al. Facile synthesis of gold trisubstituted nanocrystals with controllable sizes and dihedral angles. *Nanoscale*. 2018; 10(23): 11034-11042. doi: 10.1039/C8NR02949K.
15. Berezhytska O, Semeniv V, Sikorska K, Kamenska T, Khrokalo L, Trunova O. Synthesis and properties of new nanosystems of argentum. *Ukr Chem J*. 2021; 87(2): 95-106. doi: 10.33609/2708-129X.87.02.2021.95-106.