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"GREEN" SYNTHESIS OF NANOPARTICLES OF PRECIOUS METALS: ANTIMICROBIAL AND CATALYTIC PROPERTIES

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Здійснено "зелений" синтез монометалічних (Au, Ag) та біметалічних (Au–Ag) наночастинок (НЧ) з водних розчинів іонів металів відповідних прекурсорів із використанням відходів агропромислового виробництва (шкірки винограду). Наразі гостро стоїть проблема утилізації відходів агропромислового комплексу, раціонального природокористування та перехід до використання екологічно безпечних енергоефективних технологій. Тому спостерігається тенденція використання "зелених" технологій при одержанні наноматеріалів, що вважаються екологічно безпечними та ресурсозберігаючими. Встановлено ефективність використання харчових відходів (шкіра винограду), як відновника та стабілізуючого агента для формування наночастинок дорогоцінних металів моно- та біметалевої структури. Екстракцію біологічної сировини проводили у водному середовищі під дією короткотривалого впливу розряду низькотемпературної плазми. На основі комплексного аналізу компонентного складу екстракту встановлено, що гідроксильні, карбонільні та карбоксильні функціональні групи органічних сполук екстракту шкірки винограду, відповідають за відновлення іонів металів та стабілізацію отриманих НЧ. Встановлено, що формування моно- та біметалічних НЧ характеризується присутністю піка для Ag^0 ($\lambda_{мак}$=440 нм), для Au^0 ($\lambda_{мак}$=540 нм), Ag–Au ($\lambda_{мак}$=510 нм). Розмір та стабільність наночастинок одержаних "зеленим" синтезом оцінено в порівнянні з показниками при плазмохімічному способі формування наночасток. Встановлено антибактеріальні, каталітичні та протикорозійні властивості синтезованих наночастинок. Одержані монометалічні (Au, Ag,) та біметалічні (Au–Ag) наночастинок показали відмінну каталітичну активність для відновлення р-нітрофенолу (4-НФ) до р-амінофенолу (4-АФ) у присутності $NaBH_4$. Синтезовані НЧ продемонстрували антибактеріальну активність проти грампозитивних та грамнегативних бактерій. Отримані результати дають змогу розширити практичне застосування наночастинок металів в різних галузях виробництв та вирішити питання щодо збільшення переробки та повторного використанню неліквідних відходів

Ключові слова: водний екстракт, компонентний склад, виноград, відновлення, нітрофенол, антибактеріальні властивості, антиоксидантна активність

1. Introduction

Nowadays, one of the strategic directions of research is the production of nanosized metals of a wide range and variety of structural organization. There are distinguished monometallic nanoparticles and bimetallic nanostructures: alloys, core-shell, and a mixture of particles [1]. Among the most demanded are mono- and bimetallic nanoparticles (NPs) of noble metals (Au, Ag). Both individually and as components of composite materials, mono- and bimetalllic nanoparticles of noble metals are effective when used in various industries. Due to a wide range of physico-chemical and pronounced antimicrobial properties of NPs, they are used in water purification technologies as part of photo-catalysts [2], in sensory materials [3], anti-corrosion agents [4], cosmetics, medicine [5], etc.

The diversity and promise of the practical application of mono- and bimetallic NPs of precious metals bring forth the relevance of developing a highly efficient, environment-friendly and universal method of obtaining NPs. This method should allow controlled synthesis of NPs of mono- and bimetallic structures from available and cheap raw materials using the minimum number of technological steps. It is now widely acknowledged that the existing methods for the industrial production of nanodispersions of metals and the used reagent components are energy-consuming and, as a rule, toxic [6]. In accordance with the international standards, one of the innovative ways to reduce the amount of reagent components and replace the toxic components is the use of "green" technologies. The latter include various methods that facilitate the conditions for obtaining nanosized compounds with the use of various wastes of natural raw materials [7]. One of the main directions is the use of extracts of plant material wastes for synthesizing of nanosized metals. The advantages of the method are the renewability of the raw material base, the low cost of reagents, and their environmental friendliness.

However, the key issue in the "green" transition from laboratory studies to nanosilver production is increasing the concentration of extracts from plant-based waste and the efficiency of the produced nanoparticles. In order to increase the efficiency of extraction, traditional types of plant material processing (UV light and -radiation) are used; although, along with the advantages, they have disadvantages. Therefore, the issue of working out new energy-efficient and ecological methods to intensify the extraction of plant material for further "green" synthesis of nanomaterials is relevant.

Given the promising use of natural plant material for the synthesis of nanomaterials, the research that is aimed at further improving and developing "green" technologies for the controlled synthesis of nanoparticles of mono- and bimetallic structures is considered relevant. Such studies include selecting biological material for extraction and specifying the properties of the nanosized compounds intended for further practical application.

2. Literature review and problem statement

Currently, "green" synthesis uses a wide range of plant raw materials and agricultural processing waste. The use of organic compounds of plant origin is advantageous due to the existing polyfunctionality of the componential composition, annual renewability and environmental safety of plant materials.

In [8], nanoparticles of the complex structure Au_2Ag_2AgCl were synthesized due to the liana (Momordica charantia) leaves extract. The extraction was made by traditional maceration within 20 minutes at 70 °C. The authors revealed only the catalytic properties of the generated NPs and demonstrated the effectiveness of 2,4,6-trinitrophenols for the catalytic destruction. The authors of [9] obtained the bimetallic alloy Ag-Au with the use of fruit extract (Goji berries). The extract was obtained by maceration during boiling. Also, the authors demonstrated only the catalytic properties of the nitrophenol decay. Other properties (antimicrobial, antioxidant, etc.) of the NPs remained non-identified.

A long list of biogenic material (plant material, bacteria, and mushrooms) is suggested for the synthesis of the NPs of various metals in [10]. However, there is no data on the properties of the obtained materials and an industry for their further practical application. It should also be noted that the authors of other studies [8–10] consider only traditional methods, particularly maceration method, for obtaining extracts of the plant material. The main disadvantage of the method is incompleteness of the extraction. This allows a low yield of metal nanoparticles in further synthesis, limits polyfunctionality and calls into question the possibility of using NPs and "green" synthesis on an industrial scale. In addition, all of the tested plant materials are not waste products. The authors of [11] obtained an extract from rape (Brassicaceae) waste and studied its componential composition. The authors of [12] showed that a promising form of plant material for synthesizing organic compounds is the use of waste from grape processing. The authors determined the phyto-chemical composition of the grape skin extract and made the quantum-chemical calculations of the main components. The authors of [13] and [14] report on the use of vanillin extract and phenolic compounds, respectively, in corrosion-resistant coatings. However, it should be noted that studies [11–14] report on the use of isopropyl alcohol in the extraction, which is not common in the synthesis of nanomaterials.

At present, there is a tendency to use methods that would allow to increase the efficiency of extracting organic compounds, while simultaneously reducing the energy intensity and duration of the process by using the complex effect of physical and chemical factors on the process. The authors of [15] showed the possibility of increasing the effectiveness of NP synthesis by raising the rate of the plant material extraction. It is effective to use gamma radiation to intensify the formation of nanoparticles in the presence of plant extract [16]. However, the presented findings concern only the conditions for obtaining a NPs, and there are no data on the properties of the obtained nanomaterials. The newest method of processing homogeneous and heterogeneous systems, including plant material, is plasma discharges of various configurations [17]. However, the problem of the influence of plasma processing on various types of plant material remains unsolved.

Among the various types of plasma discharges, the most promising type is the use of low-temperature plasma discharges [18]. Its advantage is high efficiency, which is due to short-term, one-stage process and complex action of a number of physico-chemical factors (electrochemical oxidation-reduction, UV radiation, a flow of charged particles from the gas phase to the surface of the liquid medium, etc.) [19]. These factors may increase the efficiency of extraction and concentration of the obtained extracts, and, as a consequence, the cost efficiency of further synthesis of mono- and bimetallic NPs. They can also enhance the functionality of nanomaterials.

All this suggests that it is expedient to carry out research aimed at using an extract of plant material wastes, namely grape skins, obtained by the plasma discharge for the "green" synthesis of nanomaterials with different structures and polyfunctional properties.

3. The aim and objectives of the study

The research was aimed at obtaining polyfunctional mono- and bimetallic NPs of precious metals (Ag, Au) with the use of plasmochemically obtained aqueous extract from grape-processing waste (grape skins).

To achieve this goal, the authors solved the following tasks:

– to obtain an aqueous grape skin extract (GSE) in conditions of a short-term action of low-temperature plasma discharge and to study its componential composition and antioxidant properties;

– to determine the conditions for obtaining nanosized mono- (Ag, Au) and bimetallic (Ag-Au) NPs with the help of plasmochemically obtained aqueous grape skin extracts;

– to investigate the properties and to prove the polyfunctionality of the obtained mono- and bimetallic nanoparticles of metals (antibacterial and catalytic properties).

4. Materials and methods to obtain mono- and bimetallic nanoparticles. Study of the properties of NPs

4. 1. Research materials

The research was based on the use of the grape processing product – skins of the Moldova grape variety. After using this berry crop, depending on the technological process, a large amount of waste is accumulated near the processing enterprises – seeds, pulp, grape stalk and grape skins. Seeds are used to produce valuable oil, pulp – as a food additive to confectionery products, while individually grape skins are currently limited in practical use – only as a constituent in cosmetic products. Grape pulp along with phenolic compounds contains a significant amount of saturated and unsaturated acids (due to the seed press), terpene compounds, as well as aliphatic and aromatic aldehydes. Meanwhile, grape skins predominantly contain phenolic compounds, i.e. a promising source of "green" organic compounds with reducing properties, which creates conditions for the recovery of metal ions to NPs.

The total percentage of phenolic compounds, depending on the grape variety, is almost unchangeable. Changes in the main varieties do not affect the overall antioxidant capacity and reducing properties of the resulting extract. The product of processing was provided by the open joint-stock company OJSC "VINNIEFRUIT" (Kalynivka, Vinnytsia oblast, Ukraine), which is engaged in the production of juices and soft drinks. The product is provided free of charge on the request to provide industrial raw material waste for the education and research of graduate students specializing in Chemical Technologies of Cosmetics and Food Additives at the Department of Physical Chemistry of the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" (Kyiv, Ukraine). Characteristics of the grape skins are the following: dark red powder; humidity– 4.5 %.

4. 2. Characteristics of the grape skin extract obtained due to the plasma discharge

40 ml of bidistilled water were added to 1 g of dry grape skin powder and stirred. The resulting mixture was placed in a plasmochemical reactor. The scheme and the principle of the plant operation are given in [19, 20]. The mixture was treated for 5 minutes (at the amperage of I=120 mA and P=0.8 MPa), cooled and filtered. The freshly obtained aqueous extract was used immediately after its filtration. The componential composition of the grape skin extract was analyzed with the use of IR spectroscopy and liquid chromatography – mass spectrometry. The total antioxidant capacity of the extract was assessed with the help of the phosphomolybdenum method, which is based on the recovery of Mo (VI) to Mo (V) by means of the extract and, consequently, the formation of a green phosphate complex/Mo (V) at an acidic pH value. The antioxidant activity is expressed as the amount of the ascorbic acid (AsA) equivalent (mg/g of the plant extract). The ratio of the extract to the reagent is 1:10, i. e. 0.5 ml of the test extract and ascorbic acid (100 mg/ml) were mixed with 5 ml of the reagent (0.6 M of sulfuric acid, 28 mM of sodium phosphate and 4 mM of ammonium molybdate). The compensation solution contains 5 ml of the reagent and 0.5 ml of the extractant due to which the extract was obtained. All the receptacles were sealed and incubated in a water bath at 95 °C for 90 minutes. After cooling the samples to the ambient temperature, absorbance of solutions was measured against the compensation samples at 695 nm using the UV-5800PC spectrophotometer (China).

The antioxidant activity in terms of the reducing capacity was determined as follows. Fe (III) recovery was used as an indicator of electron-donor activity, which is an important sign of antioxidant properties. Extracts that have a recovering potential react with potassium ferrocyanide (Fe^{3+}) to form potassium ferrocyanide (Fe^{2+}), which subsequently reacts with iron chloride (III) to form an iron complex with a maximum absorption at 700 nm. The reaction solution was made of different concentrations of the test extract after its rotational evaporation (g) (0.005, 0.01, 0.015, 0.02, 0.025) dissolved in a suitable solvent (1 ml) and added with 1 ml of phosphate buffer (0.2 M, pH 6.6) and 1 ml of potassium ferrocyanide solution (1 %). The resulting solution was kept at 50 °C. for 20 minutes. To quickly stop the reaction, 1 ml of trichloroacetic acid (10 %) was added and cooled under running water for 5 minutes. The resulting mixture was centrifuged at 3,000 rpm for 10 minutes. From the upper layer of each solution, an aliquot of 2 ml was removed and added with 2 ml of distilled water and 0.4 ml of iron chloride solution (0.1 %). The absorbance of the solution was measured at 700 nm with the UV-5800PC spectrophotometer (China). An increasing ability of the reaction mixture to absorb radiation at a given wavelength indicates a greater reducing effect of the extract. The calibration curve was constructed with the use of ascorbic acid and the results were expressed in mg of AsA/g of the extract. The results were expressed as the mean ± standard deviation from 3 repeated measurements with ascorbic acid as a solution for comparison.

4. 3. Synthesis of mono- and bimetallic nanoparticles and their characteristics

The synthesis of metal nanoparticles required the preparation and use of 0.003 mol/l of $AgNO_3$ and $HAuCl_4 \cdot 3H_2O$ solutions. When obtaining monometallic nanoparticles (Au or Ag), 40 ml of the pre-obtained grape skin extract were added to 40 ml of solutions of the respective precursors; all this was mixed and left for 24 hours to form the NPs of Au^0 or Ag^0. When obtaining bimetallic (Ag–Au) NPs, the synthesis conditions were identical to those mentioned above. However, in the latter case, their equimolar mixture of 0.5:0.5 was used as an initial precursor. To characterize the formed nanoparticles of metals, the reaction mixture was analyzed with the use of spectrophotometry. The spectra of colloidal solutions were obtained on the UV-5800PC spectrophotometer using quartz cells in the wavelength range of 300–700 nm. The dimensional characteristics of nanoparticles and their stability were determined with the help of the Zetasizer Nano-25 analyzer (England).

4. 4. Antibacterial research on nanoparticls

Antibacterial activity of the synthesized nanoparticles was studied using the method of measuring the number of colonies of the forming units. The tested solutions of NPs (Ag, Au, Ag–Au extract and Ag–Au plasma) (15 µl) were added to the colonies of the forming units of S. aureus and E. coli (about 1.5 10^5); 50 ml of each of the formed solutions were sprayed on the surface of the plates of Luria-Bertani agar according to the procedure. Samples with distilled water and an extract without silver nanoparticles were considered as control samples. The mixtures were cultured at 37 °C in an incubator with shaking for 12 hours. After that, the counted number of bacteria colonies was compared with the control medium. Calculations were made for the quantity of the surviving bacteria [21]. The obtained data allowed calculating the inhibition rate of bacterial growth (RBG, %)=$(Vk-Vt)/Vk \times 100$ %, where Vk and Vt are the control and the test samples, respectively [22]. The research was made at the OWL University of Applied Sciences (Germany).

4. 5. Catalytic properties of the nanoparticles

In a typical catalytic reaction, 3 ml of the aqueous solution of 4-nitrophenol (0.1 mM) and 0.5 ml of the aqueous solution $NaBH_4$ (15 mM) were mixed, and then 1 ml of the aqueous suspension of pre-prepared nanoparticles was added to the reaction mixture and magnetically stirred. After that, the solution was transferred to a standard quartz cell for recording the spectra on the spectrophotometer in the wavelength range of 300–700 nm at a time interval of 2 min. at the ambient temperature.

5. "Green" synthesis findings on bimetallic nanoparticles

It is known that the "green" synthesis of nanoparticles is based on the use of reducing agents present in the composition of plant material [23, 24]. These substances are characterized by their redox potential and are able to recover cations of the dissociated metal salts. In addition, they can simultaneously act as stabilizers of the obtained NPs. Taking this into account, the research on the components of the grape skin extract involved the method of liquid chromatography – mass spectrometry – to study the componential composition of the aqueous grape skin extract obtained under the action of a plasma discharge (Table 1).

Table 1

Componential composition of the aqueous grape skin extract obtained due to a plasma discharge

Name of a compound	Residence time, min	Relative mass fraction, %
Anthocyanins		
Delphinidin-3-O-glycoside	9.7	1.2
Cyanidin-3-O- glycoside	11.8	1.1
Petunidin-3-O- glycoside	13.2	1.5
Peonidin-3-O- glycoside	15.6	0.7
Malvidin-3-O-glycoside	16.8	1.2
Delphinidin-3-O-(acetyl-glycoside)	18.2	1.4
Petunidin-3-O-(acetyl-glycoside)	22.3	1.5
Peonidin-3-O-(acetyl-glycoside)	24.6	1.6
Malvidin-3-O-(acetyl-glycoside)	25.8	1.3
Phenolic acids		
Trioxybenzoic acid	5.9	5.1
Hydroxymethylfurfural	7.7	4.7
3.4-dihydrobenzoic acid	12.7	4.5
(2R,3R)-2-[(E)-3-(3.4-Dihydroxyphenyl) pro-2-enol]oxy-3-hydroxybutanedioic acid	13.8	2.3
4-Hydroxybenzoic acid	18.0	3.2
(2R,3R)-2-Hydroxy-3-(((E)-3-(4-hydroxyphenyl)acryl)oxy) succinic acid	20.8	4.1
3.4-dioxycinnamylic acid (Caffeic acid)	23.4	2.2
2-hydroxy-3-{[(2E)-3-(4-hydroxy-3methoxyphenyl)prop-2-enol]oxy}butanedionic acid (Fertar acid)	24.3	4.2
3-methoxy-4-hydroxycinnamylic acid		2.3
4-hydroxy-3.5-dimethoxybenzoic acid (Syringic acid)	25.7	3.6
(2E)-3-(4-hydroxyphenyl)-prop-2-enoic acid (Paracumaric acid)	31.0	3.3
3.5-dimethoxy-4-hydroxycinnamylic acid (Sinapinic acid)	32.1	2.4
3-methoxy-4-hydroxycinnamylic acid (Ferulic acid)	32.5	1.8
Anthoxanthins & Stilbenes		
Procyanidin B1	13.7	2.3
Catechin	17.5	8.4
Procyanidin B2	21.4	2.9
Epicatechin	25.4	7.8
Epicatechin gallate	41.9	4.2
Quercetin-3-O- glucoside	50.4	1.6
Kaempferol-3-O-glucoside	55.6	2.9
Trans-resveratrol	59.2	4.2
Quercetin	66.2	3.6
Kaempferol	71.0	3.6

A wide range of compounds was found in the plasmochemically obtained aqueous extract of the grape skin extract (Table 1). The present phenolic acids, namely: gallic acid (9.1 %), hydroxymethylfurfural (4.7 %), 3.4-dihydroxybenzoic acid (4.5 %), 4-hydroxybenzoic acid (3.2 %), 3.4-dioxycinnamylic acid (2.2 %); anthocyanins (34 %) structurally representing glycosides at the 3-position anthocyanidins: malvidin, dolphinidin, petunidin, peonidin and cyanidin. The flavonol group is represented by quercetin and its derivative quercetin-3-O-glucoside. The extract contains catechin, epicatechins and epicatechin gallate.

The presence in the extract of the functional groups of the above organic compounds is confirmed by the analysis of the IR spectroscopy (Fig. 1). In the spectrum, one can distinguish between absorption bands in the range of 3,000–2,800 cm^{-1} – valence fluctuations and deformation fluctuations at 1,400–1,340 cm^{-1}, indicating the presence of intermolecular hydrogen bond. The presence of aliphatic groups CH_3 and CH_2 is indicated by strong absorption in the range of 2,930–2,850 cm^{-1} (valence fluctuations of groups CH_3 and CH_2) and in the range of 1,463–1,377 cm^{-1} (deformation fluctuations). The presence of absorption bands in the range of 2,880–2,650 cm^{-1}, 1,480–1,440 cm^{-1} (asymmetric valence fluctuations $-CH_2$-CO) aa well as at 975–780 cm^{-1} indicates the presence of aldehydes in the test sample. The signal in the range of 1,680–1,635 cm^{-1} corresponds to unsaturated double-bonded compounds. In the absorption bands of 1,320–1,210 cm^{-1}, where deformation fluctuations of –COOH occur, it indicates compounds with a carboxyl group. Asymmetric fluctuations of the –C–O–C group in the absorption band of 1,280–1,115 cm^{-1} confirm the presence of complex esters and lactones. The deformation fluctuations of the –CH group are observed in the range of 912–800 cm^{-1}.

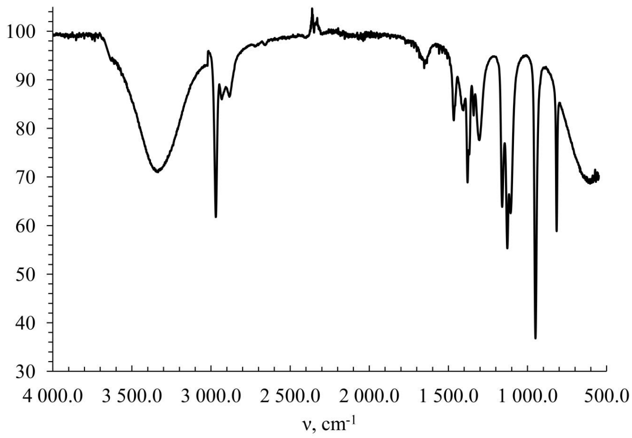

Fig. 1. The IR-spectrum of the plasmochemically obtained grape skin extract

In addition to determining the componential composition of the extract, the antioxidant properties of the extract are widely used to determine the reducing capacity of the plant extract ingredients. The results of studying the antioxidant properties of the grape extract are shown in Table 2. The obtained data testify to the presence of antioxidant properties in the plasmochemically obtained grape skin extract. The total antioxidant activity is 571±1.38 mg of AsA/g of the extract.

Table 2

The antioxidant property of the grape extract

Total antioxidant activity, mg AsA/g of the extract	Reducing capacity, mg of AsA/g of the extract				
	Concentration, mg/ml				
	0.5	1.0	1.5	2.0	2.5
571±1.38	73.2±1.38	96.1±1.01	148.3±1.41	162.3±1.96	190.5±1.79

Monometallic (Au, Ag) and bimetallic (Ag–Au) nanoparticles were received using the plasmochemically obtained grape skin extract as a reducing agent/stabilizer. The reducing of metal ions to nanoparticles and the formation of bimetallic compounds was controlled by means of UV spectroscopy as the positions of the beam-plasma discharge (BPD) maxima characterize the forms of the existing nanoparticles of metals, their size, shape, etc. [25, 26]. As Fig. 2 shows, the BPD peaks at 440 nm and 540 nm correspond to the formed nanosized particles of monometals Ag^0 and Au^0, respectively. The BPD peak in the absorption spectrum of the equimolar mixture of Au^{3+} and Ag^+ ions, which lies between the peaks of pure Au^0 and Ag^0 NPs in the plasmonic bands, indicates the formation of bimetallic alloy Ag–Au rather than a mixture of particles or a core-shell structure [26, 27].

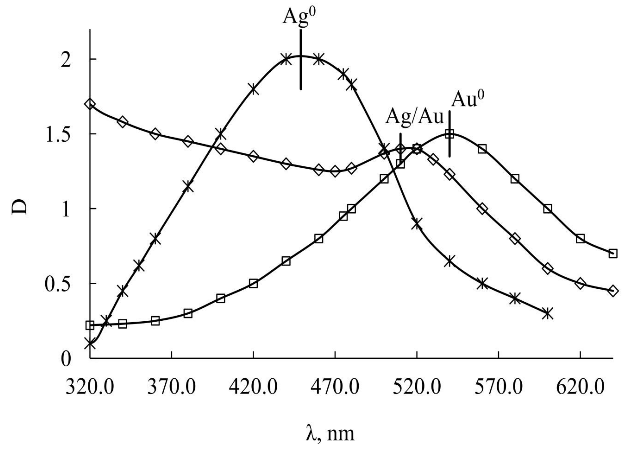

Fig. 2. Absorption spectra of monometallic (Ag, Au) and bimetallic (Ag/Au) nanoparticles synthesized using plasmochemically obtained aqueous grape extract

In [28–31], the authors demonstrated the efficiency of using plasma discharges for synthesizing monometallic and bimetallic compounds of precious metals (Au, Ag) of different core-shell compositions and alloys with various types of stabilizers. However, the authors either show antibacterial properties alone or fail to give characteristics of the resulting compounds.

Thus, in order to compare the efficiency of "green" synthesis with plasmocchemical extraction, we determined characteristics of plasmochemically obtained bimetallic compounds. This study reveals zeta potential of nanosized metals (Table 3). The resulting dispersed systems of nanoparticles are characterized by the value of zeta potential in the range from –31.0 to –40.8 mV, which is typical of stable colloidal systems [32]. Dimensional characteristics of the nanoparticles obtained in aqueous solutions were studied by the method of dynamic light scattering (DLS); they are shown in Table 1. Thus, the average size of particles obtained by the "green" method is 30.1–35.1 nm. It is found that plasmochemically synthesized bimetallic particles are much larger – their average size is 75.1 nm.

It is known that monometallic Ag, Au and bimetallic Ag–Au NPs demonstrate antibacterial properties [25, 26, 33]. We assessed antibacterial activity of the NPs synthesized using a plasmachemically obtained grape skin extract under the action of plasma discharges. The synthesized nanoparticles showed a high antibacterial effect on gram-positive and gram-negative bacteria (Table 4).

Table 3

Characteristics of metal nanoparticles synthesized using the grape extract obtained due to plasma discharges

NP	Zeta potential, ΔmV	Average NP size, nm
Ag	–31.0	32.3±3.1
Au	–28.3	35.1±1.2
Ag–Au	–40.8	30.1±2.2
Ag–Au plasma synthesis	–23.5	75.1±1.0

Table 4

Inhibition of the bacterial growth with the use of monometallic (Ag, Au) and bimetallic (Ag–Au) NPs synthesized using grape extract

Test culture	Rate of inhibition of the bacterial growth,%					
	Control		Ag^0	Au^0	Ag–Au "green" synthesis	Ag–Au plasma synthesis
	Bidystilled water	Extract				
Escherichia coli	0	13.0	97.5	56.0	93.1	82.0
Staphylococcus aureus	0	10.0	98.3	58.0	95.1	78.0

The catalytic effectiveness of the synthesized nanoparticles was studied by the model systems (the recovery of aromatic nitrocompounds in the presence of sodium borohydrate ($NaBH_4$) in aqueous solutions). The catalytic process was controlled with UV spectroscopy. Fig. 3 shows the recovery of 4-nitrophenol to 4-aminophenol with the help of the synthesized NPs.

In the spectra (Fig. 2, *a–d*), the absorption peak at about 320 nm with an arm at 400 nm corresponds to 4-nitrophenol. This peak shifts from 320 nm to 400–420 nm immediately after adding the aqueous $NaBH_4$ solution, which corresponds to the formation of 4-nitrophenolate ion. If a NP catalyst is absent and there is extract alone (Fig. 2, *a*), the absorption peak at 400 nm remains unchanged, indicating that $NaBH_4$ itself and the extract can not reduce ions of 4-nitrophenolate without a catalyst.

Catalysts (Ag, Au, Ag-Au NPs and $NaBH_4$) reduce 4-nitrophenol. This is proved by the gradual decrease in the intensity of the absorption peak at 400 nm over time. At the same time, a new absorption peak at 297–300 nm is formed in the spectra, and gradually its intensity increases. The new peak is a typical peak for the absorption of 4-aminophenol [34–37]. Thus, the research findings give the grounds to believe that catalytic reduction of 4-nitrophenol to 4-aminophenol is possible with the use of synthesized NPs.

6. Discussion of the findings on the synthesis of mono- and bimetallic NPs

The componential composition of the obtained extract, shown in Table 1, indicates the presence of a wide range of organic compounds. The latter can perform reducing and stabilizing functions in the formation of nanoparticles. Therefore, the hydroxyl, carboxyl and carbonyl functional groups of organic compounds (Fig. 1) are likely to allow the recovery of metal ions and stabilization of the NPs. In addition, the reducing ability of the extract compounds is assessed by the antioxidant activity of the plant extract. The results show that the obtained extract is active as an antioxidant (Table 2). Therefore, compounds with a reducing capacity are donors of electrons that are capable of decreasing the number of products of lipid peroxidation processes and acting as primary and secondary antioxidants.

A higher ability of the reaction mixture to absorb radiation at a given wavelength indicates a greater reducing effect of the extract. The reducing capacity of extracts increases along with the increasing concentrations.

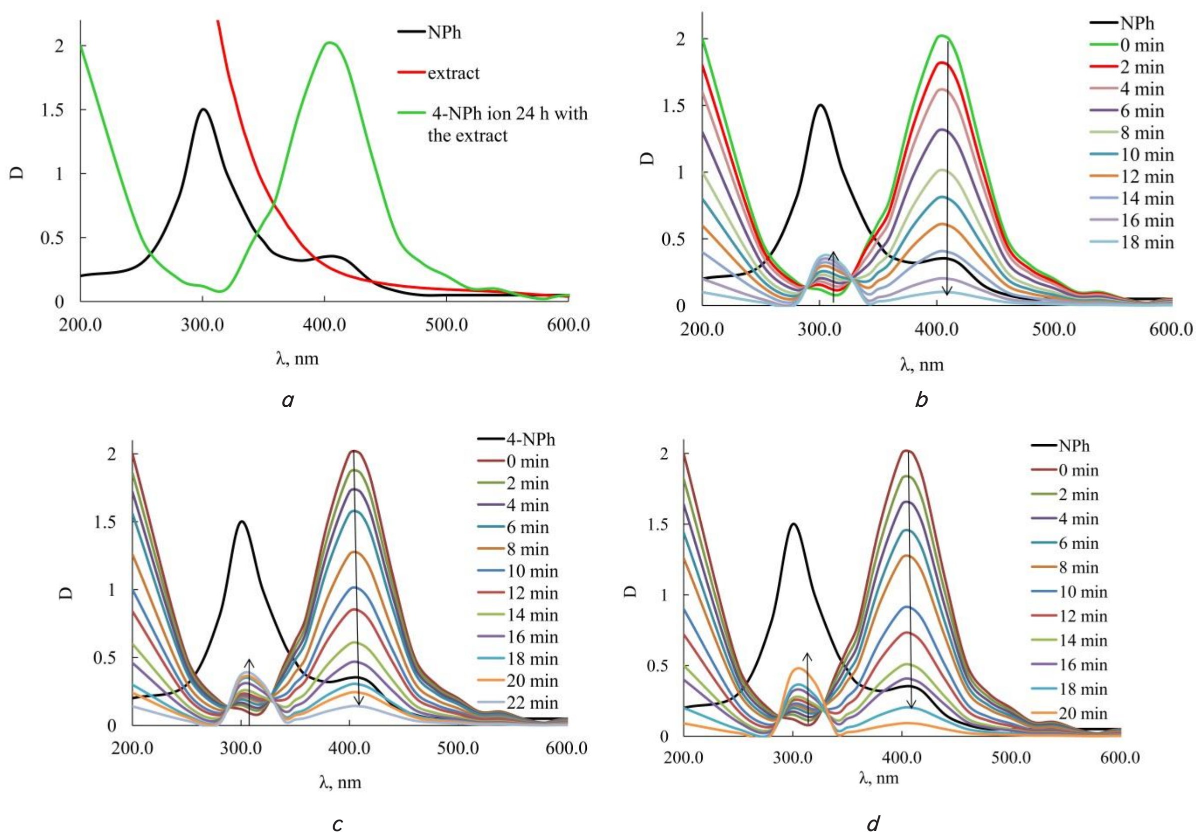

Fig. 3. Spectra for the absorption and reduction of 4-nitrophenol with the obtained nanomaterials: *a* – without NPs/an extract and with the extract; *b* – monometallic NPs Ag^0; *c* – monometallic NPs Au^0; *d* – a bimetallic alloy of Ag-Au NPs

The extract reveals its reductive potential and can serve as a potent donor of electrons, which completes the radical chain reaction [36]. Thus, the whole complex of the research data proves the expediency of using the grape skin extract for synthesizing the nanoparticles of metals.

The resulting nanoparticles were tested for their antimicrobial, catalytic and corrosion properties. Based on the results of bacterial studies, the resulting NPs are active against gram-positive (Staphylococcus aureus) 58.0–98.3 % and gram-negative (Escherichia coli) 56.0–97.5 % bacteria (Table 4). The greatest effect is achieved in the NPs of Ag, which is quite expectable. Bimetallic NPs showed higher antimicrobial effects than monometallic Au NPs. The precise mechanism of interaction of the NPs with bacteria is not completely revealed. Nevertheless, the main mechanisms are the biological resistance of NPs against microorganisms. The resulting NPs show an excellent catalytic activity in reducing p-nitrophenol (4-NPh) to p-aminophenol (4-APh) in the presence of $NaBH_4$. Depending on the type of NPs, the length of the process is 18–22 min.

7. Conclusions

1. The "green" synthesis of mono- and bimetallic NPs of precious metals used an aqueous grape skin extract. The extract obtained by the plasma discharge was used as an effective reducing and stabilizing agent. The researchers have studied the componential composition of the aqueous grape skin extract obtained under the action of a plasma discharge. They have proved a hypothesis that hydroxyl, carboxyl and carbonyl functional groups of organic compounds allow the recovery of metal ions, as well as the formation and stabilization of metal NPs.

2. The formation of mono- and bimetallic NPs is characterized by the presence of peaks for Ag^0 (λ_{max}=440 nm), for Au^0 (λ_{max}=540 nm), and for Ag–Au (λ_{max}=510 nm). The size and stability of the nanoparticles synthesized by the "green" method are assessed in comparison with the same parameters for the plasmochemical method of NP formation. It is proved that the method of "green" synthesis results in obtaining colloidal systems with the size of the formed particles twice below the ave-rage size.

3. The research on the antibacterial and catalytic properties of the obtained monometallic and bimetallic nanoparticles of metals revealed the polyfunctional properties of the synthesized nanomaterials. The resulting NPs showed their catalytic activity in reducing p-nitrophenol (4-NPh) to p-aminophenol (4-APh) in the presence of $NaBH_4$. The antimicrobial activity against gram-positive (Staphylococcus aureus) and gram-negative (Escherichia coli) bacteris makes up 76.0–98.3 %.

References

1. Revolution from monometallic to trimetallic nanoparticle composites, various synthesis methods and their applications: A review / Sharma G., Kumar D., Kumar A., Al-Muhtaseb A. H., Pathania D., Naushad M., Mola G. T. // Materials Science and Engineering: C. 2017. Vol. 71. P. 1216–1230. doi: https://doi.org/10.1016/j.msec.2016.11.002
2. Metal Nanoparticle Photocatalysts: Synthesis, Characterization, and Application / Han P., Martens W., Waclawik E. R., Sarina S., Zhu H. // Particle & Particle Systems Characterization. 2018. Vol. 35, Issue 6. P. 1700489. doi: https://doi.org/10.1002/ppsc.201700489
3. Liu X., Astruc D. From Galvanic to Anti-Galvanic Synthesis of Bimetallic Nanoparticles and Applications in Catalysis, Sensing, and Materials Science // Advanced Materials. 2017. Vol. 26, Issue 16. P. 1605305. doi: https://doi.org/10.1002/adma.201605305
4. Solomon M. M., Gerengi H., Umoren S. A. Carboxymethyl Cellulose/Silver Nanoparticles Composite: Synthesis, Characterization and Application as a Benign Corrosion Inhibitor for St37 Steel in 15% H2SO4 Medium // ACS Applied Materials & Interfaces. 2017. Vol. 9, Issue 7. P. 6376–7389. doi: https://doi.org/10.1021/acsami.6b14153
5. Nelson D., Seabra A. B. Biogenic Synthesized Ag/Au Nanoparticles: Production, Characterization, and Applications // Current Nanoscience. 2018. Vol. 14, Issue 2. P. 82–94. doi: https://doi.org/10.2174/1573413714666171207160637
6. Plant-based green synthesis of metallic nanoparticles: scientific curiosity or a realistic alternative to chemical synthesis? / Peralta-Videa J. R., Huang Y., Parsons J. G., Zhao L., Lopez-Moreno L., Hernandez-Viezcas J. A., Gardea-Torresdey J. L. // Nanotechnology for Environmental Engineering. 2016. Vol. 1, Issue 4. doi: https://doi.org/10.1007/s41204-016-0004-5
7. New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: current knowledge, their agricultural and environmental applications / Saratale R. G., Saratale G. D., Shin H. S., Jacob J. M., Pugazhendhi A., Bhaisare M., Kumar G. // Environmental Science and Pollution Research. 2017. Vol. 25, Issue 11. P. 10164–10183. doi: https://doi.org/10.1007/s11356-017-9912-6
8. Devi T. B., Ahmaruzzaman M. Bio-inspired facile and green fabrication of Au@Ag@AgCl core–double shells nanoparticles and their potential applications for elimination of toxic emerging pollutants: A green and efficient approach for wastewater treatment // Chemical Engineering Journal. 2017. Vol. 317. P. 726–741. doi: https://doi.org/10.1016/j.cej.2017.02.082
9. Green controllable synthesis of Au–Ag alloy nanoparticles using Chinese wolfberry fruit extract and their tunable photocatalytic activity / Sun L., Yin Y., Lv P., Su W., Zhang L. // RSC Advances. 2018. Vol. 8, Issue 8. P. 3964–3973. doi: https://doi.org/10.1039/c7ra13650a
10. Ingale A. G., Chaudhari A. N. Biogenic Synthesis of Nanoparticles and Potential Applications: An Eco- Friendly Approach // Journal of Nanomedicine & Nanotechnology. 2013. Vol. 04, Issue 02. doi: https://doi.org/10.4172/2157-7439.1000165
11. Study of the Mechanism of Action of the Isopropanol Extract of Rapeseed Oil Cake on the Atmospheric Corrosion of Copper / Chyhyrynets O. E., Fateev Y. F., Vorobiova V. I., Skyba M. I. // Materials Science. 2016. Vol. 51, Issue 5. P. 644–651. doi: https://doi.org/10.1007/s11003-016-9886-4
12. A comprehensive study of grape pomace extract and its active components as effective vapour phase corrosion inhibitor of mild steel / Vorobyova V., Chygyrynets' O., Skiba M., Zhuk T., Kurmakova I., Bondar O. // International Journal of Corrosion and Scale Inhibition. 2018. Vol. 7, Issue 2. P. 185–202. doi: https://doi.org/10.17675/2305-6894-2018-7-2-6
13. Vorobyova V., Chygyrynets' O., Skiba M. 4-hydroxy-3-methoxybenzaldehyde as a volatile inhibitor on the atmospheric corrosion of carbon steel // Journal of Chemical Technology and Metallurgy. 2018. Vol. 53, Issue 2. P. 336–345.

14. Self-assembled monoterpenoid phenol as vapor phase atmospheric corrosion inhibitor of carbon steel / Vorobyova V., Chygyrynets O., Skiba M., Kurmakova I., Bondar O. // International Journal of Corrosion and Scale Inhibition. 2017. Vol. 6, Issue 4. P. 485–503. doi: https://doi.org/10.17675/2305-6894-2017-6-4-8
15. Role of irradiation in the green synthesis of silver nanoparticles mediated by fig (Ficus carica) leaf extract / Ulug B., Haluk Turkdemir M., Cicek A., Mete A. // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015. Vol. 135. P. 153–161. doi: https://doi.org/10.1016/j.saa.2014.06.142
16. Effect of Gamma-irradiation on biosynthesized gold nanoparticles using Chenopodium murale leaf extract / Abdelghany A. M., Abdelrazek E. M., Badr S. I., Abdel-Aziz M. S., Morsi M. A. // Journal of Saudi Chemical Society. 2017. Vol. 21, Issue 5. P. 528–537. doi: https://doi.org/10.1016/j.jscs.2015.10.002
17. Comparative study on gamma irradiation and cold plasma pretreatment for a cellulosic substrate modification with phenolic compounds / Irimia A., Ioanid G. E., Zaharescu T., Coroab A., Doroftei F., Safrany A., Vasile C. // Radiation Physics and Chemistry. 2017. Vol. 130. P. 52–61. doi: https://doi.org/10.1016/j.radphyschem.2016.07.028
18. Contact nonequilibrium plasma as a tool for treatment of water and aqueous solutions: Theory and practice / Pivovarov A. A., Kravchenko A. V., Tishchenko A. P., Nikolenko N. V., Sergeeva O. V., Vorob'eva M. I., Treshchuk S. V. // Russian Journal of General Chemistry. 2015. Vol. 85, Issue 5. P. 1339–1350. doi: https://doi.org/10.1134/s1070363215050497
19. Plasma-chemical formation of silver nanodispersion in water solutions / Skiba M., Pivovarov A., Makarova A., Pasenko O., Khlopytskyi A., Vorobyova V. // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 6, Issue 6 (90). P. 59–65. doi: https://doi.org/10.15587/1729-4061.2017.118914
20. Plasma-chemical obtaining of silver nanoparticles in the presence of sodium alginate / Pivovarov O. A., Skiba M. I., Makarova A. K., Vorobyova V. I., Pasenko O. O. // Voprosy khimii i khimicheskoi tekhnologii. 2017. Vol. 6, Issue 115. P. 82–88.
21. Taylor P. L., Ussher A. L., Burrell R. E. Impact of heat on nanocrystalline silver dressings // Biomaterials. 2005. Vol. 26, Issue 35. P. 7221–7229. doi: https://doi.org/10.1016/j.biomaterials.2005.05.040
22. Synthesis and characterization of silver nanoparticles for antibacterial activity / Sadeghi B., Jamali M., Kia Sh., Amini nia A., Ghafar S. // International Journal of Nano Dimension. 2010. Vol. 1, Issue 2. P. 119–124. doi: https://doi.org/10.7508/IJND.2010.02.004
23. Farhadi S. Ajerloo B., Mohammadi A. Low-cost and eco-friendly phyto-synthesis of Silver nanoparticles by using grapes fruit extract and study of antibacterial and catalytic effects // International Journal of Nano Dimension. 2017. Vol. 8, Issue 1. P. 49–60. doi: https://doi.org/10.22034/IJND.2017.24376
24. Krishnaswamy K., Vali H., Orsat V. Value-adding to grape waste: Green synthesis of gold nanoparticles // Journal of Food Engineering. 2014. Vol. 142. P. 210–220. doi: https://doi.org/10.1016/j.jfoodeng.2014.06.014
25. Yallappa S., Manjanna J., Dhananjaya B. L. Phytosynthesis of stable Au, Ag and Au–Ag alloy nanoparticles using J. Sambac leaves extract, and their enhanced antimicrobial activity in presence of organic antimicrobials // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015. Vol. 137. P. 236–243. doi: https://doi.org/10.1016/j.saa.2014.08.030
26. Synthesis of Bimetallic Nanoparticles (Au–Ag Alloy) Using Commelina nudiflora L. Plant Extract and Study its on Oral Pathogenic Bacteria / Kuppusamy P., Ilavenil S., Srigopalram S., Kim D. H., Govindan N., Maniam G. P. et. al. // Journal of Inorganic and Organometallic Polymers and Materials. 2017. Vol. 27, Issue 2. P. 562–568. doi: https://doi.org/10.1007/s10904-017-0498-8
27. Core@shell Nanoparticles: Greener Synthesis Using Natural Plant Products / Khatami M., Alijani H., Nejad M., Varma R. // Applied Sciences. 2018. Vol. 8, Issue 3. P. 411. doi: https://doi.org/10.3390/app8030411
28. Obtaining of bimetallic nanoparticles by using plasma discharge / Pivovarov A. A., Skiba M. I., Makarova A. K., Vorobyova V. I. // Vibratsiyi v tekhnitsi ta tekhnolohiyakh. 2017. Issue 3 (86). P. 97–101.
29. Plasma-chemical Synthesis of Silver Nanoparticles in the Presence of Citrate / Skiba M., Pivovarov A., Makarova A., Vorobyova V. // Chemistry Journal of Moldova. 2018. Vol. 13, Issue 1. P. 7–14. doi: https://doi.org/10.19261/cjm.2018.475
30. One-pot synthesis of silver nanoparticles using discharged plasma in the presence of polyvinyl alcohol / Skiba M. I., Pivovarov O. A., Makarova A. K. Parkhomenko V. D. // Voprosy khimii i khimicheskoi tekhnologii. 2018. Issue 3. P. 113–120.
31. Plasmochemical preparation of silver nanoparticles: thermodynamics and kinetics analysis of the process / Skiba M., Pivovarov A., Makarova A., Vorobyova V. // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 2, Issue 6 (82). P. 4–9. doi: https://doi.org/10.15587/1729-4061.2018.127103
32. Silver Nanoparticles: Preparation, Characterization, And Kinetics / Ijaz Hussain J., Kumar S., Adil Hashmi A., Khan Z. // Advanced Materials Letters. 2011. Vol. 2, Issue 3. P. 188–194. doi: https://doi.org/10.5185/amlett.2011.1206
33. Marambio-Jones C., Hoek E. M. V. A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment // Journal of Nanoparticle Research. 2010. Vol. 12, Issue 5. P. 1531–1551. doi: https://doi.org/10.1007/s11051-010-9900-y
34. Microwave assisted green synthesis of silver nanoparticles using leaf extract of elephantopus scaber and its environmental and biological applications / Francis S., Joseph S., Koshy E. P., Mathew B. // Artificial Cells, Nanomedicine, and Biotechnology. 2017. Vol. 46, Issue 4. P. 795–804. doi: https://doi.org/10.1080/21691401.2017.1345921
35. Kinetic Analysis of Catalytic Reduction of 4-Nitrophenol by Metallic Nanoparticles Immobilized in Spherical Polyelectrolyte Brushes / Wunder S., Polzer F., Lu Y., Mei Y., Ballauff M. // The Journal of Physical Chemistry C. 2010. Vol. 114, Issue 19. P. 8814–8820. doi: https://doi.org/10.1021/jp101125j
36. Phenolic Compounds And Antioxidant Activity Of Wild Grape (Vitis Tiliifolia) / Jiménez M., Juárez N., Jiménez-Fernández V. M., Monribot-Villanueva J. L., Guerrero-Analco J. A. // Italian Journal of Food Science. 2018. Vol. 30, Issue 1. P. 128–143. doi: https://doi.org/10.14674/IJFS-975
37. Synthesis and applications of silver nanoparticles / Abou El-Nour K. M. M., Eftaiha A., Al-Warthan A., Ammar R. A. A. // Arabian Journal of Chemistry. 2010. Vol. 3, Issue 3. P. 135–140. doi: https://doi.org/10.1016/j.arabjc.2010.04.008