Research Article

Preparation of Silver Nanoparticles in a Plasma-Liquid System in the Presence of PVA: Antimicrobial, Catalytic, and Sensing Properties

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The preparation of stabilized silver nanodispersions under the action of short-term plasma discharge using a polyvinyl alcohol stabilizer (polyvinyl alcohol (PVA)) was investigated. The influence of the basic technological parameters such as initial Ag^+ concentration, PVA concentration, and process duration on the formation of nanoparticles and their characteristics (size and stability) were determined. The UV-Vis spectra showed the localized surface plasmon resonance at wavelengths of 400–420 nm. The SEM images showed that the shape of Ag NPs is spherical with an average particle size up to 30 nm. Ag NPs were used as a catalyst for the reduction of 4-nitrophenol (4-NP). The effect of the concentration of PNP and catalyst dosage on the value of apparent rate constant (k_{app}) for catalytic reduction of 4-NP in the presence of Ag NPs was investigated by means of UV-Vis spectrophotometry. The antimicrobial activity of Ag nanoparticles was investigated against yeast and *Escherichia coli*. The colorimetric sensor studies of plasma synthesized Ag NPs showed selective sensing of the potentially hazardous Hg^{2+} ion in water.

1. Introduction

The preparation and characterization of metal nanoparticles with different nomenclatures, structures, and properties are a major research area in various fundamental and practical fields: nanoscale science, engineering, ecology, water treatment, chemical industry, medicine, etc. [1, 2]. According to the various assessments, silver nanodispersions are among the top 10 nanomaterials in the World Low-Tech Production [3, 4]. Nowadays, numerous traditional and novel methodologies have been developed for the synthesis of Ag NPs [1, 2, 5].

The analysis of the literature [1–8] shows that all known methods have advantages and disadvantages. As a rule, when carrying out the research, the authors use different physicochemical methods and obtain silver nanoparticles with specified properties. However, during the synthesis, the choice of reagents and process conditions is not standardized by ISO quality standards.

It is undeniable that the compliance of the nanomaterials with ISO quality standards is a very important parameter at all stages of their life cycle. In addition, it is also an important indicator for potential international customers [9].

According to the ISO standards, it is recommended to opt for technology with fewer reagents, "green" and more environmentally friendly resources. The preparation of the metal nanoparticles with the help of a green chemistry method must be evaluated under three specific aspects: the choice of nontoxic solvent, an environmentally friendly reducing agent, and a biodegradable stabilizing agent [10, 11]. The method of obtaining silver nanoparticles under the action of plasma discharge corresponds to all three of

them [11–13]. The plasma reduction has been proven to be a powerful tool to produce metallic nanoparticles. The metallic nanoparticles can be prepared in an aqueous solution in the presence of a stabilizer without using chemical reducing agents. There are various types of plasma discharge. There is no single classification to the present day. The short-term (up to 5 minutes) discharge of nonequilibrium low-temperature plasma is usually used for the formation of colloidal aqueous solutions of silver nanoparticles [14–16]. The authors have demonstrated the effectiveness of using CNP for the synthesis of silver nanoparticles in the presence of different types of stabilizers: sodium alginate [17], sodium citrate [18], etc [19, 20].

However, for the development of the omnipurpose plasma technology suitable for industrial implementation, it is advisable to study the patterns and characterization of the properties of silver nanoparticles obtained with different types of stabilizers.

Analysis of the literature [21–25] indicates that one of the widely used reagent stabilizers is polyvinyl alcohol (PVA). There are a considerable number of studies in which the use of PVA is investigated both as a stabilizer and as a stabilizer-reducing agent.

Meanwhile, one major drawback of the abovementioned studies examining the use of PVA is the lack of research on the properties of the material obtained. As a rule, the authors demonstrate the already known antimicrobial properties [7–9, 26, 27]. Other important properties of silver NPs, such as catalytic ones, remain unaddressed. Research on the multifunctionality of silver NPs can be broadly used for purification and decontamination of both drinking water and wastewater from various industries.

The main goal is to determine the influence of the various conditions on the synthesis of silver nanoparticles in the presence of polyvinyl alcohol using low-temperature nonequilibrium contact plasma and on properties (antimicrobial, catalytical, and sensing) of the obtained Ag nanoparticles for the further implementation in various fields.

2. Materials and Methods

2.1. Materials.
Silver nitrate (99.8%, Kishida), polyvinyl alcohol (Mw = 40 000) (PVA; hydrolysis degree of 99.0–99.8%), and p-nitrophenol were purchased from Sigma-Aldrich, USA. Aqueous solutions of precursor were prepared using ultrapure water (Direct-Q UV, Millipore) and were utilized as starting materials without further purification.

2.2. Synthesis of Silver Nanoparticles (AgNPs).
In a typical experiment, around 37.5 ml of $AgNO_3$ salt with a molarity of 0.3–3.0 mmol/L was added dropwise to 2.5 ml of PVA solution ($C = 1.25$ g/l for 0.3 mmol/L, $C = 2.5$ g/l for 0.5 mmol/L, $C = 2.5$ g/l for 1.0 mmol/L, and $C = 5.0$ g/L for 3.0 mmol/L Ag^+). PVA solution was prepared by dissolving PVA powder in double-distilled water (at 85°C for 1 h). The solution of $AgNO_3$-PVA was in the reactor with the discharge of

plasma. A detailed diagram of the installation and image of the plasma discharge is provided in the work [28, 29].

2.3. Characterization Techniques.
The formation behaviour of Ag NPs in the PVA solution was examined by using a UV-Vis spectrophotometer (UV-5800PC) with a variable wavelength between 300 and 700 nm in 5–10 nm increments, using a 1 cm optical path at room temperature. In the study of kinetic dependencies, the amount of Ag^+ was reduced using the ion-selective electrode of Ag^+ ions (ELIS-131Ag).

Microphotographs of nanoparticles were obtained on the scanning electron microscope JEOL JSM-6510LV (JEOL, Tokyo, Japan). TEM micrograph of the sample was taken using the JEOL TEM (Model 100 CX II; Tokyo, Japan). The particle size distribution and zeta potential of the prepared Ag NPs colloid were determined by the DLS technique using the Zetasizer Nano-25 analyzer (Malvern Instruments Ltd., Malvern, England) within the range of 0.1–10000 nm. The same instrument was also used to measure electrophoretic mobility which was subsequently transformed to ζ-potential using Smoluchowski's approximation. The value of the hydrogen index of the original solutions and the obtained sols was measured using a pH meter pH-150 MI (relative measurement error of 0.5%).

2.4. Antimicrobial Activity Test.
The suspension method is used to determine the antimicrobial activity of the obtained dispersions against test microorganisms. The preparation of work dilutions of nanosilver was carried out using a buffer solution of pH 7.0. *E. coli* at a concentration of 104 CFU/cm^3 was used as the test microorganism to determine the antimicrobial action of the colloidal nanosilver solution. The duration of the exposure in the experiment was 5 min, 1 hour, 2 hours, and 3 hours. During the test, 0.1 cm^3 suspension of the test microorganisms was added to 5 cm^3 of each mixture of work dilutions. Samples with solutions were incubated at (20 ± 1)°C. At the end of the exposure time, the samples were seeded at 0.5 cm^3 into two Petri dishes with a dense nutrient medium of TSA, which were incubated at 36°C for 24 hours. The amount of CFU/cm^3 was calculated for each dilution. The test results of the colloidal solution of nanosilver were compared with the results of *E. coli* culture control, carried out similar to the experiment.

2.5. Catalytic Activity.
Separate catalytic degradation experiments were performed for the aqueous azo dyes, namely, MB and for 4- nitrophenol. As a model reaction, we selected the reduction of 4-NP to 4-AP by $NaBH_4$. $NaBH_4$ is known to stimulate catalytic reduction of p-NP by cleavage of the N–O bond for replacement with an N–H bond in an aqueous environment. The catalytic hydrogenation of PNP to PAP was carried out in a 50 mL beaker with a PNP aqueous solution (20 mL, 0.1 mM). Then, 2 mL of freshly prepared aqueous solution of $NaBH_4$ (0.2 M) was introduced into the above solution. Subsequently, 2 mL (3.0 mmol/L) of catalyst was added to the solution with magnetic stirring at room temperature (25°C). The intensity of the absorption peak at

400 nm in the UV-Vis spectrophotometer was used to monitor the process of the conversion of p-nitro phenol (p-NP) to p-aminophenol (p-AP).

2.6. Colorimetric Detection. AgNPs were evaluated as a colorimetric sensor for various metal ions by adding a uniform concentration (0.5 mL, 10^{-3} M) of metal salt solutions (Hg^{2+}) into a prepared Ag NPs solution (3 mL). Then, the absorption spectra were obtained during 10 min, and color changes were observed by the naked eye.

3. Results and Discussion

In previous studies, it has been claimed that the presence of a stabilizer reagent is obligatory for the formation of stable silver dispersions under the action of a plasma discharge. Plasma compounds are formed in a solution during the action of a plasma discharge. Previous numerical studies have shown that the duration of the discharge up to 5–7 minutes is sufficient to form nanoparticles in a discrete-type reactor (plasma parameters: pressure at 80 kPa, current strength at 120 mA, distance from the electrode to the surface was 5–7 mm, and the material of electrodes was X18H10 T).

For the unification of this assertion, similar studies have been performed for aqueous solutions with a PVA stabilizer.

Figure 1 shows the dependence of the spectrum of the obtained silver NPs on the duration of action of the plasma discharge on the initial solution of silver nitrate (0.3–3.0 mmol/l) at molar ratios of [Ag^+]:[PVA]= (1):(~0.0055) for 0.3–0.5 mmol/l, (1):(~0.003) for 1.0 mmol/l, and (1):(~0.002) for 3.0 0 mmol/l) in the presence of PVA. A dark brown suspension of colloids was formed after the plasma treatment of the reaction mixture from 10 sec up to 7 min. This dark brown color may be due to the collective vibrations of the charged particles present on the surface of nanoparticles and the resonance.

The analysis of the obtained data has led to a number of conclusions as follows:

In all studied samples (when changing the ratio Ag^+/PVA), with increase in the duration of the discharge of plasma, there is an increase in the intensity of absorption. The SPR peak is observed in the range of 410–450 nm, which is typical for nanoparticles up to 30 nm in size. This value is in good correlation with the literature [1–27, 30] reports on the spectrum of silver nanoparticles in aqueous solutions. However, the presence of only one absorption peak confirms the spherical shape of the NPs being studied. As for the absorption spectrum of unirradiated pure PVA, it has shown near zero absorption.

In all tested samples, the maximum optical density was reached in 4–6 minutes; however, in the case of a silver concentration of 3.0 mmol/L, the treatment duration of the discharge of 6–7 min contributes to a broad peak, which indicates the formation of nanoparticles with a high index of dispersion.

In the previous work [31], it was shown that the formation of silver nanoparticles without the introduction of the stabilizer reagent is a pseudo-first-order reaction and the reaction rate constant is 0.4 min^{-1}. Investigation of the kinetics of nanoparticle dispersion formation with the addition of PVA also showed that the reaction is pseudo-first order. However, the reaction rate constant is slightly higher and is ~0.55 min^{-1} (Figure 2). Such a slight increase in the constant value is likely to be associated with the possible reducing properties of Ag^+ ions, in addition to their stabilizing ability.

It is known that the properties of nanosystems depend on the size characteristics of the nanoparticles. Therefore, controlling their morphology and size is an important task. The synthesis conditions directly affect the size and shape of the nanoparticles and their polydispersity.

For the investigated ratios of the reagents, the average particle size and stability of the obtained colloidal dispersions have been established (Table 1, Figure 3). Depending on the Ag^+/PVA ratio, the solutions obtained are characterized by an average zeta potential within the range of –37.6 to –39.7 mV which indicates the high stability of the prepared Ag NPs. In addition, the measurement of the optical absorption spectrum of a colloidal NP solution over a long period (6 months) revealed no significant changes in the spectrum, indicating the stability of the NPs. The average particle size was found to be 25–30 nm.

Morphological investigation of Ag/PVA NPs is carried out using SEM and TEM (Figure 4).

The nanoparticles have a spherical shape. Figure 4 shows that the average size is smaller than the measurement method (DLS). The larger average diameter measured may be a result of the following: the adsorption of the PVA on a cluster of particles rather than on individual particles or sonication may have not fully dispersed the aggregated particles, thus resulting in larger average diameter values of the SEM measurements.

Previous studies have shown that using a stabilizer of steric type (sodium alginate) and plasma-chemical synthesis of adjusting the pH of the solution to an alkaline environment (more than 8) is desirable, as it leads to an increase in the average particle size and size distribution. Furthermore, it is known from the other studies that changes in solution pH (2–10) had no effect on ζ-potential of the sterically stabilized Ag NPs.

The initial value of the solutions' pH is 6.33–7.03, depending on the initial silver ions and PVA (Figure 5). The nature of the dependence coincides with one another, and a sharp decrease in pH to 3.5 is seen after 40 seconds of the effect of the discharge on the solution.

The modified suspension method was the optimal method for determining the antimicrobial activity of silver NP solutions [32]. The advantage of the latter in comparison with the studied method of dilutions and the method of diffusion in agar is the use of distilled water as a solvent, which minimizes inactivation of nanoparticles.

Experimental studies to determine the antimicrobial activity of a colloidal nanoparticle solution has shown that the *E. coli* test microorganism is sensitive to the action of Ag nanoparticles at concentrations of 20 to 12 $\mu g/cm^3$ (Table 2). Therefore, at the presence 20.0 μg/cm3 Ag NPs in the
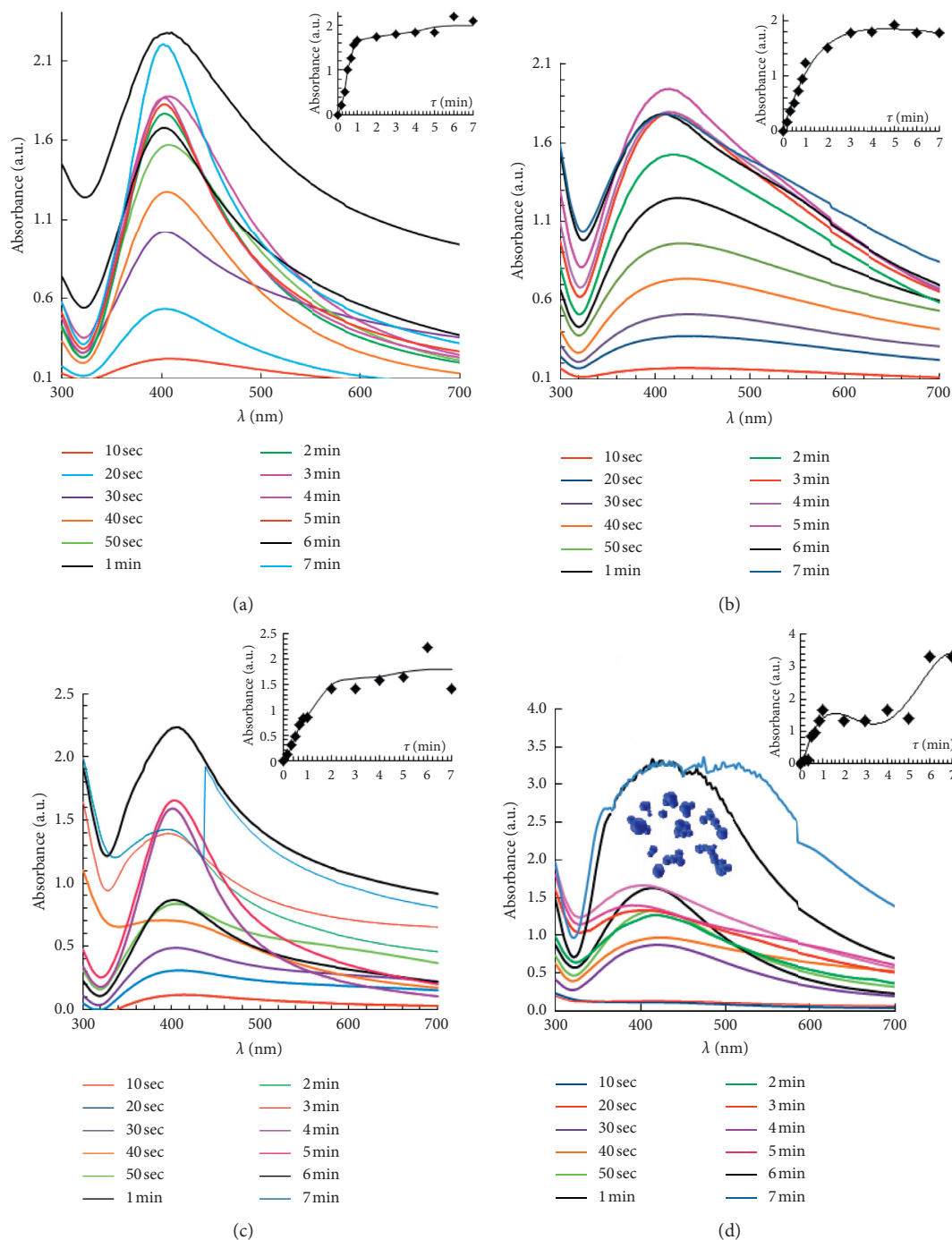
Figure 1: Absorption spectrums of silver nanodispersions with the addition of stabilizer ,PVA, at different concentrations of Ag^+: 0.3 mmol/l (molar ratio $[Ag^+]:[PVA]$ = (1):(~0.0055) (a), 0.5 mmol/l $[Ag^+]:[PVA]$ = (1):(~0.0055) (b), 1.0 mmol/l ($[Ag^+]:[PVA]$ = (1):(~0.003) (c), and 3.0 mmol/l $[Ag^+]:[PVA]$ =(1):(~0.002) (d)).

samples with fixed amount colony-forming unit (CFU) after 5 min exposition is not observed CFU. In the presence 12.0 μg /cm3 Ag NPs time for antibacterial effect more then 5 min and is about 3 hours. Exposure within 3 hours has caused a bactericidal effect on the test microorganisms. At concentrations of 3.75 μg/cm^3 and 1.875 μg/cm^3, a steady decrease in microbial load has occurred during this time. It should be

noted that antibacterial studies need further investigation by other known methods.

Phenol and its derivatives are highly stable organic compounds and very hazardous to the environment. Every year, the countries in the world produce thousands of tons of nitrophenols. These compounds are very toxic to aquatic organisms and can cause direct neurotoxicity.
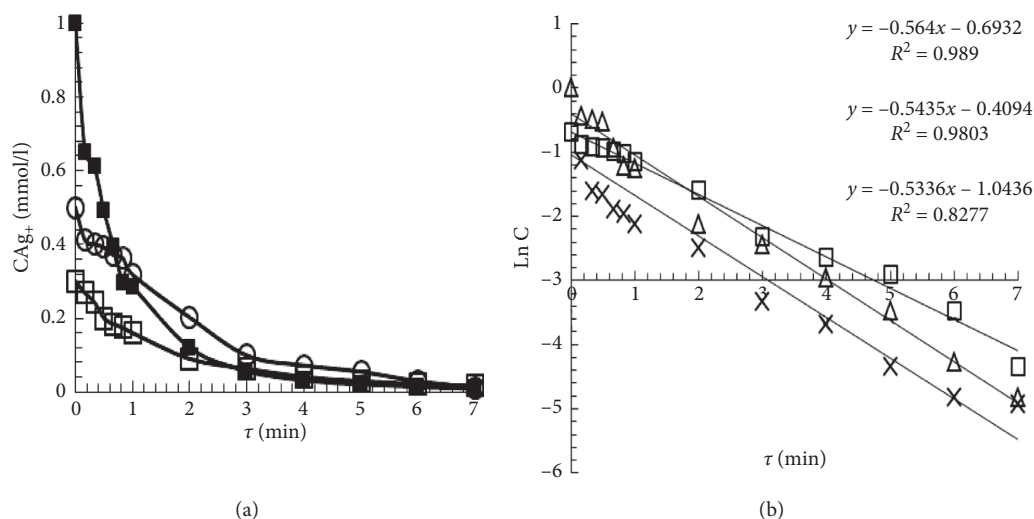
(a)

(b)

FIGURE 2: Dependence of equilibrium Ag$^+$ concentration and logarithm as a function of the duration of plasma discharge at different initial concentrations of silver ions in solution in the presence of PVA.

TABLE 1: Size of silver nanoparticles obtained under the conditions of plasma treatment (Ag$^+$/PVA) solution ($\tau = 5$ min).

C AgNO$_3$ (mmol/L)	Z-potential (mV)	Average particle size (d) of AgNPs (nm)
0.3	−37.6	30.1
0.5	−38.1	31.1
1.0	−39.7	33.0

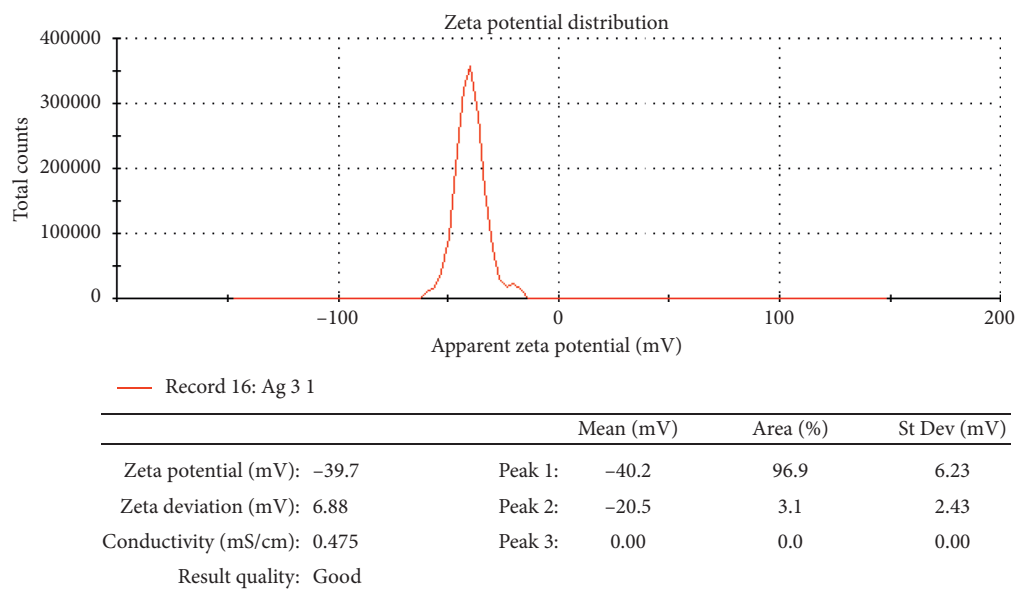|	Mean (mV)	Area (%)	St Dev (mV)
Zeta potential (mV): −39.7	Peak 1: −40.2	96.9	6.23
Zeta deviation (mV): 6.88	Peak 2: −20.5	3.1	2.43
Conductivity (mS/cm): 0.475	Peak 3: 0.00	0.0	0.00
Result quality: Good			

FIGURE 3: Zeta potential of water colloid silver/PVA (C AgNO$_3$ 1.0 mmol/L for 5 min).

It is known that the original 4-nitrophenol (4-NP) aqueous solution with light yellow color shows an absorption peak centered at 317 nm [29]. After adding NaBH$_4$ solution, the maximum absorption shifted to 400–410 nm, with a simultaneous color change to bright yellow due to the formation of p-nitrophenolate ions under the alkaline condition (Figure 5).

In the presence of a catalyst (Ag NPs), the peak at 410 nm decreases over time and is accompanied by the formation of a new peak at 298 nm. Such changes characterize the reduction of nitrophenol to 4-aminophenol (4-AP).

The linear correlation between ln (A_t/A_0) versus reduction time in minutes indicates that the reduction follows a pseudo-
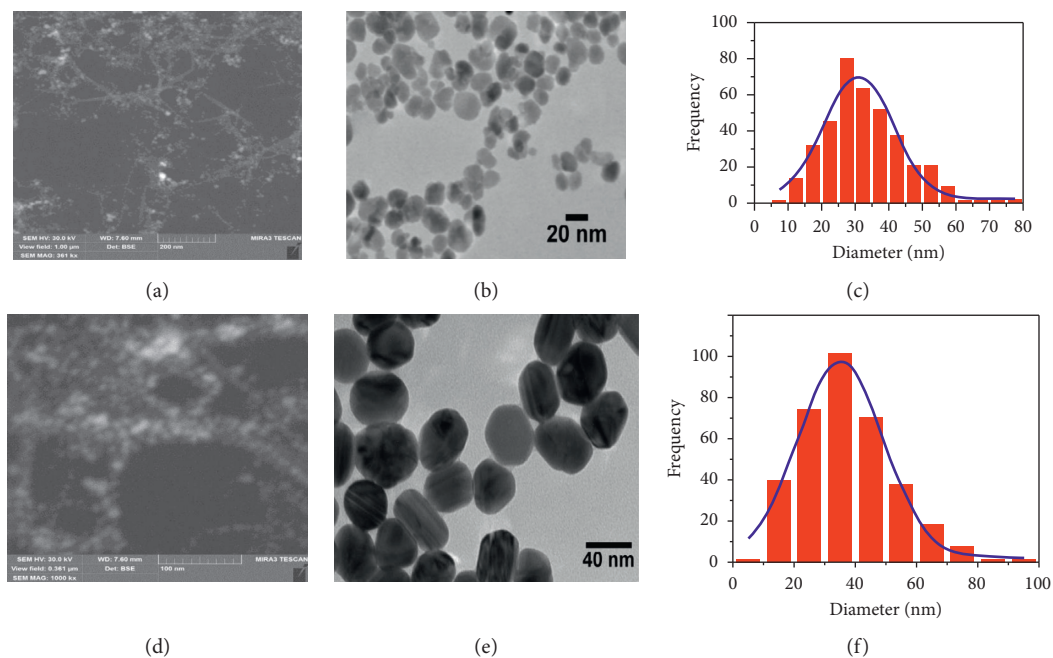
(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 4: SEM and TEM images of silver nanoparticles obtained by plasma treatment in the presence of PVA and corresponding size distribution of AgNPs (C AgNO$_3$ 0.3 and 1.0 mmol/L, $\tau = 5$ min).
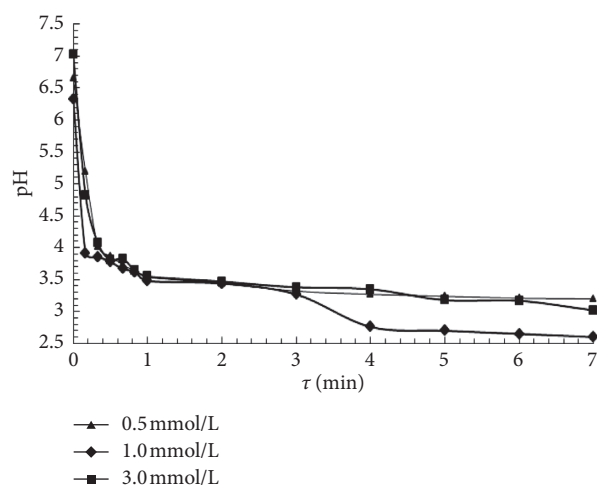

FIGURE 5: Change in the pH of the solution during the plasma treatment and formation of silver nanoparticles.

TABLE 2: Determination of the antimicrobial activity of a solution of nanoparticles against the test microorganism *E. coli* with the help of the suspension method.

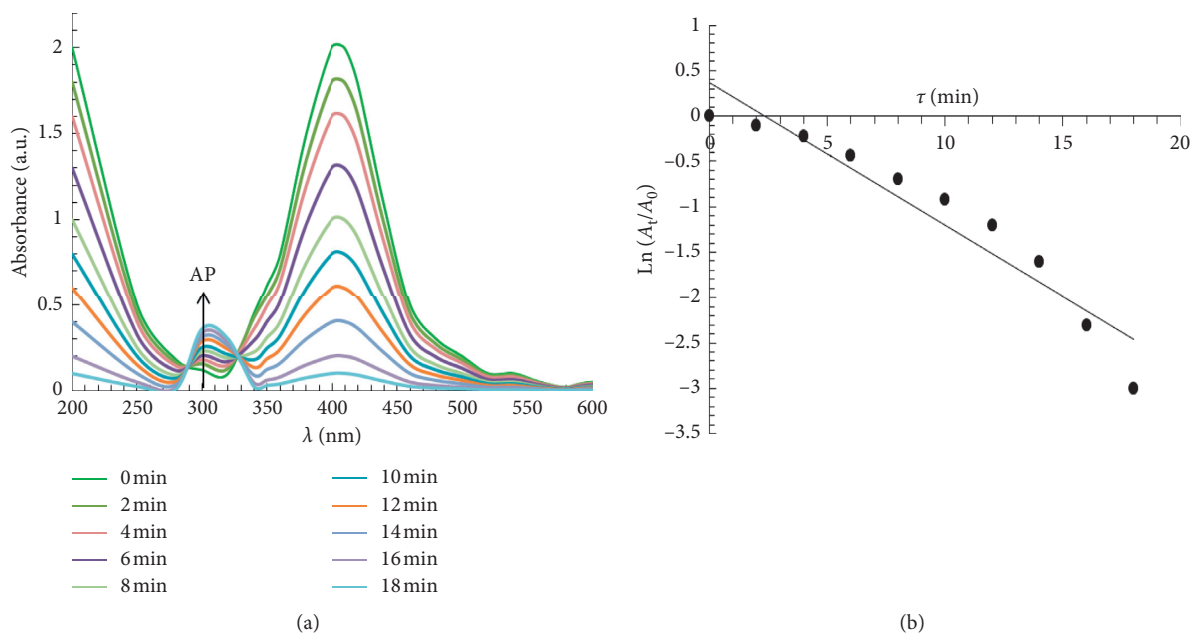| Exposure time	Concentration of silver NPs (μg/cm^3), CFU/cm^3					Test microorganism *E. coli*
	20.0	12.0	5.5	3.75	1.875	
5 min	0	25	28	26	52	65
1 hour	0	15	27	30	33	61
2 hours	0	13	24	18	19	62
3 hours	0	0	6	10	12	63

Figure 6: Catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with the Ag NPs as the nanocatalyst (a); ln (A/A_0) versus reaction time (b).
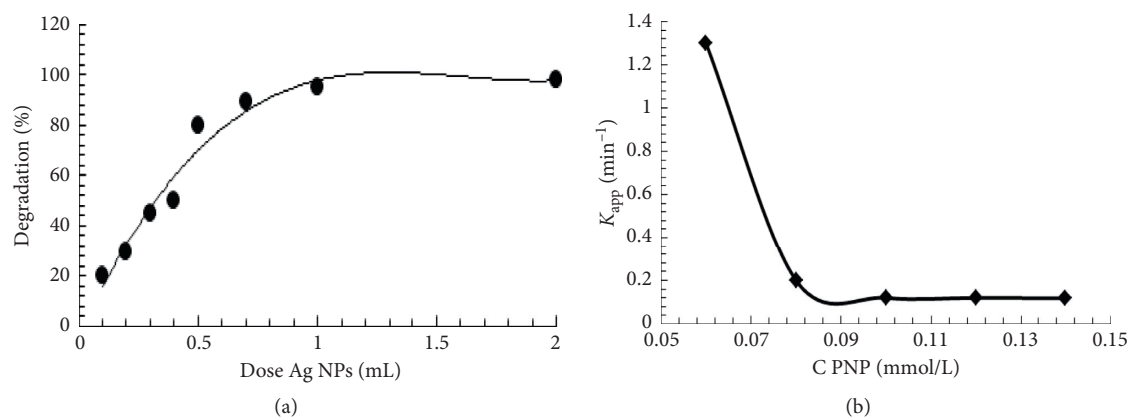

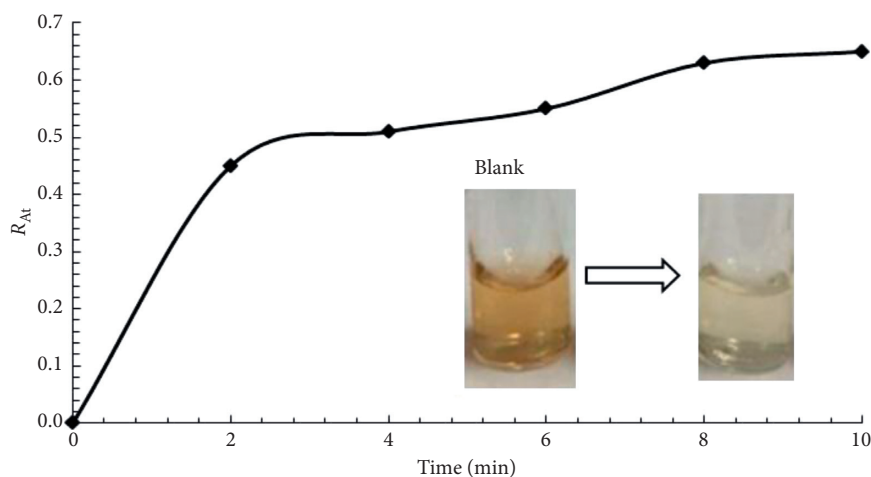Figure 7: Effects of catalyst dosage (a) and concentration of PNP (b) on the catalytic performances.

Figure 8: Relative change in absorbance, R_{At}, as a function of time at a fixed concentration of Hg^{2+}.

first-order reaction kinetics (Figure 6(b)) ($K_{app} = \ln A/A_0 = \ln$, where A and A_0 are the peak absorbances of 4-NP at 400 nm at a given time t and initial time ($t = 0$); K_{app} is the apparent rate constant ($\sim$0, 17 min^{-1} ($R^2 = 0.98$)).

The effect of the catalyst dose on the decomposition of the pollutant was investigated. Figure 7(a) shows that an increase in the amount of Ag leads to an increase in the rate of decomposition. Therefore, the introduction of 0.5 to 2 ml per 20 ml of solution into the reaction medium allows us to obtain rates of destruction of nitrophenol at the level of 80–98%. This is because more catalytic active sites can be provided with more catalyst being added into the reaction mixture. Figure 7(b) shows that the increase of the PNP concentration results in a decrease of the K_{app} value.

There is evidence of the detection of metal ions using spherical silver nanoparticles. The use of silver nanoparticles for determination of Hg has been described [33]. In most cases, the determination is based on the formation of ionic and/or coordination bonds between metal ions and nanoparticle modifiers; therefore, the type of modifier plays an important role in regulating the sensitivity and selectivity of the determination. Due to the interaction of a metal ion with modifier molecules located on the surface of silver NPs, most often "crosslinking" of nanoparticles occurs, which leads to their aggregation, which is accompanied by a strong change in the optical characteristics of the system.

It was found (Figure 8) that the addition of Hg^{2+} solution into Ag NPs decolorized the solution from dark yellow and demonstrated the selective sensing of Hg^{2+} ions.

4. Conclusions

In the present study, the synthesis of silver NPs has been demonstrated by a green and environmentally friendly approach using short-term plasma discharge and polyvinyl alcohol as a stabilizer agent. The influence of the basic technological parameters such as initial Ag$^+$ concentration, PVA concentration, and process duration on the formation of nanoparticles and their characteristics (size and stability) was determined. The effect of the concentration of PNP and catalyst dosage on the value of apparent rate constant (k_{app}) for catalytic reduction of 4-NP in the presence of Ag NPs was investigated by means of UV-Vis spectrophotometry. The antimicrobial activity of Ag nanoparticles was investigated against yeast and *Escherichia coli*. We tested Ag NPs as plasmonic sensors in water. The colorimetric sensor studies of plasma-synthesized AgNPs showed selective sensing of the potentially hazardous Hg^{2+} ion in water.

Data Availability

All data are provided in the Results section of this paper. The data used to support the findings of this study (SEM images) are included within the article and are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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