Electronic Supplementary Information

Evaluation of the antimicrobial activity of silver nanoparticles obtained by microwave-assisted green synthesis using *Handroanthus impetiginosus* (Mart. ex DC.) Mattos underbark extract

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Synthesis optimization

Microwave parameters were first optimized using a Box−BENHKEN design for three factors: time (5-15 min), temperature (100-200°C), and plant extract/$AgNO_3$ volume ratio, C_{PE}, (5-15%). The completed trials with various combinations of time, temperature and plant extract/$AgNO_3$ volume ratio are listed in Table S1. The XRD intensity of the (111) peak normalized by the intensity of the (220) peak ($I_{(111)}/I_{(220)}$) was utilized as the dependent variable for the statistical analysis through the Statistica 8.0 software.

Figure S1 shows the X-ray diffraction patterns of samples synthesized using time, temperature, and C_{PE}, parameters. Data are grouped as a function of temperatures 100, 150 and 200 °C from the left to the right panel. For all the samples, the main peaks corresponding to the face-centered cubic (fcc) structure of metallic silver (JCPDS #04-0783) were identified and indexed (between parenthesis). Only at a lower temperature (100 ºC) was the presence of the peaks at ~32° (marked with asterisks) indicating the formation of silver chloride, probably due to the spontaneous reaction of Ag^+ with chloride ions present in the plant extracts.[1] However, the low intensity of these peaks confirms the predominance of the Ag crystalline phase in all samples.

Table S1 – Parameters utilized in AgNPs syntheses and samples characteristics.

Sample	Temperature (° C)	Time (min)	C_{PE} (%)	$I_{(111)}/I_{(220)}$	d_{XR} (nm)
1	100	5	10	4.70	13.06
2	200	5	10	7.95	16.10
3	100	15	10	5.19	13.87
4	200	15	10	7.82	13.37
5	100	10	5	4.84	12.25
6	200	10	5	6.39	16.43
7	100	10	15	4.80	11.84
8	200	10	15	7.09	12.52
9	150	5	5	7.43	14.10
10	150	15	5	6.29	13.06
11	150	5	15	7.59	11.83
12	150	15	15	6.51	12.70
13	150	10	10	6.53	12.20
14	150	10	10	6.63	11.06
15	150	10	10	6.41	14.33

C_{PE} is the plant extract/$AgNO_3$ volume ratio. $I_{(111)}/I_{(220)}$ is the ratio between the intensities of peaks (111) and (220) and d_{XR} the crystalline size obtained from X-ray diffraction.

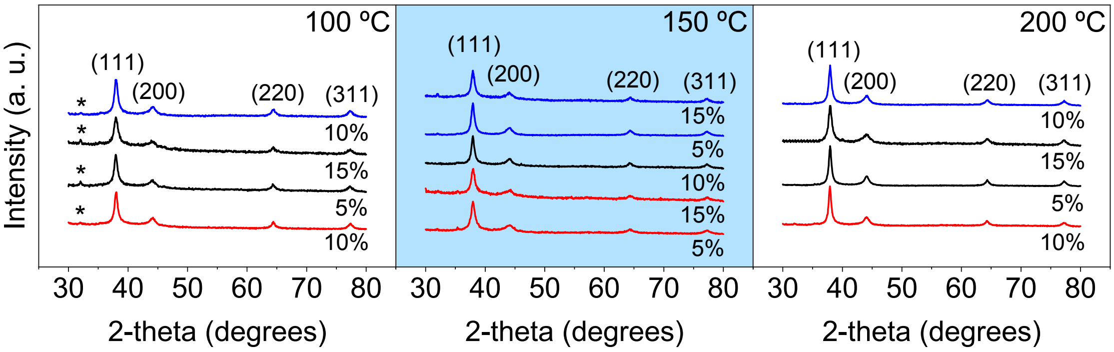

Figure S1 - XRD patterns of AgNPs synthesized at different temperatures: left panel – 100°C, center panel – 150°C and right panel – 200°C. The percent values represent (C_{PE}) the plant extract/$AgNO_3$ volume ratio. Reaction times were 5 min (blue); 10 min (black) and 15 min (red).

Besides, the crystalline sizes of AgNPs (d_{XR}), calculated by means of the Scherrer's formula on the most intense (111) peak, varied between ~11 nm to 16.4 nm depending on the combination of parameters utilized on syntheses (see Table 1). Only a qualitative influence of these parameters on the increasing size tendency was observed and followed the order: temperature > time > plant extract/$AgNO_3$ volume ratio.

Thus, to maximize the yield of syntheses, the obtained samples were monitored by the XRD intensity of the (111) peak normalized by the intensity of the (220) peak ($I_{(111)}/I_{(220)}$) – the dependent variable (see Table S1). Figure S2a shows the Pareto chart of the standardized effects in descending order (temperature > time > C_{PE}). From these results, one infers that temperature is the main factor influencing synthesis, as its linear and quadratic results cross the reference line, therefore being statistically significant at the 95% confidence level, with the response model. A contour plot of the temperature as a function of C_{PE} was also constructed to the time of synthesis equals 15 min (see Figure S2b). The regions of maximal response are represented by darker areas.[2,3]

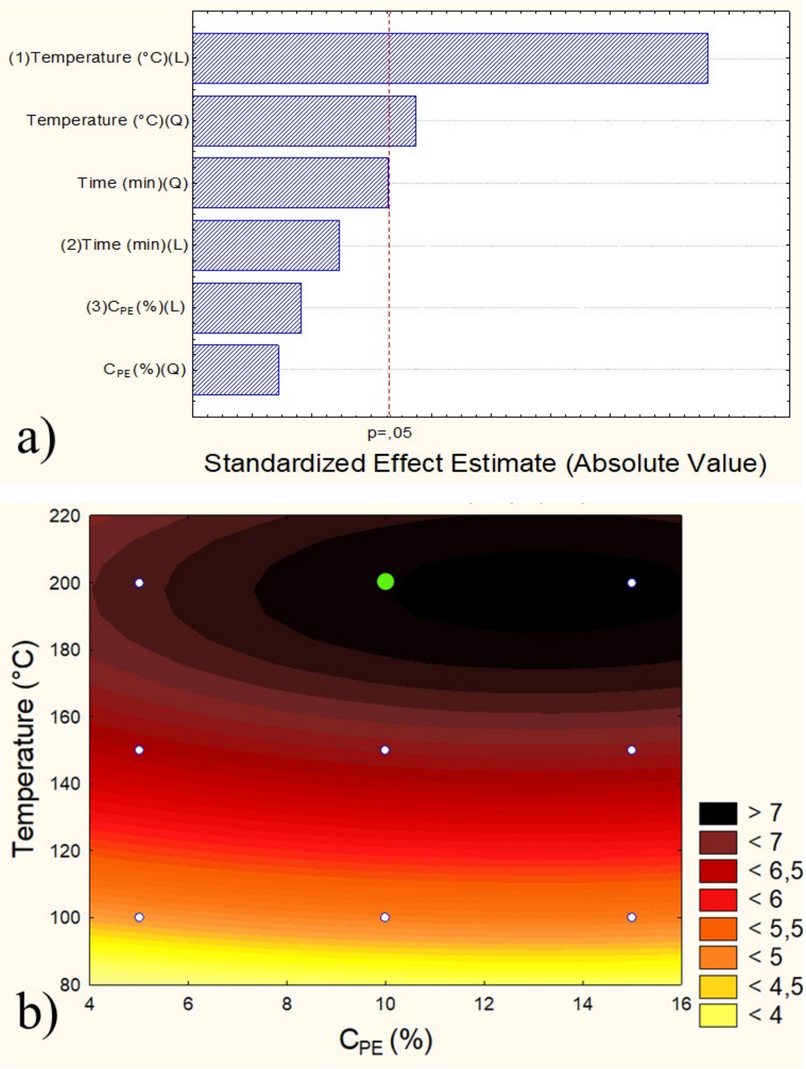

Figure S2 –Pareto Chart of the Standardized Effects (a) and fitted surface (time = 15 min). White dots are the experimental points and the intensity of ($I_{(111)}/I_{(220)}$) is represented by the color scale (b). The green dot represents the optimized synthesis conditions of AgNPs utilized for biological tests.

FTIR characterization

Figure S3 shows the FTIR spectrum of AgNPs obtained from optimized synthesis. The large peak centered at ~3360 cm^{-1} (A) can be associated to the -OH stretching vibration of alcohols and phenols moieties and/or bending stretching of hydrogen-bonded phenols and alcohols in the adsorbed molecules.[4] The peaks appearing at ~2940 and ~2875 cm^{-1} (B) are typical of C-H stretching or stretching vibrations of methyl groups of adsorbed species such as quinone molecules.[5,6] The two bands at ~2360 and 2340 cm^{-1} (C) are ascribed to asymmetric stretching mode of adsorbed CO_2 gas. In the region (D) the peak at ~1600 cm^{-1} can be attributed to amide C=O stretching. Other peaks are coming from in-plane OH bending and asymmetrical and symmetrical vibrations of COO^- moieties.[7] The peaks at ~1507 and ~1345 cm^{-1} (E) can be attributed, respectively, to the stretching vibration of C=C in aromatic rings and CH_2 groups; and at 1150-1085 cm^{-1} (F) to the C-O stretching of aliphatic ethers present in adsorbed molecules.[5] Therefore, the presence of these peaks strongly suggests functionalization of AgNPs with the plant extract molecules as is corroborated with the qualitative phytochemical analysis.

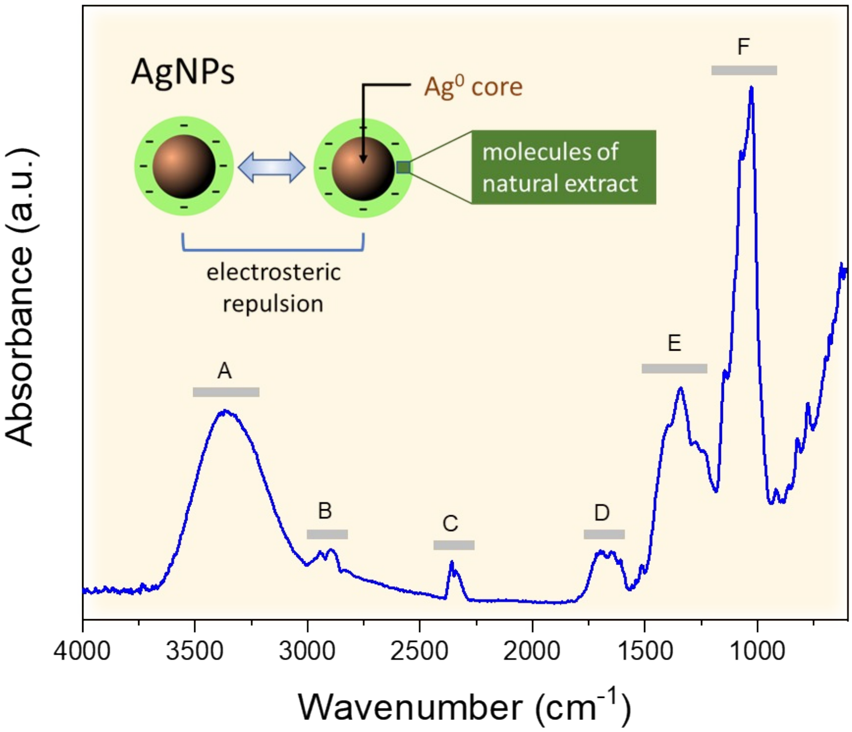

Figure S3 - FTIR spectrum of the AgNPs obtained from optimized synthesis. A-F areas indicate different regions of interest described in the text. The inset shows the design of AgNPs obtained by green synthesis.

Colloidal stability

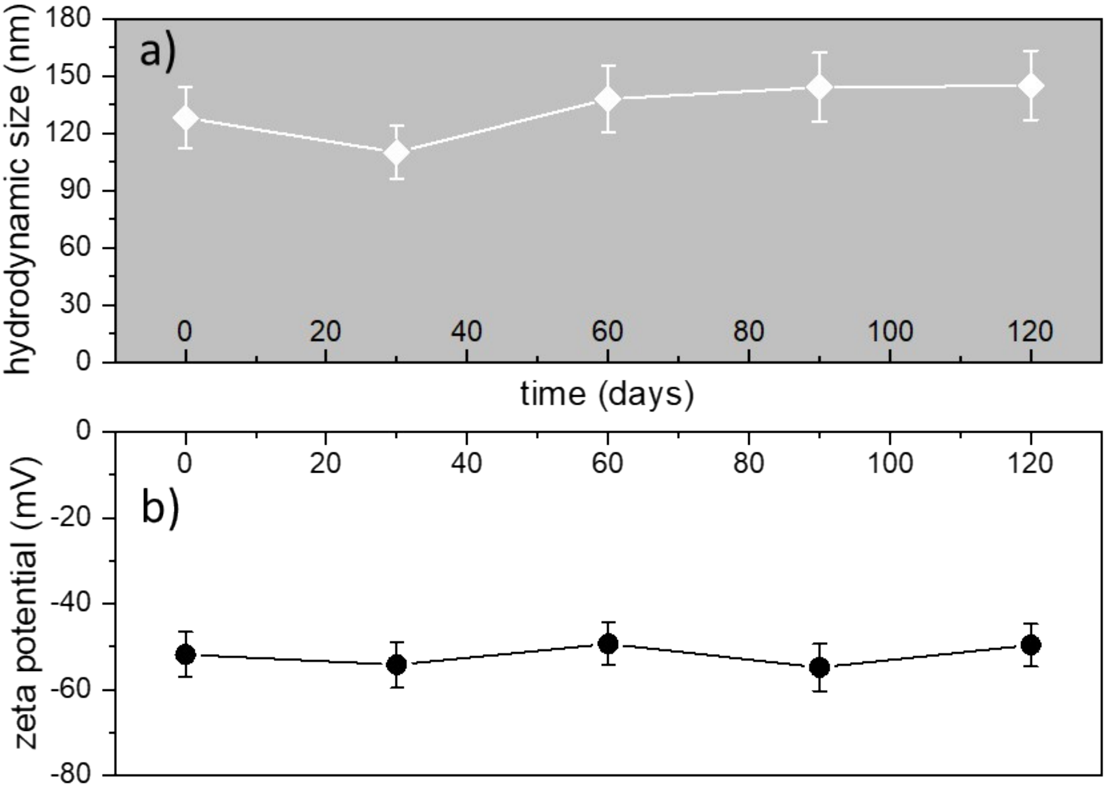

Figure S4 – Colloidal stability of the AgNPs at 25 °C for the period of 120 days in function of the hydrodynamic size (a) and Zeta potential (b).

Notes and references

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