A New Approach for the Green Biosynthesis of Silver Oxide Nanoparticles Ag$_2$O, Characterization and Catalytic Application

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Abstract

In this paper, a facile and green approach for the synthesis of silver oxide nanoparticles Ag$_2$O NPs was performed using the extract of the wild plant Herniaria hirsuta (H. hirsuta). Different spectral methods were used for the characterization of the biosynthesized Ag$_2$O NPs, ultraviolet-visible (UV-Vis) spectroscopy gave a surface plasmon resonance (SPR) peak of Ag$_2$O NPs is 430 nm, estimation of direct and indirect forbidden gap bands are respectively 3.76 eV and 3.68 eV; Fourier transform infrared (FTIR) spectral analysis revealed the groups responsible for the stability and synthesis of Ag$_2$O NPs. The morphology of Ag$_2$O NPs was studied by scanning electron microscopy (SEM) showing a nearly spherical shape of Ag$_2$O NPs, and X-ray diffraction (XRD) study confirmed the crystallinity of Ag$_2$O NPs with a crystallinity size of 15.51 nm. The catalytic activity of Ag$_2$O NPs, as well as the rings number were studied by the degradation of methylene blue dye.

Keywords: Silver oxide Ag$_2$O nanoparticles; Herniaria hirsuta; Silver nitrate AgNO$_3$; Dye degradation


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1. Introduction

Nanotechnology is defined as “the creation and use of structures, devices, and systems characterized by their distinct and varied characteristics and infinitesimal size, typically to deal with particles in the size range 1-100 nm [1]. At these scales, the material acquires properties that are unusual and often different from those of the same materials in bulk: they should be considered as new chemical compounds with different toxicities and characteristics [2]. Recently, silver-based nanomaterials have been widely considered as antimicrobial agents [3–7]. Silver oxide nanoparticles can have different applications in the form of sensors [8], photovoltaic cells [9], catalysts [10], and fuel cells [11]. These products can also be practiced as important components in optical memories [9], and plasmonic photonic devices [12]. Researchers and specialists have predicted the great role that nanotechnology will play in the development of the developing world, so the abundance of new and revolutionary ways and means, which have contributed to advances in several fields such as energy storage and transportation, pharmaceuticals and medicine [13]. Green synthesis is a modern field of biotechnology that is environmentally friendly and economical as an alterna-

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tive to chemical and physical methods that in many cases are dangerous for the environment. Because in this method, natural reagents are biologically safe, non-toxic and environmentally friendly [14], Ziziphus clinopodioides [15], Petiveria alliacea L. [16], Paeonia emodi [17], Centella asiatica and Tridax [18], Callistemon lanceotus (Myrtaceae) [19] and many others have been used in the biosynthesis of metal oxide nanoparticles [20].

In the green synthesis of metal oxide nanoparticles, researchers have used plant extracts widely available in nature. Due to its speed, environmental efficiency and low cost, which are known as "vital plants". It has the power to absorb minerals while respecting the safety levels [21]. These methods include algae, microbes such as fungi, bacteria, and viruses as reducing agents [6,22]. The current method has more than one advantage as it is an economical technique that is solvent and surfactant-free [21].

In recent years, several studies have been conducted in the field of nanotechnology that exploits green plant materials and extracts for the biosynthesis of metal oxide nanoparticles to avoid chemicals responsible for environmental pollution. The biosynthesis of metal nanoparticles is carried out by a green method, using different plant fractions as reducing and stabilizing agents. Among the many metallic nanoparticles that have been studied, silver oxide is a valuable material used in various fields because of its unique characteristics. Therefore, it occupies great importance in the field of nanomaterials. Its characteristics are photoelectric, catalysis and drug delivery [23,24], cathode in rechargeable batteries [11]. The increase of the industrial activities implies always a great pollution of the environment by chemicals is due to an insufficiency of treatment systems, simple and less expensive solutions are then strongly required, among them we find the nanoparticles which already showed their potential in the treatment of organic pollutants such as the blue of methylene which is very used in several sectors: chemistry, pharmacology, medicine, biology, textile [25]. The ignorant use of this substance causes serious damage to human health and the environment [26,27].

In this study, for the first time silver oxide nanoparticles Ag$_2$O NPs were synthesized and studied by the aqueous extract of H. hirsuta plant. The characterizations of the obtained Ag$_2$O NPs nanoparticles were analyzed using standard techniques such as UV-Vis, FT-IR, XRD and SEM. In addition to a study of their optical properties and their catalytic activity for dye degradation were evaluated.

2. Materials and Methods

2.1 Materials

The precursor chemicals used were: silver nitrate AgNO$_3$ (99.9%, oxford LAB FINE CHEM. India), the plant H. hirsuta was harvested from the province of Ouezzane in the North of Morocco, sodium hydroxide (98%, LOBA CHEMIE PVT.LTD. India). The glassware used was washed with acetic acid and rinsed with distilled water. Two mortars one in porcelain and the other in zirconium.

2.2 Preparation of the Extract of the Plant H. hirsuta

The H. hirsuta plant was harvested during the June, dried and stored in the dark at room temperature, after about two months the H. hirsuta plant was washed twice with distilled water and dried at room temperature for 48 h, ground to a fine powder. 10 g of the H. hirsuta plant was added to 400 mL in a 500 mL beaker. The mixture was shaken vigorously at 5000 rpm and under room temperature overnight. The extract obtained was filtered through a piece of tissue and stored in a container. Finally, the filtrate was centrifuged at a speed of 10,000 rpm under room temperature to obtain a clear brown supernatant and stored in a container away from light for further use.

2.3 Biosynthesis of Silver Oxide Nanoparticles (Ag$_2$O NPs)

In a 250 mL beaker, 20 mL of the silver nitrate solution AgNO$_3$ (4.5 g, 0.04 mol) was added to 60 mL of the plant extract H. hirsuta while stirring at 5000 rpm at room temperature for 10 min. The formation of biosynthesized Ag$_2$O NPs was observed by the change of color and the appearance of a brown-black precipitate after a duration of 5 min and confirmed by UV-vis spectroscopy after adjusting the pH = 8 by sodium hydroxide solution (0.1 M). Finally, the mixture was centrifuged at a speed of 10,000 rpm under room temperature to remove the supernatant, the precipitate was washed twice with distilled water and methanol then dried in the oven at a temperature of 70 °C overnight, and stored in a glass container for further analysis.

2.4 Characterization of Silver Oxide Nanoparticles (Ag$_2$O NPs) Biosynthesized

2.4.1 UV-vis spectroscopy

The production of Ag$_2$O NPs was monitored using UV-visible spectroscopy
measurements were recorded in the wavelength range of 250 to 900 nm and at room temperature. Its stability was monitored by UV-vis spectroscopy using distilled water as a control in a quartz cell.

2.4.2 X-ray Diffraction (XRD)

Crystal structure of the biosynthesized Ag$_2$O NPs was carried out by an X-ray powder diffractometer (Phaser D2 Diffractometer, Broker, USA), with Cu-Kα radiation of wavelength $\lambda = 0.15406$ nm in the range of 10°−80°, operating at 30 KV and 10 mA.

2.4.3 Fourier transform infrared spectroscopy FT-IR

Different functional groups were observed by FTIR spectral analysis Varian 800/Gladiatr model (Scimitar Series, Australia/Pike Technologies, USA) such as carbonyls, amines, phenols and amides which could be bioreducers for the synthesis of Ag$_2$O NPs.

2.4.4 Scanning electron microscopy SEM

The morphology and shape of synthesized Ag$_2$O NPs were studied using scanning electron microscopy coupled with EDS (SEM-JEOL IT500HR) with the following characteristics: Landing Voltage 15.0 kV, WD 11.0 mm, Magnification x800, Vacuum Mode High Vacuum.

2.5 Catalytic Activity of Biosynthesized Ag$_2$O NPs

2.5.1 Catalytic degradation of methylene blue dye

The silver nanoparticles obtained by the green method, tested for the reduction of methylene blue in the presence of sodium borohydride (NaBH$_4$) and white light at room temperature. First, 3 mL of diluted methylene blue was analyzed in the visible ultraviolet, two optical absorption peaks appeared at 611 nm and 663 nm. To study the catalytic effect of biosynthesized silver nanoparticles Ag$_2$O NPs, 2.25 ml of NaBH$_4$ solution ($6 \times 10^{-6}$ M) (considered as a reducing agent) was added to 3 mL of methylene blue solution ($2 \times 10^{-6}$ M), then the addition of biosynthesized silver nanoparticles (80 mg/L). The degradation process was monitored by spectrophotometry in a wavelength range of 400-800 nm every 5 min for 30 min. The decolorization was observed by the decrease in the absorbance intensity of the solution at maximum length ($\lambda_{\text{max}}$). The experiments evaluated the catalytic efficiency of the biosynthesized Ag$_2$O NPs nanocatalysts.

3. Results and Discussion

3.1. Characterization of Silver Oxide Nanoparticles Ag$_2$O NPs

3.1.1 UV-vis spectroscopy and optical bandgap

Preliminary studies suggest that photo-chemical screening of *H. hirsuta* plant extract evidences the presence of polyphenols, flavonoids and condensed tannins [28]. The as-prepared colloidal solution of Ag$_2$O and the plant extract were analyzed by UV-Vis spectroscopy (see Figure 1). In fact, the spectrum of plant extract showed two peaks at 300 nm and 670 nm. After the reaction, the spectrum of Ag$_2$O NPs revealed a peak located at 430 nm. This peak corresponds to the characteristic surface plasmon resonance absorption band of Ag$_2$O [29].

3.1.2 Determination of the optical bandgap

In general, the optical band gap of a semiconductor can be determined by plotting the absorption coefficient against the photon energy which could be estimated using Tauc’s formula (Equation (1)) [30]:

\[
(\alpha h\nu) = K (h\nu - E_{g})^{n}
\]

where $\alpha$ is the absorption coefficient, $h\nu$ is the incident photon energy, $K$ is a constant, $E_{g}$ is the optical band gap in electron volts (eV) and $n$ is an exponent that can take two values depending on the nature of the electronic transition, *i.e.* $n = 2$ for a direct transition, and $n = 1/2$ for an indirect transition as shown in Figure 2 and Figure 3 [31,32].

![Figure 1. UV-visible Spectrum (b) of Ag$_2$O NPs biosynthesized and (a) of plant Extract of *H. hirsuta*.](image-url)
3.1.3 Estimation of the Urbach energy

The Urbach energy refers to the width of the band tails of localized states. The Urbach energy is determined from Equation (2) from the slope of the linear part of the plot of ln against the photon energy (Figure 4) [33]. The results of the direct and indirect bandgap, as well as the Urbach energy, are presented in Table 1.

\[
\ln(\alpha) = \frac{h \nu}{E_u} + \ln(\alpha_0)
\]  

(2)

Figure 2. Determination of the optical bandgap for the direct transition using the Tauc method.

Figure 3. Determination of the optical bandgap for the indirect transition using the Tauc method.

Table 1. The values of direct, indirect bandgap and Urbach energy of the biosynthesized Ag\(_2\)O NPs.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Direct Optical bandgap</th>
<th>Indirect Optical bandgap</th>
<th>Urbach energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.76</td>
<td>3.68</td>
<td>1.23</td>
</tr>
</tbody>
</table>

3.1.4 Fourier transform infrared spectroscopy (FTIR)

Identification by FTIR analysis shows the potential presence of reducing and stabilizing biomolecules in the extract of the plant H. hirsuta. In the resulting FTIR spectrum (Figure 5) several absorption bands are presented, which correspond to the functional groups of the biomolecules existing in the plant extract of H. hirsuta. Seven main absorption peaks were observed, the broad peak centered at 3400 and 3533 cm\(^{-1}\) are assigned to the O–H stretching vibrations of flavonoids and alkaloids, the intense peak at 1123 and 1687 cm\(^{-1}\) are due to
the C=O stretching and N−H bending vibrations of the primary amide group which often exist in proteins [34]. The two peaks located at 1392 cm\(^{-1}\) pharmaceuticals and medicine and 1621 cm\(^{-1}\) are attributed to Nitro-banding NO and COC stretching vibrations of the aromatic ring respectively [35]. In addition, the peaks located at 673 cm\(^{-1}\) and 650 cm\(^{-1}\) were respectively attributed to Ag−O bending vibrations and C−H out-of-plane bending vibrations [25].

The FTIR results show that the extract of \textit{H. hirsuta} plant contains many different functional groups, such as: carboxyls, carbonyls, amides and phenols, which could be used as bioreducing and capping agents for the synthesis of Ag\(_2\)O NPs [28].

3.1.5 X-ray diffraction (XRD)

The X-ray diffraction pattern of biosynthesized Ag\(_2\)O NPs is shown in Figure 6. Several Bragg reflection peaks were observed in the XRD pattern located at 2 values of 27.28\(^{\circ}\), 33.36\(^{\circ}\), 55.93\(^{\circ}\), 66.52\(^{\circ}\) and 70.01\(^{\circ}\) corresponding to the (110), (111), (220), (311) and (222) planes of Ag\(_2\)O silver oxide of face-centered cubic crystal structure (JCPDS, File No. 00-012-0793) [20]. The crystallite size of the biosynthesized Ag\(_2\)O NPs nanoparticles was calculated using Scherrer’s formula Equation (3), considering the most intense peak located at the \(\theta\) value of 33.45\(^{\circ}\):

\[
D = \frac{0.9 \times \lambda}{\beta \cos \theta}
\]  

where \(D\) is the crystal size (nm), \(\beta\) is the total width at half the diffraction peak maximum.

Figure 6. XRD diagram of biosynthesized Ag\(_2\)O NPs.

Figure 7. (a) FESEM images of spherical biosynthesized Ag\(_2\)O, (b,c) corresponding EDS elemental mapping of O and Ag, (d) EDS spectrum of NPs Ag\(_2\)O biosynthesized.
(FWHM) of the most intense diffraction peak, $\lambda$ is the X-ray wavelength (for Cu-Kα $\lambda=1.5406$ Å), and $\theta$ is the Bragg diffraction angle. Its value was 17.16 nm, and the average crystal size is 15.51 nm.

3.1.6 Morphological study by scanning electron microscopy (SEM)

SEM was used to study the morphology of Ag$_2$O NPs and their morphological size. In Figure 7 (a-c) the SEM images and elemental mapping of Ag$_2$O NPs. It was observed that most of them have a spherical shape. And in Figure 7 (d), EDS analysis indicates that the elements present in the synthesized product are oxygen O and silver Ag, the element Ag more abandoning than the element O.

3.2 Catalytic Activity for BM Degradation

The catalytic hydrolysis of MB dye in the presence of NaBH$_4$ was examined to confirm the catalytic activity of Ag$_2$O NPs. The catalytic degradation is monitored by UV-Vis spectroscopy. By adding the Ag$_2$O nanoparticles into the reaction mixture, the catalytic reduction of the dye takes place after a few minutes. The strong blue color of the MB solution fades and becomes colorless after 35 minutes during the degradation process Figure 8. The degradation efficiency is calculated by the following formula (Equation (4)):

$$D\% = \left(\frac{C_0 - C_t}{C_0}\right) \times 100$$

where $C_0$ is the initial concentration of MB and $C_t$ the immediate concentration in the sample. The presence of amide groups of Ag$_2$O NPs in the electron transfer of BH$_4^-$ anions to MB cations, which increases with time, which was also similar to the previously reported Ag$_2$O NPs [36,37]. The initial absorption peak at 663 nm was attenuated with time, which demonstrates the catalytic activity of the Ag$_2$O NPs product (Figure 10). Figure 9 schematically shows the mechanism of the catalytic degradation process of MB dye. The number of cycles of use of biosynthesized Ag$_2$O nanoparticles for the photocatalysis of MB is equal to 4 (Figure 11).

Analysis of the kinetic data of the degradation reaction showed that the reaction kinetics is pseudo-first order. The reaction rate is determined by the following relationship:

$$\ln \left(\frac{C_t}{C_0}\right) = \ln \left(\frac{A_t}{A_0}\right) = -K_{app} \times t$$

where $C_t$ ($A_t$) and $C_0$ ($A_0$) represent the concentration (absorbance) of the MB dye after and before degradation, respectively. The slope of Figure 8. UV-vis spectrum for the reduction of MB using biosynthesized Ag$_2$O NPs.

Figure 9. Schematic of the catalytic degradation process of MB dye by Ag$_2$O NPs.
the curve determines the value of $K_{app}$ (min$^{-1}$). The linear plot of $\ln \left(\frac{C_t}{C_0}\right)$ versus time (Figure 12) affirms the kinetic theory, where the value of $K_{app}$ is 0.020 min$^{-1}$ [36,38]. The catalytic performance of silver oxide nanoparticles is related to their specific morphology that allows the rapid movement of electrons on the catalyst surface, and their small size (average size of 15.51 nm) ensures a large specific surface area that facilitates the dye degradation reaction by the silver oxide nanocatalyst, which reaches the rate of 88.6% after a duration of 35 min. Then, these two characteristics of biosynthesized Ag$_2$O NPs accelerate the degradation process of the methylene blue dye.

4. Conclusion

In this study, for the first time the green synthesis of silver oxide nanoparticles was successfully achieved using the aqueous extract of the wild plant *Herniaria hirsuta*. The process is easy, fast, cheap, environmentally friendly, and does not require any organic solvent or surfactant. Therefore, this synthesis method is more advantageous than traditional methods for the synthesis of Ag$_2$O nanoparticles. The shape of the biosynthesized Ag$_2$O nanoparticles is almost spherical, of cubic crystalline nature, and the average crystal size is 15.51 nm, which implies that they will be of great interest to the research community. Moreover, the Ag$_2$O nanoparticles prepared exhibit a better catalytic activity for the degradation of the MB dye under standard conditions which approached the rate of 89% due to their morphology and their small size. The biosynthesized Ag$_2$O NPs are of great importance in wastewater treatment (dye degradation), medicine, cosmetics, paints, plastics and textiles.

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References


