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Synthesis and Characterization of Silver Nanoparticles Prepared with Carrasquilla Fruit Extract (Berberis hallii) and Evaluation of Its Photocatalytic Activity

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Abstract: In this study, silver nanoparticles (AgNPs) were obtained using a green-chemistry procedure. For this protocol, the Carrasquilla extract (CE) (Berberis hallii) and a AgNO₃ solution were used as the reducing agent and the metal precursor, respectively. The as-prepared AgNPs after characterization were then used to evaluate the degradation of the methylene blue (MB), the safranin (SF), and the mixture of both dyes in the aqueous phase under solar light irradiation. The photocatalytic activity of AgNPs for the degradation of the MB (k = 0.0092 min⁻¹) was higher than the SF (k = 0.00016 min⁻¹) due to the susceptibility of the thiazine ring of the MB to photodegradation contrasted to the phenylphenazine of the SF. However, SF was mostly removed by adsorption with a maximum uptake of 2907 mg/g. Overall, this eco-friendly and green conversion of silver ions to metallic elements avoids the use of toxic chemicals and could be applied for the degradation/adsorption of dyes used in several industrial processes.

Keywords: nanoparticle; synthetic dye; plant extract; photocatalysis

1. Introduction

Recently, silver nanoparticles (AgNPs) have attracted interest in the field of environmental remediation [1–4]. The chemical preparation of nanoparticles is based on the reduction of metallic salts using reducing agents that can be synthetic or from biological sources such as plant extracts [5–7]. These phyto extracts are the reducing agents that promote the formation of nucleation centers and the incorporation of neighboring sites into the nucleation to produce different morphologies of nanoparticles [8,9]. Multiple studies have been carried out with fruits such as Capparis petiolaris [10], Terminalia chebula [8], Passiflora tripartita [11] to demonstrate the formation of nanoelements. Plants are a natural source of secondary metabolites like flavonoids that are responsible for the red, purple, and blue colors of flowers and leaves [12]. It is well known that plant extracts are economic resources that do not generate by-products in the environment [4,5,7–11] so they are being used more often in the fabrication of nanostructures. The Carrasquilla (Berberis hallii) fruit of the Berberidaceae family found in the highlands of the Andes at an altitude of 2400 m, is a black-purple spherical drupe and is used as a food for birds [13,14]. The main phenolic compounds in fruits of Berberis species are anthocyanins, mainly delphinidin, cyanidin, petunidin, peonidin, and malvidin glycosides, and catechin [15], and can also be used in the green nanotechnology field as a source of reducing natural agents. On the other hand, organic dyes are used in the textile industry including azo, anthraquinone, oxazine, thiazine, or stilbene groups in their structures [16], giving them a recalcitrant or non-biodegradable character. To our knowledge, there has not been reported any study re-
lated to the synthesis of AgNPs nanoparticles using the Carrasquilla extract as the reducing agent and its application on the degradation or removal of organic dyes.

2. Results and Discussion

2.1. Polyphenol Content and Scavenging Activity of the Extract

A suitable extraction method able to withdraw the largest quantity of polyphenol content is essentially that one to enhance the reducing capability of the silver ions to silver nanoparticles. In this study, methanol-hydrochloric acid at a ratio of 9:1 (v/v) was used as the extraction solvent, as other studies have recommended it is an excellent solvent for polyphenol extraction [17,18]. Table 1 summarizes the results of total polyphenols and the antioxidant activity (antioxidant activity) of the CE. The original pH of the extract (Table 1) was acidic (2.9 ± 1.03) and after mixing with the silver solution, an increase in pH to values well above 3.0 was observed (pH 6.95 and 4.17 for 1 mM and 10 mM Ag\(^+\), respectively). This change to less acidic pH may be due to the generation of OH\(^-\) during the reduction of Ag\(^+\) by the polyphenols [19].

Table 1. Polyphenol content, DPPH scavenging activity, and pH of the Carrasquilla extract and AgNPs.

| Samples                        | Total Phenols (mg GAE/0.2 g CE) | Antioxidant Activity (%) with 0.2 g CE | pH          |
|--------------------------------|---------------------------------|---------------------------------------|-------------|
| CE extract                     | 1% = 258.44 ± 0.19              | 1% = 47.52 ± 0.04                     | 2.9 ± 1.03  |
| AgNps with 10 mM of AgNO\(_3\) | No applicable                   | 1% = 5.98 ± 0.02                      | 4.17 ± 0.03 |

2.2. Characterization of Silver Nanoparticles

The CE, the silver precursor solution, and the as-prepared AgNPs are shown in Figure 1a. During the biosynthesis of AgNPs, a gradual change in the black-greenish color to brownish-black in the reaction mixture (see Figure 1a) ascertains the formation of silver nanoparticles at pH 9.5 and 12.5 and temperature of 40 °C after 1 h of incubation. Even more specifically, the polyphenols (~258 mg GAE/0.2 g) (Table 1) mainly cyanidin-glycosides and peonidin and catechin of the CE [15] are the antioxidants (scavenging activity~47%) (Table 1) that may act as primary reducing and stabilizing agent for the synthesis of the AgNPs through the reaction Ag\(^+\) + e\(^-\) → Ag\(^0\) (E\(^0\) = −1.80 V vs. NHE) [20] as occurs for iron and copper oxides, silver, and gold nanoparticles [21–24]. In Figure 1b, the UV-Vis patterns for AgNPs prepared with different concentrations of the CE at pH 12.5 are seen. It is observed that the optimum concentration of the extract is 20 mg/mL. Silver nanoparticles prepared with this CE concentration show a single surface plasmon absorption band with a maximum at 400 nm indicating the presence of spherical Ag nanoparticles. It is well documented for spherical AgNPs the blue shift is around 390–450 nm [4]. Yet, as the concentrations of the CE increase (40 and 60 mg/mL), AgNPs are produced with maximum absorbance peaks (0.49–0.40) and the plasmon absorption bands moved to 380–390 nm. This blue shift indicates a reduction in the mean diameter of the silver nanoparticles [19]. Similar surface plasmon resonance spectra of AgNPs in UV-Vis were obtained in previous studies [25,26]. Figure 1c shows the visual and UV-Vis spectra of AgNPs incubated at 40 °C for 1.0 h at different pH values. It is observed that increasing pH from 9.5 to 12.5, the wavelength of peaks reduces from 450 to 390 nm and intensity of absorbance peaks increases from 0.2 to 0.3. The observed absorbance peaks produce a single surface plasmon resonance (SPR) band of spherical and monodisperse AgNPs. Mie theory stated that a single SPR band results in spherical nanoparticles in contrast two or more SPR bands lead to variation in shape [27]. A basic pH in addition to producing colloidal nanoparticles shows a larger displacement towards the UV zone, ensuring a higher level of energy and particle size control [28]. Somchaidee and Tedsree [29] demonstrated the same absorbance increase when changing the pristine pH of the extract to alkaline pH due to the presence of deprotonated phenolic groups (at higher pH deprotonation increases), which have a
reduction potential greater than the regular polyphenols. Moreover, AgNPs prepared with 10 mM solution, 20 mg/mL of extract and pH 12.5 show the highest peak (~0.63 at ~410 nm) compared to that one prepared with 1 mM of silver precursor (~0.23 at ~398 nm) (Figure 1d). It is expected more Ag atoms are available for the formation of nanoparticles using 10 mM AgNO₃ solution, 20 mg/mL of extract and pH 12.5, incubation time of 1 h, and 40 °C of temperature.

DLS (Dynamic Light Scattering) analyses were performed to evaluate the hydrodynamic diameter of silver nanoparticles (Insets Figure 2). Particle size of nanoparticles prepared with 1 mM AgNO₃ solution (Inset Figure 2a) shows a wide distribution (122.7 ± 117.94 nm) whereas the size distribution is narrowed (40.83 ± 29.8 nm). Moreover, in Figure 2a,b, TEM analysis demonstrated that AgNPs prepared with 10 mM AgNO₃, are multiform in shape (Figure 2b) and show homogeneity. In contrast, AgNPs synthesized with 10 mM AgNO₃, are fully square, circle and rod forms (Figure 2b) and show homogeneity.

![Figure 1](image1.png)

**Figure 1.** (a) A photograph of the CE extract, AgNO₃ solution and AgNPs; UV-Vis spectra of the as-synthesized AgNPs with: (b) different extract concentrations and pH 12.5; (c) different AgNO₃ concentrations (1 mM and 10 mM precursor solutions) with 20 mg/mL of extract and pH 12.5, incubation time of 1 h, and 40 °C of temperature.

![Figure 2](image2.png)

**Figure 2.** Cont.
Figure 2. (a) STEM micrographs of AgNPs prepared with 1 mM of AgNO₃ and (b) STEM micrographs of AgNPs prepared with 10 mM of AgNO₃.

In Figure 3, the XRD (X-Ray Diffraction) pattern of AgNPs prepared with 1 mM AgNO₃ solution (black line) shows reflection peaks at 37.96°, 44.09°, 64.32° and 77.29° corresponding to crystalline planes <111>, <200>, <220> and <311>, respectively while for the AgNPs prepared with 10 mM AgNO₃ solution (red line), the diffraction angles are 37.93°, 44.18°, 64.47° and 77.16°. Results demonstrate that both types of AgNPs are linked to the crystalline planes of face centered cubic (fcc) structure of the silver metal and closely correlates to the reported reference values of the Joint Committee on Powder Diffraction Standards (JCPDS PDF no: 89-0713). These peaks are similar to those nanoparticles prepared by green synthesis using Shora [10], Rosa hybrida petal [30], cochineal [31] extracts. The remaining diffraction peaks at 2θ = 28.23°, 31.54°, 40.44°, and 64.32° for the AgNPs synthesized with 1mM AgNO₃ solution and 2θ = 27.58°, 32.02°, and 37.93° for the AgNPs synthesized with 10 mM AgNO₃ solution, are difficult to directly attribute to the correspondent silver phase. However, these peaks can be related to silver oxide (Ag₂O) and contaminants such as sylvine (KCl) and halide (NaCl) (see Figure S1), which are a common occurrence in plant-based synthesis [32] and can be effectively removed by performing multiple washing cycles with deionized water.

Figure 3. XRD patterns of the silver nanoparticles prepared with 1Mm AgNO₃ and 10 mM AgNO₃ solutions.

Figure 4 shows the cyclic voltammetry of the CE at a concentration of 20 mg/mL and two types of AgNPs (prepared with 1 mM & 10 mM AgNO₃ solutions) within a range potential of −1.2 to 1.2 V. The extract exhibited a reduction peak at −0.53 V in the cathodic zone and two oxidation peaks are observed at −0.18 and −0.34 V in the anodic region.
in the aqueous medium. Moreover, the small potentials observed at 0.83 V for AgNPs prepared with 1 mM AgNO₃ solution and 0.86 V for AgNPs synthesized with 10 mM AgNO₃ solution in the anodic section (Inset Figure 4), are due to the oxidation of hydroxyl groups in the A-ring of the flavonoid molecule, as suggested by Zhang et al., 2011 [33]. The as-synthesized AgNPs at basic pH show low oxidation because bands of the extract were extinguished during the redox reaction. As a substitute, characteristic peaks of the silver band (Ag⁺) and Ag₂O are observed at 0.15 V and −0.01 V for AgNPs prepared with 1 mM AgNO₃ solution and 0.16 V, −0.06 V for AgNPs synthesized with 10 mM AgNO₃ solution.

Note that the existing value of the last Ag₂O band is increased due to a larger ratio of precursor to extract. These byproducts may be resulted from the: (a) limited reducing power of the extract polyphenols (E₀ = 0.3–0.8 V) [34] to reduce Ag⁺ to Ag⁰ (E₀ = −1.80 V vs NHE) [35] and (b) alkaline pH used in the synthesis of AgNPs. Under an alkaline environment, the formation of AgOH is triggered [36] that in turn decomposes into Ag₂O due to the favorable energetics [37]. This tendency has also been reported during the synthesis of AgNPs prepared with the cochineal extract (*Dactylopius coccus costa*), in which the increase in the band of Ag₂O was due to a low volume of extract for the reduction of AgNO₃ [31]. Furthermore, the energy gap and ionization potential of the green synthesized AgNPs using the CE were estimated using optical and electrochemical techniques [38]. Based on the maximum potentials (0.83 V for AgNPs prepared with 1 mM AgNO₃ and 0.86 V for AgNPs synthesized with 10 mM AgNO₃), the HOMO and the LUMO energy levels were determined (Table 2).

### Table 2. Energy levels of the molecular orbital of AgNPs.

| Sample                  | HOMO (eV) | GAP (eV) | LUMO (eV) | Wavelength (nm) |
|-------------------------|-----------|----------|-----------|-----------------|
| AgNPs with 1 mM AgNO₃  | 5.08 ± 0.02 | 3.03     | 2.05 ± 0.02 | 409             |
| AgNPs with 10 mM AgNO₃ | 5.03 ± 0.01  | 2.99     | 2.09 ± 0.01  | 414             |

These results show that the AgNPs synthesized with 10 mM AgNO₃ and 20 mg/mL of CE extract exhibit a smaller energy gap (ΔE₉) and thus have better photon absorbance (ΔE₉ = 2.99 eV) than the counterpart of AgNPs prepared with 1 mM and 20 mg/mL of the
extract ($\Delta E_g = 3.03$ eV) in the UV-Vis region. The $\Delta E_g$ value of 2.99 eV for AgNPs prepared with 10 mM AgNO$_3$ solution falls within the typical range of values for colored materials (<3 eV). Thus, this material requires less energy for an electron to be transferred from the valence band into the conduction band [39] and is commonly used for the degradation of organic dyes.

The FTIR spectra of the dry aqueous CE and AgNPs were also investigated (Figure 5 and Table 3). The two materials have the characteristic absorption bands in the high frequency region of 4000 to 3000 cm$^{-1}$, which can be attributed to O–H stretching vibration. The peak at 3270 cm$^{-1}$ of AgNPs indicates the presence of the phenolic compounds that reduce Ag$^+$ to Ag$^0$. The polyphenols are from the Carrasquilla extraction solution that convert the silver in solution into nano-silver particles. Bands at 2110 cm$^{-1}$, 1931 cm$^{-1}$ and 1918 cm$^{-1}$ are ascribed to C–H stretching of methyl, methylene and methoxy groups by the mixture of anthocyanins [39], –CH and C=C stretching of aromatic compounds [40]. Note that these peaks are displayed in both materials (CE and AgNPs). Nevertheless, the peaks on the nanoparticles are more visible because the change of the pH to a value greater than 12. This alkaline environment enables the anthocyanins to be chemically modified and facilitated the formation of AgNPs. The new band at 1332 cm$^{-1}$ on the AgNPs can be associated to amine group C–N [41] resulting from the synthesis using the CE and AgNO$_3$ solution.

![Figure 5. FTIR patterns of the dried CE extract and the AgNPs synthesized using 10 mM AgNO$_3$ and chemical structure of the CE molecule.](image)

Table 3. Molecular organic groups of the CE extract and the as-prepared AgNPs with 10 mM AgNO$_3$.

| Bands cm$^{-1}$ | CE Extract | AgNPs 10 mM AgNO$_3$ | Molecular Group | References |
|----------------|------------|----------------------|-----------------|------------|
| 3270           | 3270       | -OH$_1$              | stretching the phenolic group | [8]         |
| 2933           | 2933       | -OH$_2$, -CH$_3$, -CH$_2$ aliphatics | [8]           |
| 2102           | 2102       | C-H stretching, methyl, methylene and methoxy groups | [8]           |
Table 3. Cont.

| Bands cm⁻¹ | Molecular Group | References |
|------------|-----------------|------------|
| CE Extract | AgNPs 10 mM AgNO₃ |             |
| 1988       | -C=N alkenes    | [39]       |
| 1906       | -CH₃           | [39]       |
| 1711       | C=O carbonyl    | [39]       |
| 1596       | C=C aromatics   | [39]       |
| 1513       | C=C aromatics   | [39]       |
| -          | -C=N stretch, amine | [8,39]   |
| 1017       | -C=O bond      | [39]       |
| 818        | aromatic ring, C-H bending | [4]       |
| 767        | aromatic ring, C-H bending | [4]       |

The peaks on the CE spectrum at 1711 cm⁻¹ and 1596 cm⁻¹ are accredited to C=O double bond carbonyl and aromatics, respectively. The peaks on the CE spectrum at 1711 cm⁻¹ and 1596 cm⁻¹ are designated to C=O double bond carbonyl and aromatics, respectively. And the peak at 1017 cm⁻¹ corresponds to the C–O esters group of the pyran nucleus of C-ring [8,41] as observed in the molecule of the CE (Inset Figure 5). In addition, bands at 818 cm⁻¹ and at 767 cm⁻¹ are linked to the aromatic ring and ethyl group [40], respectively. These organic functional groups from the CE solution could bind to the surface of silver nanoparticles and act as capping and stabilizing agents, thus significantly enhancing the properties of the nanoscale particles.

2.3. Mechanism of Reduction of Ag⁺ to AgNPs by the Phytocompounds of Carrasquilla Extract

In the green synthesis process of AgNPs, using the extract of Carrasquilla fruit as reducing agent, it was observed there was a blue shift of the absorption peak when the pH of the extract was raised to 12. This phenomenon is likely due to the breaking of the C-ring, formation of a C=O bond and a hydroxyl; while in the B-ring there is an O⁻ in the 5′ position of the anthocyanins, a phenolic compound that is a main component of the Carrasquilla fruit [15]. During the formation of AgNPs, the C=O group forms a complex with Ag⁺ and then is oxidized to COO⁻ at the same time Ag⁺ is reduced to AgNPs (Figure 6).

Figure 6. Schematic diagram for biosynthesis of AgNPs using CE extract.

2.4. Analysis of the Degradation of Dyes in Artificially Contaminated Water

The as-synthesized silver nanoparticles were then assessed on the degradation of the MB and the SF dyes in artificially contaminated water. Figure 7a shows the changes in the absorption spectra during degradation of the MB in the presence of the AgNPs (prepared with 10 mM AgNO₃). A sharp decrease of peaks intensity at a wavelength of 654 nm after 40 min of treatment was observed and after 90 min of treatment, 85.5% of degradation was achieved under solar lamp irradiation. This implies that the conjugated
system of phenothiazine species and the benzene ring structure of methylene blue were easily decomposed under solar light irradiation [42]. Also, after treatment the MB aqueous solution became colorless, typical of leucomethylene blue [8].

Comparable catalytic reactions of AgNPs prepared with T. chebula extract on methylene blue solution have been reported in other studies [8]. Moreover, results of the photocatalytic activity of AgNPs, explained on the basis of band gap (<3.0 eV) of the as-prepared NPs, could be attributed to the absorption of more photons from the solar irradiation that produce of more reactive oxygen species (ROS), which in turn degrade more efficiently the dyes, thus enhancing the photocatalytic activity of the silver nanomaterials. In contrast, the same nanoparticles degraded less the SF dye under otherwise similar experimental conditions as above (Figure 7b). A degradation of 57.24% was obtained after 90 min of treatment, suggesting the SF molecule was more resistant to photodegradation because it holds a phenyl phenazine group and the characteristic pink color of the SF dye molecule did not change but it turned less intense. Further, kinetics tests were carried out with both dyes under solar light irradiation. Results of the MB and the SF degradation in the presence of AgNPs fitted well a first-order model (Figure 7c,d) with equivalent rate constants of k = 0.0092 min$^{-1}$ and 0.00016 min$^{-1}$, respectively. Although the degradation kinetic models for both dyes were the same, the rate for the SF is approximately two-fold lower than the rate for the MB. Hence, degradation of the MB can be mainly attributed to the photocatalytic activity of the AgNPs. However, a significant degradation of the MB under dark conditions (test performed during 30 min) was also observed (Figure 7a). To further explain this finding, adsorption tests with the MB dye and AgNPs, under dark environment, were run (Figure S2a). Results indicated that a maximum of 140.85 mg/g of the dye was adsorbed (Figure S2b and Table 4) after 90 min of treatment. Thus, it can be implied that the MB dye was removed from water by a combined mechanism of adsorption and photodegradation.

**Figure 7.** Degradation of: (a) MB and (b) SF dyes assisted by AgNPs prepared with 10 mM AgNO$ _3$ solution, (c) Linearized first-order kinetics for the MB and (d) for the SF, treated with AgNPs prepared with 10 mM AgNO$ _3$ solution.
Table 4. Langmuir, Freundlich isotherm constant for the adsorption of Methylene Blue.

| Time (min) | Langmuir qmax (mg/g) | KL | R² | RL | Freundlich KF (mg/g) (L/mg)¹/n | n | R² |
|-----------|----------------------|----|----|----|---------------------------------|---|----|
| 90        | 140.85               | 27.94 | 0.99 | 2.24 × 10⁻⁴ | 17.12 | 2.5 | 0.90 |

On the contrary, the SF removal was mostly due to adsorption as confirmed by tests run under dark conditions (Figure 7b). The maximum adsorption of SF dye at equilibrium was ~2907 mg/g (Figure 8b and Table 5). Constant values of the Langmuir and Freundlich adsorption isotherms (Figure 8c and Table 5) confirmed favorable adsorption conditions for the SF dye since the dimensionless separation factor, R_L, was in the range of 0–1 for the Langmuir isotherm [43] and the heterogeneity factor, n, was greater than 1.0 for the Freundlich isotherm [44]. To complement this study, the adsorption kinetics of the SF dye on AgNPs was conducted (Figure 8a). It was observed that up to 60 min of the kinetic test, the uptake of the SF showed a sharp slope. Nonetheless, with the progress of time, the adsorption rate for the dye became less due to probably saturation of reactive sites. The best fit for the kinetic data was the pseudo-second order model (Figure S3b) as the correlation coefficients for the linear plots of t/qt against time are greater than 0.93 for all tests (Table 6). The pseudo-second order rate constant, k₂, values decreased from 0.85 to 0.01 g/mg/min and the calculated-equilibrium adsorption capacities (qₑ) increased from 143.06 to 909.09 mg/g for the initial SF concentrations of 10 to 160 mg/L (Table 6).

**Figure 8.** (a) Adsorption kinetics of the SF on the AgNPs under dark conditions, (b) Adsorption isotherms for the SF under dark, (c) Linearized Langmuir and Freundlich isotherms for the SF after 90 min of equilibration.
Table 5. Langmuir, Freundlich isotherm constant for the adsorption of Safranin.

| Time (min) | Langmuir $q_{max}$ (mg/g) | $K_L$ | $R^2$ | Freundlich $K_F$ (mg/g) (L/mg)$^{1/n}$ | $n$ | $R^2$ |
|------------|---------------------------|------|------|----------------------------------------|----|------|
| 90         | 2906.9                    | 2.8×10^-3 | 0.6  | 13.87                                  | 1.21 | 0.96 |

Table 6. Constants of the pseudo-first order and pseudo-second order models for different initial concentrations of the Safranin dye.

| Co (mg/L) | $q_{e,exp}$ (mg/g) | Pseudo First Order Kinetic Model $q_{e,cal}$ (mg/g) | $K_1$ (min^-1) | $R^2$ | Pseudo Second Order Kinetic Model $q_{e,cal}$ (mg/g) | $K_2$ (g/mg min) | $R^2$ |
|-----------|--------------------|---------------------------------------------------|----------------|------|---------------------------------------------------|-----------------|------|
| 10        | 131.73             | 94.70                                             | 0.011          | 0.58 | 143.06                                            | 0.85            | 0.98 |
| 20        | 146.60             | 142.79                                            | 0.013          | 0.99 | 142.86                                            | 0.14            | 1.00 |
| 40        | 298.27             | 297.66                                            | 0.001          | 1.00 | 333.33                                            | 0.30            | 0.95 |
| 80        | 532.93             | 529.30                                            | 0.003          | 0.61 | 588.24                                            | 0.23            | 0.94 |
| 160       | 931.67             | 929.25                                            | 0.001          | 0.74 | 909.09                                            | 0.01            | 1.00 |

Thus, the sorption system was a pseudo-second order model, based on the assumption that the rate-limiting step could be chemisorption via electrostatic interaction between the cationic dye and the negatively charged polyphenolic compounds that cover the AgNPs. Similar results were reported for the SF adsorption using Fe$_3$O$_4$ magnetic nanoparticles modified with sodium dodecyl sulfate [45].

Lastly, Figure 9a showed the spectrum of the control sample (SF + MB) and the mixture of both dyes treated with AgNPs under simulated solar irradiation. Two main peaks at the wavelengths of 664 nm for MB and 518 nm for SF were clearly observed. Evidently, as seen in Figure 9a, without adding AgNPs, there was no reaction of any dye as reported by Sonawane et al. 2017 [46]. Furthermore, the degradation of MB and SF is similar to the profile obtained when both dyes were independently studied. Visually, it was observed that there was no change in the purple color of the initial mixture of both dyes but the intensity was less after treatment, implying there was no chemical transformation but only adsorption of the dye on the surface of the AgNPs similar to the SF individual tests. A second-order kinetics model fitted more accurately the results of the simultaneous degradation of both dyes. Change in the order of the reaction for this test compared to the individual ones carried out with each dye can be attributed to the increase of the solution concentration.

Figure 9. Cont.
3. Materials and Methods

3.1. Chemical and Materials

Carrasquilla fruits were collected in the town of Sangolquí, Ecuador 0°21’31.7” S 78°24’39.6” W. Silver nitrate and thiazine group dye methylene blue were purchased from Spectrum Chemical Mfg. Corp (98–103%, California, CA, USA). Diazine group dye safranine and sodium hydroxide were purchased from SAFE-D chemicals (~100%, Vernon Hills, IL, USA), and Fisher Scientific (98.9%, Bergen, NJ, USA), respectively.

3.2. Preparation of the Carrasquilla Extract

Carrasquilla fruits were washed several times with deionized water to remove impurities. For extract collection, clean fruits were mixed with methanol-hydrochloric acid at a ratio of 9:1 and kept for 72 h under ambient conditions. Before being used for the synthesis of nanoparticles, the extract was filtered with Whatman paper of 125 µm and concentrated in a rotary evaporator (Buchi R-210, büchi labortechnik AG, Flawil, Switzerland) at 60 mbar, 40 °C and 125 rpm until all solvent was recovered. The extract was stored at 4 °C for further use.

The phenolic content of CE was determined following the Folin-Ciocalteu method. In brief, 0.5 mL of the extract (0.2 g/10 mL CH3OH : H2O) diluted 1% (CH3OH : H2O) was reacted with 0.5 mL of Folin-Ciocalteu reagent, followed by the addition of 4 mL 1 M sodium bicarbonate. Thereafter, the solution was heated in a water bath at 45 °C for 15 min and the absorbance was measured at 765 nm [17,18].

3.3. Synthesis of Silver Nanoparticles

Several weights of the dry extract were dissolved in distilled water (10, 20, 40, 60 mg/mL). One milliliter of each concentration at pH of 7.5, 9.5 or 12.5 was added to 10 mL of 1 m or 10 mM of silver nitrate solution (AgNO3) contained in falcon tubes and incubated for 1 h in a water bath at 40 °C to complete the synthesis. The content was observed on a UV-vis spectrophotometer Specord S600 (AnalytikJena, Jena, Germany) to verify the nanoparticles formation. Subsequently, falcon tubes with synthesized nanoparticles were purified in a centrifuge at 10,000 rpm for 15 min and then at 12,000 rpm for additional 15 min. AgNPs samples were then collected up to 20 mL and lyophilized (LiShinBioBase lyophilization) for later use.

3.4. Antioxidant Activity Test

The antioxidant activity of the CE and AgNPs was determined by the reduction method of the 2.2-diphenyl-1-picrylhydrazyl to 2.2-diphenyl-1-pricrylhydrazine radical [47] with minor adjustments. 0.2 mL of the extract (0.2 g/10 mL CH3OH : H2O) diluted 1% (CH3OH : H2O) was mixed with 4 mL of 0.1 mM DPPH, homogenized and
incubated in the dark at room temperature for 1 h. The absorbance of the mixtures was measured in the UV-Vis spectrum at 517 nm [33]. Methanol was used as a positive control. The ability of the sample to scavenge DPPH radical was determined by Equation (1) [10,47].

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\text{Scavenging activity} \ (\% ) = \left\{ \frac{\text{Abs control} - \text{Abs sample}}{\text{Abs control}} \times 100 \right\} \tag{1}
\]

3.5. Characterization Studies

A CE extract sample of 20 mg/mL and purified AgNPs samples were monitored periodically, with the UV-Vis spectrometer Specord S600 (AnalytikJena, Jena, Germany); hydrodynamic size of the AgNPs was measured using the DLS (Horiba LB-550); analysis of the crystalline structure of the AgNPs was carried out by XRD diffractometer (PANalytical Inc, Malvern, United Kingdom) operating in a \( \theta-2\theta \) configuration in the Bragg-Brentano geometry and equipped with a copper X-ray tube (\( K\alpha \) radiation = 1.54056 Å) operating at 40 kV and 45 mA; morphology of the nanoparticles was performed by the transmission electron microscope in the TEM (FEI Spirit Twin) at an acceleration voltage of 80 kV. The electrochemical tests were conducted with a potentiostat (Metrohm Autolab PGSTAT 128N, Metrohm AG, Herisau, Switzerland) coupled with three electrodes and through cyclic voltammetry curves, the highest occupied molecular orbital (HOMO) of the sample was determined. These analyses were carried out in a 0.1 M KCl bottom electrolyte solution with a scanning speed of 0.05 V/s, in the standard hydrogen electrode (SHE) vs saturated calomel electrode (SCE) range of \(-1.2 \text{ to } 1.2 \text{ eV}\). It is appropriate to refer the resulting potential values (E) to the SHE. The conversion of the SHE to vacuum scale can be accomplished by theoretical and experimental means with relaxation of thermodynamic rigor [38]. The energy band gap (\( \Delta E_g \)) was determined in the position of maximum absorption of the AgNPs. Then, the lowest unoccupied molecular orbital (LUMO) was determined by the difference between HOMO and \( \Delta E_g \) (LUMO = HOMO − \( \Delta E_g \)) [48].

FTIR studies of the CE and AgNPs were carried out (Agilent Cary 630 FTIR spectrometer, Santa Clara, CA, USA) with a number of scans of 128, 180-degree reflection configuration and the wavelength in the range of 350–4000 cm\(^{-1}\). Samples were prepared with several concentrations of dyes and AgNPs to obtain band representations.

3.6. Degradation of Dyes Assisted by Silver Nanoparticles

The degradation capability of AgNPs was evaluated using Methylene Blue (MB) and Safranin (SF) dyes under a solar light lamp and in a dark environment. For the MB tests, AgNPs prepared with 10 mM AgNO\(_3\) were re-suspended and contacted with a 3 mL sample of each dye (10 mg/L) in 5 mL vials. Measurements of the absorption peak of the MB were performed at 664 nm. Also, the SF tests were carried out using the same AgNPs; the measuring absorbance was 518 nm. Then, samples were placed under dark conditions for equilibration overnight at constant agitation of 100 rpm. Next, most of the samples were exposed to a solar lamp (Neutronics 94023A, PV Measurements, Inc. 245 Mill Road Point Roberts, WA, USA) at 30 cm beam light distance and power of 387 W (see Figure S4) and a few ones were placed under dark to investigate the degradation of the dyes without light irradiation. Aliquots of 10 \( \mu \)L were taken at 10, 30, 60 and 90 min and analyzed in the UV-Vis spectrum to verify the degradation of the dyes. Percentage of degradation was calculated using Equation (2) [10,11] and the rate of degradation was estimated using the first-order and the second-order kinetic reactions, according to Equation (3) [11] and Equation (4) [48]. All tests were conducted by triplicate and a control sample consisting of only 3 mL of dye without AgNPs was used.

\[
\eta = \frac{A_o - A_t}{A_o} \times 100 \tag{2}
\]

\[
\ln \left( \frac{A_o}{A_t} \right) = kt \tag{3}
\]
where $\eta$ is the dye degradation rate of MB and SF in percentage, $A_o$ is the initial absorbance concentration (mg/L), $A_t$ the absorbance at time $t$ (mg/L), $t$ the time reaction (min) and $k$ is the first-order rate constant (1/min) and (mg/L-min) for the second-order reaction.

To find out the influence of experimental conditions in the degradation of both dyes, a series of weights of nanoparticles tests were used. For tests with MB and SF dyes, 0.17 and 0.05 mg/mL of lyophilized silver nanoparticles were utilized, respectively; and for tests with the mixture of MB + SF, 0.10 mg/mL of AgNPs was employed.

Adsorption isotherms were conducted under dark conditions using 160, 80, 40, 20, 10 mg/L of the MB with 2 mg of AgNPs, while the same concentrations of the SF were used with 0.5 mg of AgNPs. Samples were placed in a rotor (Heidolph Unimax 1010) at 40 rpm. Aliquots of 200 µL were taken after 60, 90, and 1440 min of treatment and analyzed in the spectrum Specord S-600. For the adsorption isotherm tests, Equation (5) was used to calculate the adsorption of the dye at equilibrium, $q_e$ (mg/g) [49]. All tests were conducted by triplicate.

\[
q_e = \frac{V(C_i - C_e)}{m}
\]  

(5)

where $V$ is volume of the water (L), $m$ is mass of the AgNPs (g), $C_i$ refers to the initial concentration of dye in solution (mg/L) and $C_e$ is the equilibrium concentration of the dye in solution.

Langmuir and Freundlich adsorption models were applied to fit data of the isotherm tests.

**Langmuir:**

\[
q = \frac{q_{max}KLC}{1 + KLC}
\]  

(6)

**Freundlich:**

\[
q = K_F C^{1/n}
\]  

(7)

where $q$ (mg/g) is the dye adsorbed on the AgNPs, $q_{max}$ (mg/g) and $K_L$ (L/mg) are the Langmuir constants; $K_F$ (mg$^{1-1/n}$ L$^{1/n}$/g) and $n$ are the Freundlich constants of the dye adsorption on the AgNPs.

Additionally, adsorption kinetics were conducted under dark conditions using 160, 80, 40, 20, 10 mg/L of the SF and 0.5 mg of AgNPs. Samples were placed in a rotor (Heidolph Unimax 1010) at 40 rpm. Aliquots of 200 µL were taken at 30, 60, 90, and 1440 min and analyzed in the spectrum Specord S-600. For the adsorption kinetic tests, pseudo-first order and pseudo-second order reactions (Equation (8) and Equation (9), respectively) were used to calculate the constants of the adsorption on AgNPs, $k_1$ and $k_2$ and $q_e$ (mg/g) [50].

\[
\ln(1 - qt/q_e) = -k_1t
\]  

(8)

\[
t/q_t = 1/k_2(q_e)^2 + (1/q_e)t
\]  

(9)

4. Conclusions

In the fabrication of silver nanoparticles using the proposed green-based chemical process, the following experimental conditions produced the best results: an extract concentration of 20 mg/mL, 10 mM of AgNO$_3$ solution, pH~12.5 and an incubation time of 1 h followed by lyophilization. The resulting AgNPs exhibited spherical or nearly aspherical morphology with sizes of 40.83 ± 29.8 nm, a fcc crystalline structure and once supplied into a solution of the MB under solar light irradiation at 664 nm, caused 85.57% of degradation. The conjugated system of phenothiazine species and the benzene ring structure of the MB were decomposed and the dye solution became colorless after the treatment. In contrast, the same AgNPs degraded only 57.24% of the SF at 518 nm of wavelength under solar light exposition, suggesting that there was no modification in the molecular structure of the dye, as the color of the degradation product slightly changed. However, the SF was
better removed from water by adsorption (~2907 mg/g). The constant values of adsorption isotherms (R^L_1 = 0.70 for Langmuir and n > 1 for Freundlich) validated a favorable adsorption of the dye. Based on these results, it can be concluded that the catalytic and adsorption activity of AgNPs over textile dyes depends on the method of synthesis, size, and morphology. Also, the crystalline structure and the specific surface area of particles are important properties in catalysis as well as in adsorption. Moreover, it is important to consider the chemical structure of the dyes.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/catal11101195/s1, Figure S1: Composition of AgNPs calculated from XRD patterns for: (a) 1 mM AgNO\(_3\) and (b) 10 mM AgNO\(_3\) Figure S2: (a) Adsorption isotherms for the MB dye treated with AgNPs under a dark environment; (b) Linearized Langmuir isotherm for the adsorption of the MB dye under dark and Linearize Freundlich isotherm isotherm model for the adsorption of the MB dye under dark for the adsorption of the MB dye under dark; Figure S3. (a) Pseudo-first order model for the adsorption kinetics of SF dye on AgNPs; (b) Pseudo-second order model for the adsorption kinetics of SF dye on AgNPs; Figure S4: Scheme of the Neutronics solar lamp.

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