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PLASMA-CHEMICAL-ASSISTED SYNTHESIS OF SILVER NANOPARTICLES USING GRAPE POMACE WASTE

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Dispersions of silver nanoparticles (AgNPs) were prepared by two methods: a chemical reduction using plasma-chemically obtained water extract of grape pomace as a reducing and stabilizing agent and one-pot plasma-chemical-assisted synthesis using a grape pomace in an aqueous medium. The UV-vis spectrum of AgNPs exhibited a surface plasmon absorption at about 405−420 nm, which originated from the formation of AgNPs. The UV-visible absorption spectral characteristics of silver nanoparticles prepared under different Ag^+ concentrations and durations of synthesis were studied. The results demonstrated that the synthesis via both methods provides the formation of AgNPs at the investigated concentrations of Ag^+ (0.25−6.0 mmol/L) during 5−10 min. Dynamic light scattering and scanning electron microscopy were employed to measure the hydrodynamic size and morphology of silver nanoparticles in suspensions. The prepared AgNPs were spherical with an average particle size of about 20−33 nm. The results of powder X-ray diffraction method revealed that Ag nanoparticles had a face-centered cubic crystal structure. The catalytic performance of the AgNPs were ascertained in the reduction of 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride.

Keywords: silver nanoparticle; low-temperature nonequilibrium plasma; grape pomace; catalytic degradation; nitrophenol.

Introduction

Metal nanoparticles (NPs), especially silver nanoparticles (AgNPs), have attracted a great attention both in the area of scientific researches and in industrial applications due to their excellent properties. The synthesis of AgNPs is generally carried out by various physical or chemical methods, such as reduction in solutions, thermal decomposition of silver compounds, microwave-assisted and photochemical reactions in the reverse micelles, etc. [1]. Despite on success of these methodologies, they have many limitations, including expensive chemical reagents and potential hazardous impact on the environment. These detrimental effects can be minimized by using an environmentally friendly facile approach.

Green nanotechnology integrates the principles of green chemistry and green engineering to produce eco-friendly safe nanoparticles that do not use toxic chemicals during a synthesis protocol [2]. Green synthesis uses environmentally compatible materials, such as bacteria, fungi and plants to synthesize the nanoparticles. However, the usage of plant extracts is more advantageous due to preventing risks and complications in the maintenance of cell cultures, when the reaction time decreases from days to hours. Various plants wastes have been utilized for the synthesis of AgNPs [1,2].

Grape is one of the world's largest fruit crop with a global production of 68 million tons [3], only about 38 million tons of which are further processed. Annually, around 2.5 million tons of grape pomace is generated. Grape pomace (GP) mainly consists of peels (skins), seeds and stems that correspond to 20−25% of the grape weight crushed to produce wine. In recent years, the management of food waste processing has emerged as a major concern. One of the food waste, grape pomace, as a great source of bioactive compounds, might be used for more environmentally-friendly processes in the synthesis of nanomaterials. However, an analysis of the pertinent literature revealed actual issues and

shortcomings that limit the advancement of the green synthesis [1−4]. Major issues are associated with the source/type and concentration of the plant extracts and waste materials. The formation of NPs by using plant extracts proceeds, as a rule, in two stages: preparation of the extract and its subsequent use as a reducing/stabilizing agent. Maceration of solid material with different solvents is the most common method to prepare extracts [5]. These techniques often involve several extraction steps, thus take a lot of time. Different extraction techniques have been studied in an effort to increase the yield, including e.g. ultrasound-assisted extraction from grape stems, superheated liquid extraction from vine shoots and fluidized-bed extraction from grape canes [6].

Some scientists used additional influences on the reaction mixtures directly at the stage of the NPs formation and/or extract preparation. As an example, a variety of radiation sources emitting in the gamma, UV, vis or microwave ranges are used to synthesize AgNPs in the presence of plants extracts [7,8]. Among these, plasma-chemical treatment exhibits low instrumental requirements and allows simultaneously treating various samples in a short time [9].

Among plasma-chemical discharges, the contact nonequilibrium low-temperature plasma is a promising option from the point of view of practical application. Plasma discharge is generated between the electrode in a gaseous phase and a liquid surface, where another electrode is located [10]. Therefore, chemical transformations on the phase boundary are determined by the combined effect of the electrochemical oxidation-reduction, initiated photolysis reactions, the UV radiation and a flow of charged particles from the gaseous phase to the surface of the liquid medium. These factors may increase the extraction efficiency and concentration of the resulted extracts, and, as a consequence, the efficiency of a further synthesis of AgNPs.

The main goal of this work was to determine the synthesis conditions and catalytic properties of silver nanoparticles prepared via green methods using the grape pomace extract and the plasma-chemical treatment at the stages of extract preparation and directly for the NPs formation.

Material and methods

Green synthesis of silver nanoparticles with the use of plasma-chemical treatment at the different stages was performed by two following methods.

According to the first method, grape pomace, stored in plastic bags at 4^0C before treatment, was dried at 100^0C for 48 h and grounded to obtain a fine powder. The bidistilled water (40 mL) was added to 1 g of dry GP powder and thoroughly stirred. The resulting mixture was placed in a plasma-chemical reactor. The scheme and the operating principle of the industrial plasma-chemical reactors were given elsewhere [10,11].

The mixture was treated by contact nonequilibrium low-temperature plasma for 5 min (at the amperage of I=120 mA and the pressure of P=0.8 MPa), cooled and filtered. The freshly obtained GP water extract was used immediately after filtration. These extracts will be mentioned below as the plasma-chemically obtained grape pomace water extracts (PC GPWE). AgNO$_3$ solutions was used as As Ag$^+$-ions source (C_{Ag}=0.025−6.0 mmol/L). In a typical reaction procedure, 40 mL of GP extract was added to 40 mL of AgNO$_3$ solution under stirring during 0.1 min. The obtained mixture was heated to 75°C for an appropriate time. The change of color to the brown for AgNO$_3$−PC GPWE mixture indicated the formation of AgNPs. This method will be mentioned below as chemical synthesis using plasma-chemically obtained grape pomace water extract (the method I).

In accordance to the second method, 40 mL of AgNO$_3$ aqueous solution with the concentration of 0.25−6.0 mmol/L was added to 1 g of dry GP powder under stirring. The resulting mixture was treated by contact nonequilibrium low-temperature plasma for 5 minutes (at the amperage of I=120 mA and the pressure of P=0.8 MPa), cooled and filtered. This method will be mentioned below as the plasma-chemical-assisted synthesis using grape pomace in the aqueous medium (the method II).

The final product was a colloidal dispersion of silver nanoparticles in both methods. AgNPs obtained by chemical synthesis were centrifuged at 5000 rpm for 5 min. The dried powders were used for further characterization.

The spectra of colloidal solutions were recorded using a spectrophotometer UV-5800PC (FRU, China) equipped with quartz cuvettes in the wavelength range of 200−700 nm.

The particle size distribution, polydispersity index and zeta potential of the prepared AgNPs colloids were determined by the dynamic light scattering technique using an analyzer Zetasizer Nano-25 (Malvern Instruments Ltd., Malvern, England) within the range of 0.1−10000 nm. For the hydrodynamic diameter measurement, 1 mL of the sample was transferred into a disposable plastic cuvette and automatically equilibrated in the instrument for 2 min. The data were recorded in triplicate. Microphotographs of nanoparticles were obtained by means of a scanning electron microscope

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JEOL JSM-6510LV (JEOL, Tokyo, Japan).

To test the catalytic activity of AgNPs, the reduction of 4-nitrophenol (4-NP) was monitored as follows: 1.5 mL of 4-NP solution (0.15 mM) was mixed with 1.0 mL of $NaBH_4$ solution (0.02 M) in a cell for UV-Vis measurements. The color immediately changed from light yellow to deep yellow; then, 0.5 mL of AgNPs solution was added to the above mixture. The intensity of the absorption peak at 400 nm was used to monitor the process of conversion from 4-nitrophenol to p-aminophenol.

Results and discussion

The most common technique used to elucidate and confirm the formation of silver nanoparticles is UV-Vis spectroscopy. Generally, metal nanoparticles, due to their nano dimension, exhibit surface plasmon resonance phenomenon, where the metal electrons in the conduction band oscillate collectively in the resonance at a certain wavelength of incident light. Colloidal silver nanoparticles demonstrate the absorption peak in the wavelength range from 380 to 450 nm, depending on the complex dielectric constant of the metal, the cluster size and an environment [12]. Obviously, the concentration of silver nitrate plays an important role in the formation of the silver particles [13]. In order to illustrate the effect of silver nitrate concentration, different concentrations of $AgNO_3$ were used to synthesize silver nanoparticles.

Figure 1 presents the UV-Vis absorption spectra of AgNPs prepared by two methods described above at different concentrations of $AgNO_3$ (0.25−6.0 mmol/L). The pure extract shows a maximum absorbance at λ<300 nm, which may be due to the functional compound extracted from GP. The presence of absorption peak in the range of 405−420 nm in the presented curves indicates the AgNPs formation after reaction with plasma-chemically obtained GPWE (Fig. 1,a).

As can be seen in Fig. 1, the growth of silver nitrate concentrations from 0.25 to 6.0 mmol/L leads to an increase in the intensity of absorbance peak. Increasing intensity suggests that more nanoparticles are formed. However, while the concentration of silver nitrate changes from 1.0 to 3.0 mmol/L, the intensity of absorbance peaks changed only slightly. This may be explained by the exhaustion of the reducing agent. With an increase in Ag^+ concentration up to 6.0 mmol/L, the peaks intensity slightly increases and a pair of absorption peaks at 424 nm and 550 nm is formed. This indicates that aggregation occurs in this reactive system and the nanoparticles are well dispersed.

The plasma-chemical-assisted synthesis with grape pomace in the aqueous medium under the second method also leads to the formation of silver nanoparticles (Fig. 1,b). The absorption spectra of colloidal solutions showed a highly symmetric single absorption band with a maximum at 422 nm and a steadily increasing of intensity as a function of reaction time without any shift in intensity. This indicates a narrow and uniform size distribution of the synthesized AgNPs with the spherical shape, which is confirmed by relatively low polydispersity indexes.

The dependences of the absorbance (at λ_{max}) in the recorded UV-Vis absorption spectra of AgNPs synthesized on the treatment duration are shown in Fig. 2.

It was established that a gradual increase in the absorbance is observed for both synthesis methods and different $AgNO_3$ concentrations during first 5−10 min of the synthesis, which indicates the growth of AgNPs content with increasing treatment duration. However, plasma-chemical-assisted synthesis is more effective than the chemical synthesis and the time
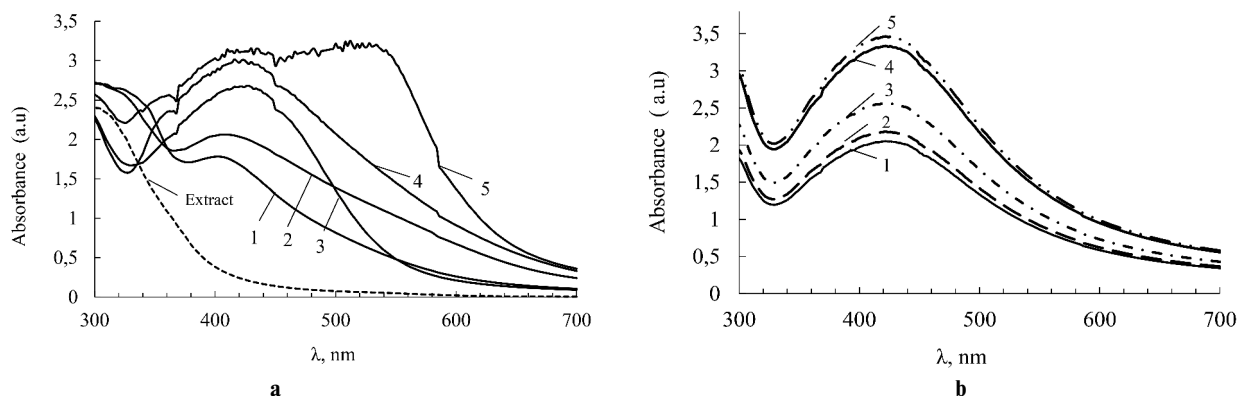

Fig. 1. Absorption spectra of silver colloidal solutions prepared by different methods and Ag^+ concentrations: (a) chemical synthesis using plasma-chemically prepared grape pomace water extract; and (b) plasma-chemical-assisted synthesis using grape pomace in the aqueous medium: Ag^+ concentration (mmol/L): 1 − 0.25, 2 − 0.5, 3 − 1.0, 4 − 3.0 and 5 − 6.0
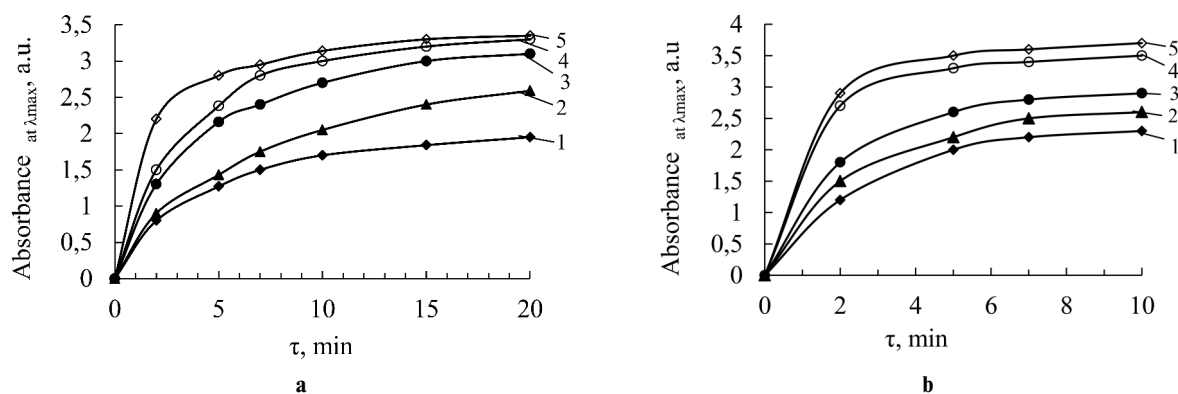
Fig. 2. Dependence of the absorbance (at λ_{max}) of prepared colloidal solutions of AgNPs on the synthesis duration under different preparation methods and Ag$^+$ concentrations: (a) chemical synthesis using plasma-chemically obtained grape pomace water extract; and (b) plasma-chemical-assisted synthesis using grape pomace in the aqueous medium. Ag$^+$ concentration (mmol/L): 1 − 0.25, 2 − 0.5, 3 − 1.0, 4 − 3.0 and 5 − 6.0 (τ=10 min)

for the conversion of Ag$^+$ into nanoparticles decreases by two times (5−7 min).

The dynamic light scattering technique was used to determine the mean particle size and polydispersity index (Table). The particle size distribution was evaluated for different Ag$^+$ concentration by both methods. It was shown that silver nanoparticles with a narrow size distribution were formed. The obtained data indicate that the average diameter of the nanoparticles formed via both methods is equal to 20−33 nm and slightly grows with increasing initial Ag$^+$ concentration. The polydispersity index of AgNPs prepared by the plasma-chemical-assisted method was 0.18−0.23, which indicates the stability of the nanoparticles.

The particle size and polydispersity index of prepared silver nanoparticles

C AgNO$_3$, mmol/L	Average particle size, d$_{AgNPs}$, nm		Polydispersity index	
	Method I	Method II	Method I	Method II
0.25	27.0	20.0	0.25	0.18
0.50	28.9	22.2	0.27	0.20
1.00	30.0	24.3	0.31	0.21
3.00	31.1	27.7	0.31	0.22
6.00	33.0	29.1	0.58	0.23

The SEM images of the prepared AgNPs are shown in Fig. 3,a,b. The observed morphology of the samples indicates that spherical nanoparticles are formed.

The microstructure of the synthesized AgNPs was investigated by XRD technique (Fig. 4). The AgNPs powder was obtained under the following conditions: τ=10 min and C(AgNO$_3$)=6.0 mmol/L.

The XRD peaks at 27.81^0, 32.16^0, 38.1^0, 46.1^0, 54.55^0, 66.74^0, and 76.84^0 correspond to 210, 122, 111, 200, 142, 220, and 311 crystalline planes for cubic crystalline structure of metallic silver (JCPDS card number 04-0783), respectively. The intensity of the peaks reflects a high degree of crystallinity of the silver nanoparticles.

Various nitro-aromatic compounds are extensively used in textile, paper, pharmaceutical, cosmetic, leather, plastic and food industries. According to the report generated by the US environment protection Agency (EPA), 4-nitrophenol belongs to the most widespread and dangerous nitro-aromatic wastes and toxic chemicals [15]. Thus, the reduction reaction of 4-nitrophenol to 4-aminophenol (4-AP) is a very important issue.

To evaluate the catalytic performance, the synthesized AgNPs were used for the degradation of 4-nitrophenol, an anthropogenic pollutants that is harmful to the environment. Though the reduction of 4-NP to 4-AP by using aqueous NaBH$_4$ solution is thermodynamically favorable (E^0 is equal to 0.76 V and 1.33 V vs. NHE for 4-NP/4-AP and H$_3$BO$_3$/BH$_4$, respectively), the potential barrier due to a large potential difference between donor and acceptor molecules decreases the feasibility of this reaction. It is well-known that the metal AgNPs catalyze this reaction by facilitation of electron transfer from the donor, BH$_4$, to the acceptor, 4-NP.

The data given in Fig. 5,a,b show that 4-NP reveals the absorbance peak at ~317 nm, which shifts to 400 nm in the presence of NaBH$_4$ due to the formation of 4-nitrophenolate ion in the alkaline medium caused by NaBH$_4$. The progress of the reaction was monitored by the UV-Vis absorption spectroscopy and confirmed visually by the disappearance of the yellow color of 4-NP. The

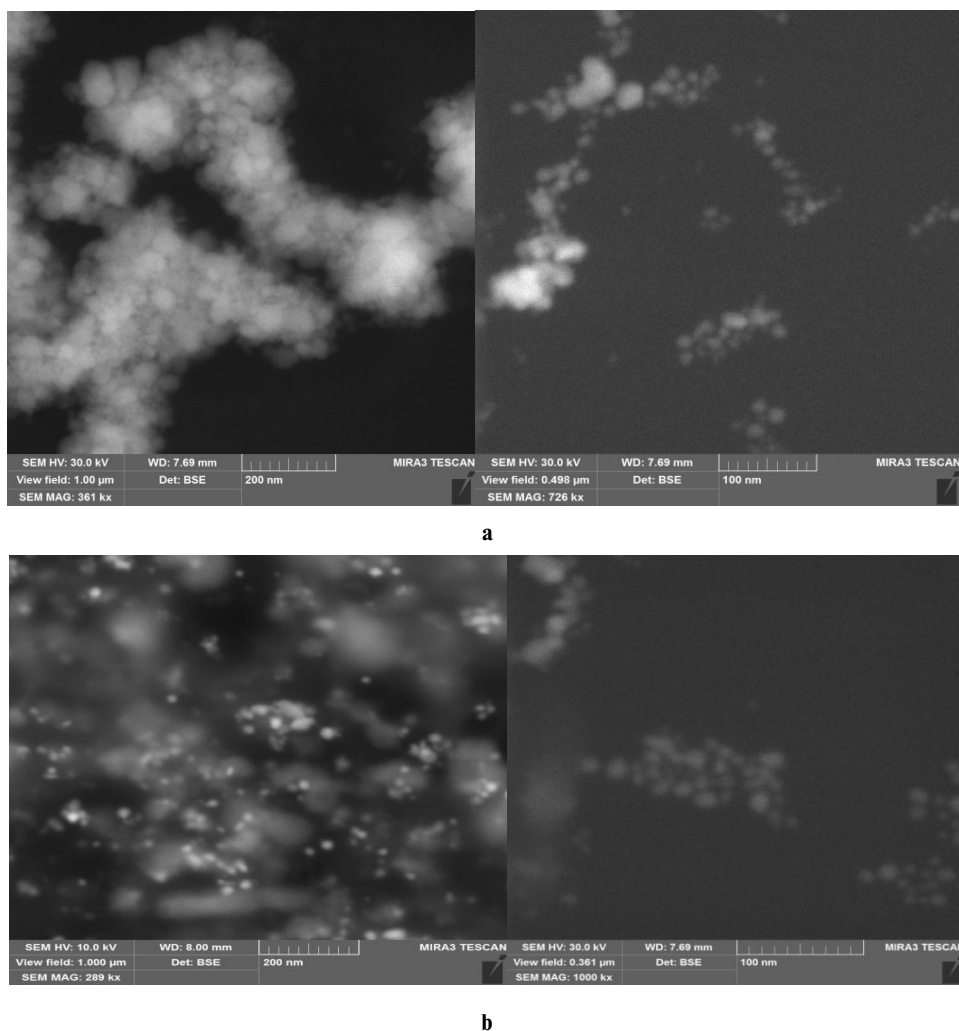*M.I. Skiba, V.I. Vorobyova, O.A. Pivovarov, K.O. Sorochkina, A.S. Shakun*

a

b

Fig. 3. SEM images of prepared silver nanoparticles: (a) chemical synthesis using plasma-chemically prepared grape pomace water extract and (b) plasma-chemical-assisted synthesis using grape pomace in an aqueous medium ($C(Ag^+)$=3.0 mmol/L and τ=10 min)
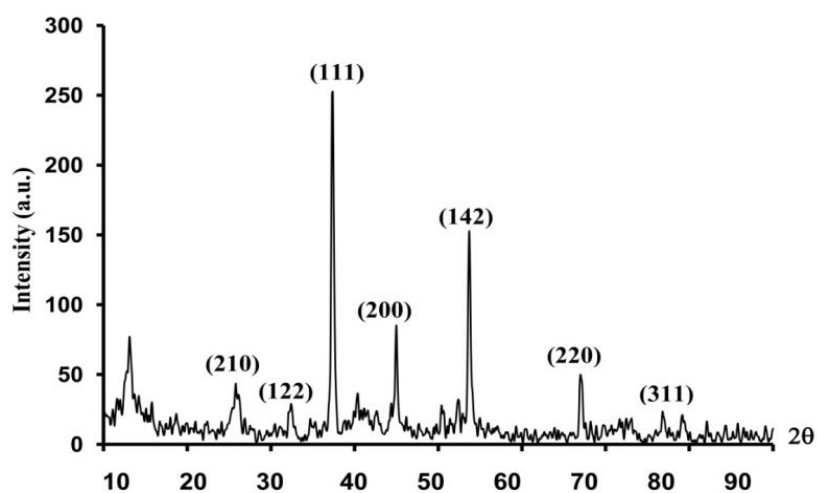

Fig. 4. X-ray diffraction pattern of silver nanoparticles (plasma-chemical-assisted synthesis using grape pomace in an aqueous medium ($C(Ag^+)$=3.0 mmol/L and τ=10 min)
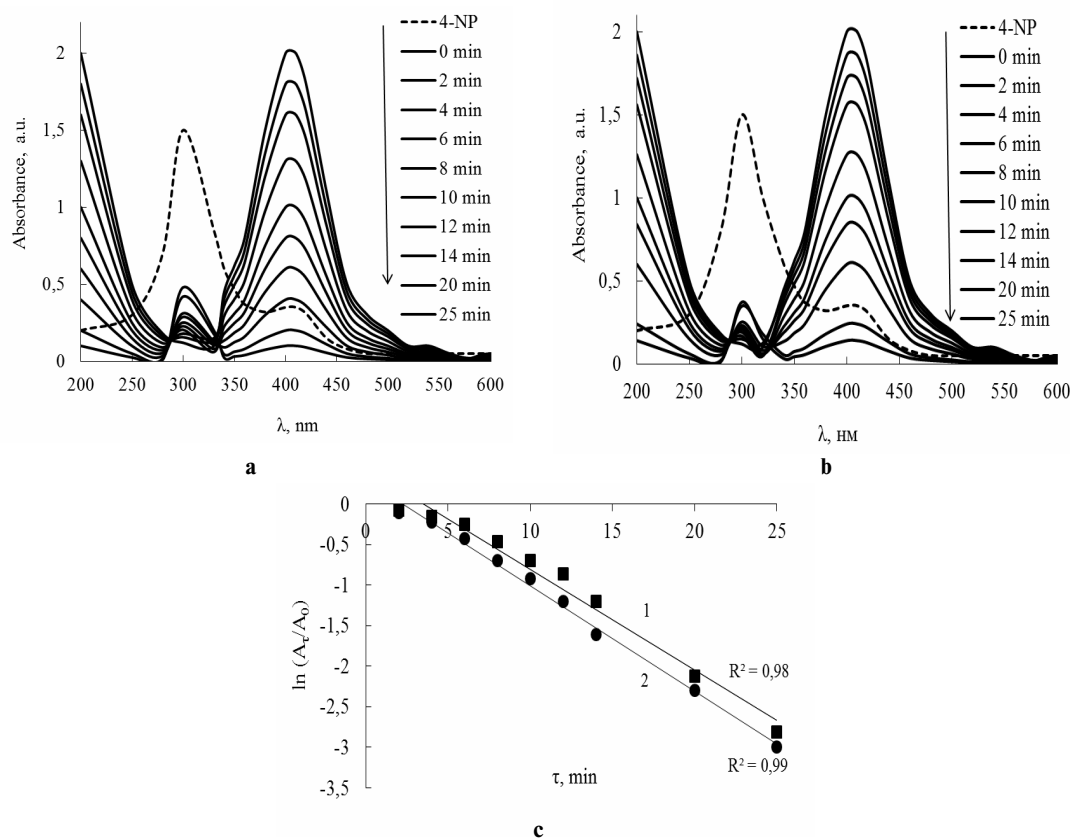
Fig. 5. Time-dependent UV-visible spectra for the catalytic reduction of 4-NP by NaBH₄ in the presence of AgNPs obtained using two different methods: (a) chemical synthesis using plasma-chemically obtained grape pomace water extract; and (b) plasma-chemical-assisted synthesis using grape pomace in the aqueous medium. (c) Plots of ln(A_t/A_0) vs. time for the reduction of 4-NP by NaBH₄ in the presence of AgNPs

introduction of nanoparticles leads to the rapid decrease in the absorption peak intensity at 400 nm, and, at the same time, to the concomitant appearance of a new peak at 298 nm, which indicates the formation of the reduction product, 4-AP. The reaction is completed within 20−25 min in the presence of AgNPs.

The control of the above reaction was performed by taking water instead of the nanoparticle solution. The peak at 400 nm remained unchanged even after 3 days that confirmed the catalytic role of the nanoparticles for the above reduction reaction.

Since the concentration of NaBH₄ significantly exceeds 4-NP, the reduction rate, probably, is independent of NaBH₄ concentration. Therefore, the catalytic rate constant in this case can be evaluated by studying the pseudo-first-order kinetics with respect to 4-NP concentration. Figure 5, c shows that there is a good linear relation between ln(A_t/A_0) and time after the induction time; the catalytic rate constants is 0.11−0.13 min⁻¹.

Conclusions

The environmentally friendly technique was developed to produce metal nanoparticles using green synthesis methods. UV-visible absorption spectral characteristics of the silver nanoparticles prepared at different Ag⁺ concentration and synthesis duration were determined. The UV-Vis spectrum of AgNPs exhibited a surface plasmon absorption at about 405−420 nm, which originated from the formation of AgNPs. The prepared AgNPs were spherical with the average particle size of about 20−33 nm. The crystal structure of the synthesized nanoparticles corresponded to the face-centered cube according to the data of powder XRD analysis. The catalytic performance of AgNPs was illustrated in the reaction of degradation of a pollutant, 4-nitrophenol. Thus, our study offers an effective and eco-friendly approach to the purification of the environment from organic pollutants.

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ПЛАЗМОХІМІЧНИЙ СИНТЕЗ НАНОЧАСТИНОК СРІБЛА З ВИКОРИСТАННЯМ ВІДХОДІВ ПЕРЕРОБЛЕННЯ ВИНОГРАДУ

М.І. Скиба, В.І. Воробйова, О.А. Півоваров, К.О. Сорочкіна, А.С. Шакун

Дисперсії наночастинок срібла (AgНЧ) були одержані двома методами: хімічним відновленням з використанням попередньо плазмохімічно одержаного водного екстракту відходів перероблення винограду як відновлюючого і стабілізуючого агента та одностадійним плазмохімічним синтезом з використанням відходів перероблення винограду у водному середовищі. УФ-спектри AgНЧ показали поглинання в діапазоні 405−420 нм, що обумовлено утворенням AgНЧ. Досліджено спектральні характеристики УФ-видимого поглинання наночастинок срібла, одержаних при різних концентраціях Ag⁺ і тривалості синтезу. Результати показали, що синтез обома методами забезпечує формування наночастинок срібла при досліджуваних концентраціях Ag⁺ (0,25−6,0 ммоль/л) протягом 5−10 хв. Динамічне світлорозсіювання і сканувальну електронну мікроскопію було використано для вимірювання гідродинамічних розмірів і морфології наночастинок срібла в суспензіях. Встановлено, що одержані Ag НЧ є сферичними із середнім розміром частинок близько 20−33 нм. Результати рентгеноструктурного аналізу порошку показують, що наночастинки Ag мають гранецентровану кубічну кристалічну структуру. Каталітичні властивості наночастинок були досліджені шляхом відновлення 4-нітрофенолу до 4-амінофенолу в присутності боргідріду натрію.

Ключові слова: наночастинки срібла, низькотемпературна нерівноважна плазма, вичавки винограду, каталітичне руйнування, нітрофенол.

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