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Catalytic performance of Ag, Au and Ag-Au nanoparticles synthesized by lichen extract

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Abstract: In the present study, the green chemistry approach for the biosynthesis of Ag, Au and Ag-Au bimetallic nanoparticles (NPs) was applied using lichen extract [*Cetraria islandica* (L.) Ach.]. The lichen extract acts both as a reducing and stabilizing agent. The monometallic and bimetallic NPs were characterized by transmission electron microscopy (TEM), ultraviolet-visible (UV-Vis) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The results showed that NPs were successfully synthesized and the prepared structures were generally spherical. The synthesized nanostructures exhibited excellent catalytic activities towards reduction of nitrophenols (4-nitrophenol; 4-NP) to aminophenols (4-aminophenol; 4-AP) with sodium borohydride (NaBH_4). It was determined that bimetallic NPs exhibit more effective catalytic activity than monometallic Ag and Au nanostructures. This is the first report on 4-NP reduction with Ag, Au and Au-Ag NP catalysts prepared by lichen extract.

Keywords: bimetallic nanoparticles; biosynthesis; catalysis; *Cetraria islandica* (L.) Ach.

1 Introduction

Nanoparticles (NPs) have very interesting electrical, optical, magnetic and chemical properties with respect to their bulk counterparts [1]. For this reason, studies on NPs have been increased rapidly and NPs have been introduced to a variety of application areas [2, 3]. NP synthesis is carried out with two general approaches; top-down (pyrolysis, lithography, etc.) and bottom-up (chemical vapor deposition, sol-gel technique, electrodeposition, chemical reduction, etc.) methods. Due to its low cost,

simplicity and mild synthesis conditions, a bottom-up approach, the chemical reduction method, is a widely preferred technique for synthesis of metal NPs. Chemical reduction of metal salts and stabilization of particles may be realized by chemicals that are harmful to the environment and human health as they contain chemicals such as sodium borohydride (NaBH_4), N,N-dimethylformamide and trisodium citrate [1, 4]. For this reason, there has been increasing interest in alternative chemicals that are benign for human health and the environment. As a result of those studies, green reducing and stabilizing agents have been developed [1]. These green agents can be classified into two types as microorganisms and plants [5]. Plants are gaining more popularity due to their simplicity and scalability [3, 7].

It has been reported that Ag, Au monometallic and Ag-Au bimetallic NPs synthesized by green approaches can be applied in various fields such as catalysts, electronics and biosensors [3, 8]. As the Fermi potential of the NPs becomes more negative, compared to their bulk states, a significant change in the reduction potential for metal NPs is observed. This feature allows them to act as catalysts in electron transfer processes [9]. It is also indicated that bimetallic NPs exhibit better catalytic activity and selectivity compared to monometallic NPs [3, 8].

Dyes are important environmental pollutants that are commonly used in textiles, cosmetics, food, leather and plastics industries [4]. The decomposition of the nitro and azo compounds in these dyes takes a very long time and they can accumulate in the soil and stay without decaying for many years [4]. Nitrophenols, such as 4-nitrophenol (4-NP), are widely used in the production of dyes, medications and insecticides. They are major threats to humans and the environment due to their carcinogenic and mutagenic properties [10]. Many processes have been developed to remove the dyes based on photoelectric decay, adsorption, microwave assisted decay and photocatalytic reduction. However, all of these processes require using organic solvents and consuming high amounts of energy. As a result, an alternative effective and environmentally friendly method is needed for reducing nitrophenol to replace those inconvenient methods [2, 4, 9]. Under these circumstances, modern methods based on bio-green synthesized NPs to reduce these dangerous dyes are an attractive alternative approach, because they do not need

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complicated synthesis procedures and can be operated under mild conditions [4].

4-Aminophenol (4-AP), a reduction product of 4-NP, has a wide range of applications in a variety of industries, such as photographic developer, corrosion inhibitor, drying agent, analgesic and antipyretic drugs. For this reason, nitrile reduction with borohydride is preferred in the presence of suitable catalysts. As an alternative route, monometallic or bimetallic noble metal NPs proved to be effective catalysts for 4-NP reduction [10].

Many studies have been carried out to synthesize metallic NPs using biological materials in the literature [4, 6–8, 10–16].

Lichen is one of the interesting plant groups which is a symbiosis of algae and fungi [17]. With their variety of sources, the number of lichen species in the world reaches around 25,000 [18]. The habitat and substrates of the lichens are very broad. They exist in different parts of earth, from polar to tropical regions, from high mountains to shores and from deserts to very cold regions. Lichens can grow and develop in soil, rocks and stones, trees, bark, bones, timber, walls of houses, monuments, tiles, tombstones, glass and old iron tools. Lichens digest the calcareous and granite rocks gradually with lichen acids which exist in their chemical structure. They accumulate radioactive elements in their thallus, and are resistant to high radioactive doses. For this reason, lichens are extremely important plants in terms of ecology. It is also an unusual plant used in medical, dye and perfumery industry, food, folklore and decoration [17, 18].

In this study a lichen species *Cetraria islandica* (L.) Ach. extract was used as reducing and stabilizing agent for preparation of Ag, Au monometallic and Ag-Au bimetallic NPs. *C. islandica* (L.) Ach. is a lichen species that exists abundantly in the mountainous parts of northern European countries. It also grows in forestland in Central Anatolia. It consists of lace-like serrated pieces with a green color and contains 15% moisture [17, 18]. The efficiency of *C. islandica* (L.) Ach. extract to synthesize Ag NPs was investigated before [16] by our research group. In this study, the catalytic activities of Au, Ag and bimetallic Ag-Au NPs prepared using *C. islandica* (L.) Ach. extract on 4-NP reduction were investigated for the first time.

2 Materials and methods

2.1 Material

Fresh *C. islandica* (L.) Ach. was collected from Turkey (Yapraklı, Çankırı). Chloroauric acid (HAuCl_4), silver nitrate (AgNO_3), 4-NP and

NaBH_4 were purchased from Sigma-Aldrich (Germany). Deionized water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$) was used for preparation of all aqueous solutions obtained from the Young Lin aquaMAX-ultra ultrawater purification system (South Korea).

2.2 Preparation of lichen extracts

Collected samples of lichens from the natural environment were cleaned under an optical microscope to remove surface impurities and then crushed into small pieces with liquid nitrogen. After size reduction, 6 g of powdered lichen was extracted in 80 ml of ethanol. The prepared *C. islandica* (L.) Ach. extract was filtered and stored at 4°C to further use for NP synthesis.

2.3 Synthesis of Ag and Au NPs

10 ml of 1.5 mM HAuCl_4 and AgNO_3 solutions were used for the synthesis of monometallic Au and Ag NPs, respectively. *C. islandica* (L.) Ach. extract (1 ml), which is a reducing and stabilizing agent, and 0.5 M NaOH solution, to adjust the pH of the reaction mixture (pH ~ 10), were added to the metal salt solution. Then, the reaction mixture was stirred at 80°C under continuous mixing for 30 min. The color of the resulting solutions of Au NPs and Ag NPs changed to purple and yellowish brown, respectively [16].

2.4 Synthesis of Au-Ag bimetallic NPs

10 ml of 1.5 mM HAuCl_4 and AgNO_3 solutions were used for the synthesis of Ag-Au bimetallic NPs. The molar ratios of the Ag and Au solutions were changed to 1:1, 1:2, 2:1 and these bimetallic NPs are defined as Ag50Au50, Ag33Au67 and Ag67Au33, respectively. *C. islandica* (L.) Ach. extract (1 ml) and 0.5 M NaOH solution (pH ~ 10) were added to the reaction mixture which was stirred at 80°C under continuous mixing for 30 min.

2.5 Catalytic experiments (catalytic activity of Au, Ag and Ag-Au bimetallic NPs)

The catalytic activities of Ag NPs, Au NPs and Au-Ag bimetallic NPs on the reduction of 4-NP to 4-AP were investigated. 9.52 ml of $9.6 \times 10^{-5} \text{ mM}$ 4-NP aqueous solution was freshly prepared and mixed with excess NaBH_4 (0.1 M and 0.48 ml). Yellow dye solution (2.7 ml) was added in a standard quartz cuvette. To initiate the reducing of 4-NP, 200 μl of prepared monometallic (Ag, Au) or Ag-Au bimetallic NPs solution was added to the above mixture. The reduction was monitored by ultraviolet-visible (UV-Vis) spectra and the yellow solution was decolorized in time, during the reduction.

2.6 Characterization of Au, Ag and Ag-Au bimetallic NPs

The formation and catalytic activities of the Ag, Au and Ag-Au bimetallic NPs were monitored by UV-Vis (model: Shimadzu-UV 1601,

Japan) in a range between 200 nm and 900 nm, 200 nm and 500 nm, respectively. Transmission electron microscopy (TEM) images were taken by a Fei Tecnai G² Spirit Bio(TWIN) (USA) operated at an accelerating voltage of 80 kV. Infrared spectra of *C. islandica* (L.) Ach. extract and NPs samples were obtained with a Fourier transform infrared (FTIR) (model: Shimadzu FTIR 8400-S, Japan) in the range between 400 cm⁻¹ and 4000 cm⁻¹.

3 Results and discussion

Synthesis of Ag, Au monometallic and Ag-Au bimetallic NPs were carried out with facile and one pot reduction approach. *C. islandica* (L.) Ach. was used as a reducing agent without the need for another stabilizing agent. Figure 1 shows UV-Vis spectra of Ag, Au monometallic and Ag-Au bimetallic NPs. The presence of a surface plasmon resonance (SPR) band of monometallic and bimetallic NPs represented that metal NPs were successfully prepared with *C. islandica* (L.) Ach. For monometallic Ag (Ag100Au0) and Au (Ag0Au100) NPs, the SPR band maxima of NPs are 410 nm and 534 nm, respectively. By contrast, SPR bands of bimetallic NPs are between the absorption bands of Ag and Au monometallic NPs. Furthermore, it redshifts with increasing Au content. SPR band maxima of Ag67Au33, Ag50Au50 and Ag33Au67 NPs are 412 nm, 519 nm and 523 nm, respectively. These results are compatible with many studies in the literature [12, 19]. UV-Vis spectroscopy is a useful tool to discover whether the prepared bimetallic NPs have alloy, core-shell structure or a heterogeneous mixture of their monometallic counterparts. UV-Vis spectra of all bimetallic NPs have

one absorbance band that is positioned between SPR bands of monometallic Ag and Au NPs. It is well known that a heterogeneous mixture of monometallic Ag and Au causes the formation of two absorption bands that represent related monometallic NPs. Core-shell NPs exhibit two distinct absorption bands or one absorption band that is positioned at a similar wavelength with metal on the shell, depending on the thickness of the shell metal. By contrast, alloy NPs have only one absorption band between SPR bands of monometallic Ag and Au NPs and its position redshifts with increasing Au amount in the NPs structure. As a result of these findings, the prepared bimetallic NPs may have an alloy structure [19]. The UV-Vis spectra of all monometallic and bimetallic NPs have another absorption band near 300 nm that arises from components of *C. islandica* (L.) Ach., such as fumarprotocetraric acid, licheterinic acid and usnic acid, etc. [20]. This proves interaction between *C. islandica* (L.) Ach. and the prepared NPs that refer to an effective stabilizing role of the extract. The UV-Vis spectra of the prepared NPs does not change for several weeks which shows effective and stable stabilization of prepared NPs by *C. islandica* (L.) Ach.

To obtain catalytically efficient metal NPs, the aim was to synthesize stable monometallic and bimetallic NPs that have a small size and narrow size distribution. Figure 2 shows TEM images and Figure 3 shows particle size distribution of Ag, Au monometallic and Ag33Au67 bimetallic NPs. Monometallic Ag and Au NPs have a spherical structure. For both Ag and Au monometallic NPs, more than 97% of the prepared NPs are between 6 nm and 19 nm. By contrast, bimetallic Ag-Au NPs have both spherical and polygonal structures. More than 98% of the Ag33Au67 bimetallic NPs are between 6 nm and 21 nm. Ag33Au67 NPs display uniform contrast and homogenous electron density within whole NP volumes, indicating that the prepared bimetallic NPs have an alloy structure [7, 21]. Both monometallic and bimetallic NPs prepared with *C. islandica* (L.) Ach. extract have narrow particle size distribution with small mean sizes that provide a high active surface area for catalyst application. Table 1 shows mean particle size and particle size distribution of Ag-Au bimetallic NPs prepared by green reducing agents in the literature. *C. islandica* (L.) Ach. exhibits smaller mean size and narrower particle size distribution with respect to most of the studies from the literature. These results indicate that as an effective reducing agent for reduction of metal ions for preparation of metal NPs, *C. islandica* (L.) Ach. extract is also an effective stabilizing agent for preparation of stable NPs.

Figure 1: Ag (Ag100Au0), Au (Ag0Au100) monometallic and Ag67Au33, Ag50Au50, Ag33Au67 bimetallic nanoparticles prepared by *Cetraria islandica* (L.) Ach. extract.

Figure 2: Transmission electron microscopy (TEM) images of: (A, B) Ag nanoparticles, (C, D) Au nanoparticles and (E, F) Ag₃₃Au₆₇ bimetallic nanoparticles.

FTIR spectra are useful to identify which functional groups or mechanisms are responsible for preparation and stabilization of metal NPs. It is known that *C. islandica* (L.) Ach. is rich in polysaccharides and secondary metabolites such as protocetraric acid, fumarprotocetraric acid, lichesterinic acid, protolichesterinic acid, etc. [29, 30]. Figure 4 shows FTIR spectra of dried *C. islandica* (L.) Ach. extract and Ag₃₃Au₆₇ NPs. The FTIR spectra of *C. islandica* (L.) Ach., shows absorption

bands of O-H stretching vibration peak (3400 cm^{-1}), C-H stretching vibrations of aliphatic acids (2924 cm^{-1} and 2854 cm^{-1}), C=O chain ester vibration (1743 cm^{-1}), C=O phenyl ester vibration (1690 cm^{-1}), C=O aldehyde vibration (1651 cm^{-1}), C=C vibration (1573 cm^{-1}), CH_2 , CH_3 band (1443 cm^{-1}) and C-O methyl ester vibrations (1273 cm^{-1} , 1072 cm^{-1}) [31]. For the FTIR spectra of Ag₃₃Au₆₇, appearance of the highly intensive band at 1383 cm^{-1} is assigned to the C=O mode of carboxylic acid and the

Figure 3: Particle size distribution of (A) Ag nanoparticles, (B) Au nanoparticles and (C) Ag-Au bimetallic nanoparticles.

Table 1: Mean particle size and particle size distribution of Ag-Au bimetallic nanoparticles prepared by green reducing agents from the literature.

	Reducing agent	Mean size (nm)	Particle size distribution (nm)
Shankar et al. [22]	Neem (<i>Azadirachta indica</i>) leaf broth	–	50–100
Ganaei et al. [23]	<i>Antigonon leptopus</i>	–	8–176
Raju et al. [24]	Macerase enzyme	9	4–20
Xia et al. [10]	Degraded <i>Pueraria</i> starch	32 ± 1.6	–
Zheng et al. [25]	Yeast cells	–	9–25
Yallappa et al. [26]	<i>Jasminum sambac</i> leaf extract	–	20–50
Abdel Hamid et al. [3]	<i>Potamogeton pectinatus</i> L.	6.6 ± 2.4	–
Tamuly et al. [13]	<i>Piper pedicellatum</i> C.DC	–	3 ± 0.2 – 45.3 ± 1.6
Kumari et al. [7]	Pomegranate fruit extract	12	–
Song and Kim [27]	Persimmon (<i>Diopyros kaki</i>) leaf extract	–	50–500
Karthika et al. [28]	<i>Guazuma ulmifolia</i> bark	–	10–20
This study	<i>Cetraria islandica</i> (L.) Ach. extract	13	6–21

methyl interactions in large branched molecules that provide stabilization and capping of prepared NPs. This result confirms oxidation of phenolic compounds within *C. islandica* (L.) Ach. extract as a result of reduction of metal ions to form quinones [12].

3.1 Catalytic property

Both monometallic and bimetallic NPs are effective catalysts for many reactions. In order to investigate the catalytic activity of Ag and Au monometallic and Ag-Au

Figure 4: Fourier transform infrared (FTIR) spectra of dried *Cetraria islandica* (L.) Ach. extract and Ag33Au67 nanoparticles.

bimetallic NPs with different metal compounds, the conversion of 4-NP to 4-AP was chosen as a model reaction. For thermodynamically favorable 4-NP reduction with NaBH_4 , the large standard reduction potentials between -0.76 V (4-NP/4-AP) and -1.33 V ($\text{H}_3\text{BO}_3/\text{BH}_4^-$) hinder the progress of the reaction. As a result of this obstacle, it is well known that the reduction of 4-NP reaction with NaBH_4 is only possible with addition of a suitable catalyst to the reaction system. After of the adsorption both BH_4^- and 4-NP on catalyst particle surfaces, metal NPs can provide electron transfer from the donor BH_4^- to the acceptor 4-NP to catalyze the reaction [31, 32].

Before the catalytic studies, the possible effects of reducing agents [NaBH_4 and *Cetraria islandica* (L.) Ach.] were examined. After addition of NaBH_4 to 4-NP solution, nitrophenolate anions occurred with an absorption band at 400 nm. Addition of excess NaBH_4 did not alter the absorption band of 4-NP, even after several hours, which confirms that reduction of 4-NP to 4-AP reaction is not possible without a metal NP catalyst. For effective determination of the reaction rate constant of monometallic and bimetallic NPs, the possible effect of *C. islandica* (L.) Ach. On the reduction reaction was also examined before catalytic experiments. As an effective reducing agent, *C. islandica* (L.) Ach. extract had no effect on the 4-NP absorption band absence of metal NP catalyst. Figure 5 shows the UV-Vis spectra of the catalytic conversion process of 4-NP to 4-AP by NaBH_4 with Ag, Au, Ag67Au33, Ag50Au50 and Ag33Au67 NP catalysts. After addition of both monometallic and bimetallic NPs to the reaction solution, the 4-NP absorption band at 400 nm decreased gradually, while a new absorption band at 298 nm occurred, which indicates formation of 4-AP. This alteration of the absorption bands confirms successful conversion of 4-NP to 4-AP. For Ag monometallic NPs and

Ag-rich Ag67Au33, the reduction reaction rate is significantly lower with respect to Au monometallic and Au-rich Ag50Au50 and Ag33Au67 bimetallic NPs. By contrast, Ag NPs also exhibited lowest conversion of 4-NP to 4-AP (Figure 5A). Alloying Ag with Au (Ag67Au33) significantly increased the conversion rate of 4-NP (Figure 5C). Increasing the Au atoms within bimetallic NPs [Ag50Au50 (Figure 5D) and Ag33Au67 (Figure 5E)] and using monometallic Au NPs as catalyst (Figure 5B) leads to complete reduction of the 4-NP absorption band at 400 nm.

As a result of addition of excess concentration of NaBH_4 , the reducing reaction of 4-NP follows pseudo first order kinetics. Therefore, it is possible to calculate the reaction rate constant by measuring the absorbance of 4-NP at 400 nm using Eq. (1):

$$\ln\left(\frac{A_t}{A_0}\right) = -kt \quad (1)$$

A_0 and A_t are absorbance of 4-NP at $t=0 \text{ s}$ and measured absorbance values at different reaction times, respectively, and $k \text{ (s}^{-1}\text{)}$ pseudo first order is the rate constant. Figure 6 shows $\ln(A_t/A_0)$ vs. reaction time (t) plot [31]. For all nanocatalysts, good linear fitting of $\ln(A_t/A_0)$ to reaction time values were obtained. The reaction rate constant can calculated with the relationship between $\ln(A_t/A_0)$ - t by applying Eq. (1). The rate constants for Ag, Ag67Au33, Au, Ag50Au50 and Ag33Au67 NP catalysts are 0.0023 s^{-1} , 0.0052 s^{-1} , 0.0123 s^{-1} , 0.0132 s^{-1} and 0.0302 s^{-1} , respectively. The rate constants show that monometallic Au NPs have better catalytic activity than monometallic Ag NPs. For bimetallic NPs, the composition of NPs has a great effect on catalytic activity, increasing the Au content in alloy NPs which caused increase in catalytic activity. Moreover, Ag50Au50 and Ag33Au67 bimetallic NPs exhibited an enhanced performance with respect to monometallic Ag and Au NPs. Both monometallic and bimetallic NPs have similar shape, mean particle size and particle size distribution. The enhanced catalytic performance of bimetallic Ag-Au NPs may arise from the higher ionization potential of Au (9.22 eV) than Ag (7.58 eV) that causes electronic charge transfer from Ag to Au and which leads to an increase in the electron density on the NP surface [7, 33].

4 Conclusion

In summary, as a green agent, *C. islandica* (L.) Ach. proved to be an effective reducing and stabilizing agent

Figure 5: Ultraviolet-visible (UV-Vis) spectra of reduction of 4-nitrophenol (4-NP) by sodium borohydride (NaBH_4) with (A) Ag, (B) Au, (C) Ag₆₇Au₃₃, (D) Ag₅₀Au₅₀ and (E) Ag₃₃Au₆₇ nanoparticle catalysts.

Figure 6: Plot of $\ln(A_t/A_0)$ vs. reaction time (t).

for preparation of monometallic Au and bimetallic Ag-Au NPs for the first time in the literature. Both prepared stable monometallic and bimetallic NPs have small mean diameters and narrow particle size distribution, and can be effective candidates for application as catalysts in many reactions. In this study, the catalytic activity of monometallic Ag, Au and bimetallic NPs prepared with *C. islandica* (L.) Ach. towards conversion of 4-NP to 4-AP was investigated. As a result of the synergic effect arising from alloying Ag and Au atoms, Au rich bimetallic NPs (Ag₅₀Au₅₀ and Ag₃₃Au₆₇) exhibited higher catalytic performance with respect to their monometallic counterparts. These results demonstrate that NPs synthesized

by *C. islandica* (L.) Ach. have great potential for catalytic applications.

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